New Block Copolymers of Isobutylene by Combination of Cationic and Anionic Polymerizations

DISSERTATION

zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften (Dr. rer. nat.)
in Fach Chemie der Fakultät für Biologie, Chemie und
Geowissenschaften
der Universität Bayreuth

vorgelegt von

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Geboren in Tampico / Mexiko

Bayreuth, 2004

Die vorliegende Arbeit wurde in der Zeit von April 2000 bis Oktober 2003 in Bayreuth am Lehrstuhl Makromolekulare Chemie II unter Betreuung von Herrn Prof. Dr. Axel H. E. Müller angefertigt.

Vollständiger Abdruck der von der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigten Dissertation.

Dissertation eingereicht am:
Zulassung durch die Promotionskommission:
Wissenschaftliches Kolloquium:

Amtierender Dekan: Prof. Dr. O. Meyer

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1. Introduction

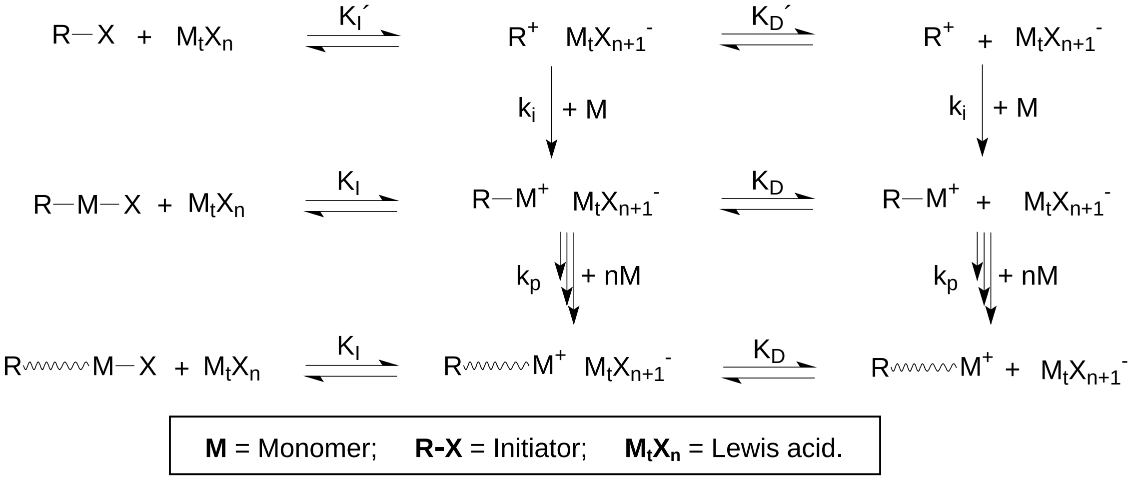
Besides the well known application of isobutylene for producing polymers with this as the basic monomer (oligo- and polyisobutylenes, butyl rubbers, isobutylene copolymers with butenes, styrene, etc.), together with alkylphenols, it participates in synthesis of other technically important products: methyl-*tert*-butyl ester, methacrylic acid, methacrylates, aliphatic diamines, a sequence of insecticides, etc. Widening fields of application indicate continuous growth of the isobutylene demand. Just in the USA, the deficit of isobutylene in 1995 was about 8 million tons.

Keeping in mind the industrial production of a rather wide range of isobutylene polymers and composites with isobutylene as starting material, we can talk about the existence of a self-contained field of low-tonnage isobutylene chemistry; in this case it should be taken into account that there are a number of traditional fields that are bound to application of high-molecular polyisobutylene and butyl rubber, which will continue in use with no alternative.

1. 1. Controlled / living cationic polymerization

1. 1. 1. General concepts of controlled/living cationic polymerization

The polymerization of a monomer like isobutylene can be divided into different steps, each having its own characteristic rate constant as shown in scheme 1. 1. and 1. 2. As mentioned above, undesired side reactions, such as transfer and termination have to be taken into account in some systems as shown in scheme 1. 2. It is then the relative ratios between rate constants in a system that decide whether or not it is a controlled/living or conventional cationic polymerization.

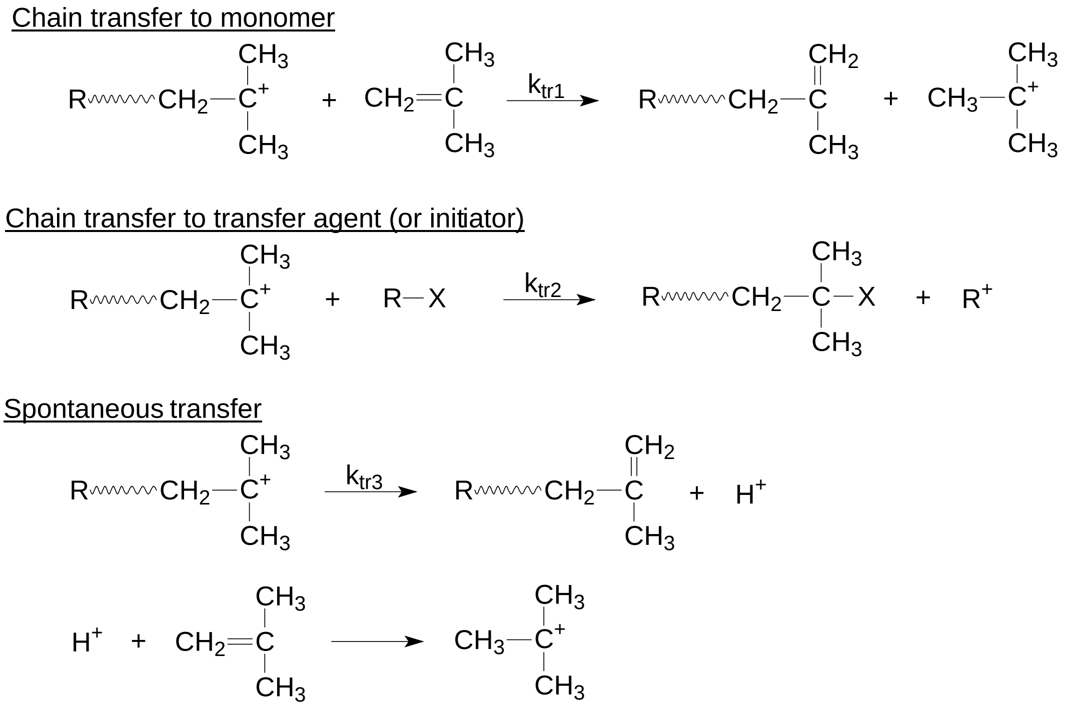


Scheme 1. 1.: Elemental reaction steps in cationic polymerization.

It is important to know how the polymerization proceeds, i.e. how the chain end incorporates the monomer during the propagation if we assume ideal conditions. A living polymerization with a dynamic equilibrium between inactive (dormant) and active species seems to be the most plausible mechanism as represented in scheme 1. 1. taking the fundamental experimental/kinetic facts into consideration [1]. The existence of this equilibrium is a central topic later when influence of coinitiator and solvent is discussed. If we ignore the equilibrium between the active and inactive species, this scheme also includes the "ideal" living polymerization. It is impossible to distinguish between the two ways of living polymerizations, if the rates of exchange between active and inactive species are much higher than the rate of propagation. The rates of propagation for ideal living polymerization and living polymerization with reversible termination is expressed by the following equations:

$R_p = k_{app}[P^*][M]$,
in "ideal" case, $[P^*] = [I]_o$
and with reversible termination:
$P' + C \rightarrow P^* \Rightarrow K_I = P^*/(P'.C)$, taking the following assumptions into account;
$P^* << P'$, $P' \approx I_o$, and $C \approx C_o \approx [M_tX_n]_o \Rightarrow K_I = P^*/(I_o.C_o)$,
$[P^*] \approx K_I[M_tX_n]_o[I]_o$ (neglecting dissociation of ion pairs),

where $[P^*]$ is the concentration of living chain end, $[P']$ the concentration of dormant i.e. inactive chain ends, $[I]_o$ the initial initiator concentration, $[C]_o = [M_tX_n]_o$ the initial catalyst concentration, and K_I the equilibrium constant of ionization. Since the number of polymer chains does not change during polymerization ($[P] = [I]_o$), DP_n is independent of the way it proceeds. The equilibrium between inactive and active species is usually stronger shifted toward the inactive ones ($K_I << 1$). This is indirectly verified by the fact that in polymerization of isobutylene in the presence of electron donors (EDs), quenching with methanol does not give methoxy but a chlorine end group[2].

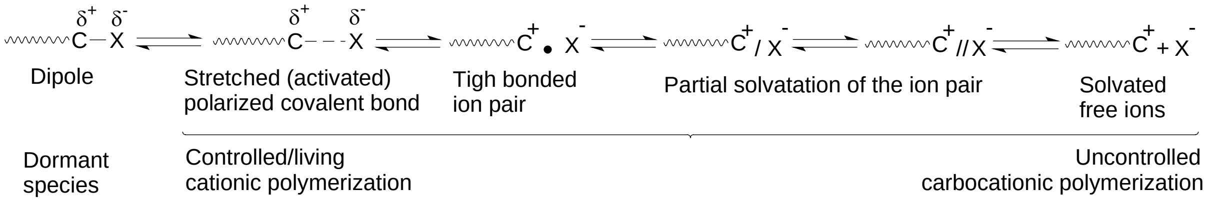


Scheme 1. 2.: Potential side reactions in living cationic polymerization of isobutylene.

Transfer can take place in three ways as seen in scheme 1. 2., to monomer, to transfer agent or spontaneous transfer due to the elimination of a proton at the chain end. In all cases the ionicity of the chain end is important, and the latter two types of transfer reactions can be totally suppressed by addition of electron donor. Transfer to monomer is not as simple as described in scheme 1. 2. Actually one can distinguish between three different transfer reactions with regard to monomer[3]. The purpose of mentioning these reactions is that experiments with isobutylene[3] have proved that temperature has a distinct influence on which kind of reaction dominates. In addition to temperature, parameters like solvent and additives also control the outcome of these reactions.

An important detail which has to be noted here is that quenching/termination of a controlled/living cationic polymerization of isobutylene with methanol can be interpreted as a deactivation of the Lewis acid. $M_t(OR)_n$ is a much weaker acid than M_tCl_n. Therefore, after the formation of $M_t(OR)_n$ the degree of ionization of the chain end is very low. Quenching/termination can also be carried out in a controlled way which gives the possibility to prepare polymers with well-defined endgroups. This is a crucial point since the aim in out study is to use the tailored PIBs for subsequent anionic polymerization. One of the most important undesired reactions when aromatic initiators (or styrene as monomer) are used is the formation of indanyl skeleton[4]. This reaction can be avoided by the use of sterically hindered initiators, e.g. tBuDiCumCl instead of DiCumCl. The parameter which affect this reaction have been investigated with DiCumCl[4] and DiCumOH[5]. The results show that low temperature and low polarity of the reaction medium favors the wanted end-product (even at –70°C in pure CH_3Cl solvent as much as 32% mono-indane and 21% di-indane adducts are observed).

An important feature of controlled/living cationic polymerization is the ionicity at the reaction center both in the ion generating and propagating step. The Winstein spectrum (scheme 1. 3.) is frequently used to elucidate the different kind of propagating species which can exist in a polymerization system. One important aspect considering the equilibria is that the rates of exchange between the species have a strong effect on MWD of the end product [6].



Scheme 1. 3.: The Winstein spectrum.

Total control is not achieved until each step is mastered. This means initiation shall only be performed by the added initiator and not by moisture or impurities like phosgene (which can be formed by oxidation of the solvent, such as methylene chloride). If more than one type of initiator is present, Poisson MWD can not be attained, instead a polymodal MWD will appear. Therefore, it is important to work under relatively pure conditions. Furthermore, initiation has to be rapid, at least comparable to propagation, if narrow MWD should be reached[2,7-9]. The next critical event is propagation (the nature of the propagating chain end) which, considering the scheme 1. 3. and the concept introduced in scheme 1. 1. can be guided into the wanted direction by additives like electron donors (EDs).

1. 1. 2. Monomers

Isobutylene is the most explored monomer which is polymerized by controlled/living cationic polymerization, but of course other types of monomers can also be used. The requirement for polymerization to develop a carbocation which can be sufficiently stabilized (resonance forms/hyperconjugation). The monomer as an element in a polymerization system can possess several function[10]. A slow decomposition has been detected when [M] approaches zero, indicating that monomers have some kind of stabilization effect on the growing chain end due to the formation of a monomer/chain end complex. An interesting detail regarding this effect could be the results (e.g. MWD) obtained by a continuous monomer addition. Some research concerning this topic has been pursued[11], but the results are not really satisfactory (PDI=1.2-1.4). However, such process might be important for industrial application in the future.

Two types of monomers, olefins (e.g. isobutylene, indene and different kinds of styrene derivatives) and vinyl ethers can be polymerized by controlled/living cationic polymerization. Amphiphilic block copolymers with (meth)acrylates cannot be prepared by cationic polymerization alone, since the ester group of these monomers does not have the ability to stabilize a cation at the chain end. Secondly, the oxygens of the ester group will complex the Lewis acid leading to a deactivated coinitiator and thereby to termination. Particularly the limitation with regard to monomers is a central topic for this project, since block copolymers containing meth(acrylate) segments are of special interest. To overcome this problem, the block copolymers have to be prepared from PIB macroinitiators using either group transfer polymerization or anionic polymerization for the second monomer.

1. 1. 3. Initiating system

The initiator and the coinitiator are the key elements in the controlled/living cationic polymerization system. As described before, a necessary demand to a system where narrow MWD is wanted (PDI<1.2) is that the rate of initiation is much higher than the rate of propagation. For that reason different type of initiating systems exist depending on the monomer used, i.e. olefins and vinyl ethers.

Figure 1. 1. illustrates some of the most used initiators in living cationic polymerization of isobutylene, but they can also be used with other vinyl monomers like styrene derivatives. In the case of the cumyl type initiators, mono-, di- and trifunctional ones are frequently used, which makes it possible to synthesize linear AB and ABA or star-shaped $(AB)_3$ block copolymers[2]. Recently, polyfunctional cumyl type initiators, so-called calix[n]arenes (n=4-8), have been used for the synthesis of PIB-multiarm stars[12].

X′ = $-CH_3$, $-OSiR_3$, $-OCH_3$, -Cl, -H
X = -Cl, $-OCH_3$, -OH, -OAc
R = Saturated/unsaturated alkyl groups

Figure 1. 1.: Typical initiators used in controlled/living cationic polymerization of isobutylene.

The catalyst or coinitiator which is the second part of an initiating system is a Lewis acid (Friedel-Crafts acid), such as $TiCl_4$, BCl_3, $AlCl_3$, $SnCl_4$ or Zn halide[2,13]. The right selection of Lewis acids depends on different factors like the monomer, the M_n of the wanted polymer and the solvent(s), since the crucial point is the acidity of these acids which affects the ionization equilibrium between inactive and active species (see scheme 1. 1.) and thereby, the kinetic events (see scheme 1. 1. and 1. 2.). In addition to this it is also important to note the influence of these processes, in some quenching reactions of the living PIB[14-17].

Especially BCl_3 and $TiCl_4$ are of interest for the polymerization of isobutylene. The BCl_3 system give good results in the low M_n range (M_n = 1000-3000)[18,19]. At higher M_n values precipitation is observed (usually gives broader MWD) because the solvent has to be relatively polar (CH_2CH_2 or CH_3Cl, in which PIB has a low solubility) in order to obtain a certain degree of ionization (see scheme 1) (BCl_3 is a weaker Lewis acid than $TiCl_4$). $TiCl_4$ is normally considered to give the best results for M_n >10000, where the solvent is a mixture of n-hexane and a polar component normally in the range 60:40 to 40:60. Some experiments have been made with $TiCl_4$[20] where prepolymers having Mn in the wanted range where prepared. However, compared to a two-step procedure using BCl_3 in the first one together with $TiCl_4$ in the second one[21,22] the MWD is somewhat broader.

Actually, BCl_3 does not only function as a coinitiator. In some systems it can also initiate the polymerization itself due to self-ionization ($2\ BCl_3 \rightarrow BCl_2^+ + BCl_4^-$)[23,24]. The initiator BCl_2^+ is incorpored into the polymer resulting in a functional head group which can undergo further reactions[25]. This initiating system can compete with, e.g. TMPCl/BCl_3 under certain conditions, leading to two initiating species simultaneously present in the polymerization media. Therefore, careful selection of experimental conditions is necessary in order to minimize the direct initiation with BCl_3 for example, by addition of additives like electron donors (EDs).

1. 1. 4. Solvents

The choice of a solvent or a mixture of solvents is restricted to a few possibilities in controlled/living cationic polymerization of isobutylene, namely because of the solubility of the polymer and the influence of the solvent polarity on the ionization equilibrium of the initiator and the living chain end (see scheme 1. 1.). Another aspect will shall be kept in mind is that the solvent as well as any of the other elements can affect the central steps in a polymerization (for instance can cause transfer). CH_2Cl_2 and a mixture of CH_2Cl_2:n-hexane (40:60 v/v %) are often used. The main problem with CH_2Cl_2 is a relatively high concentration of moisture (about 10^{-3}M). This problem is more or less eliminable with the use of a proton trap. The second complication is that PIBs with a M_n >2500-3000 begin to precipitate in pure CH_2Cl_2 and thereby result in uncontrolled reaction conditions. n-Hexane on the other hand dissolves PIB and is therefore used when high molecular weight material is prepared. However, the presence of n-hexane shifts the equilibrium between inactive and active species toward the inactive one and that is the reason why a strong Lewis acid like $TiCl_4$ is needed when such a solvent mixture is used. Since n-hexane normally is purchased as a technical product special purification is necessary to remove 1-hexene which acts as termination agent. Other solvents like CH_3Cl and CH_2ClCH_2Cl are also well-known solvents for cationic polymerizations.

In general, the change from a non-polar to a polar solvent or visa versa has remarkable effects on kinetic events due to shifts of the equilibria shown in scheme 1. 1. The rate of propagation as well as the rate of initiation are both proportional to the respective ionization constant ($R_p \propto k_p.K_I$, $R_i \propto k_i.K_I'$). Some experiments with vinyl ethers[26] show that the apparent rate constant in CH_2Cl_2 is 40 times higher than in CH_2Cl_2:n-hexane (1:9). MWD is also affected by the solvent. Broader MWD is obtained in a non-polar solvent[7] because K_I and K_I' are influenced by the polarity to a different extent in this case. The kinetics can even be totally modified in some cases when the solvent is changed. For instance, with respect to reaction orders in monomer[27]. The reaction order of different vinyl ethers is zeroth order in n-hexane and first order in toluene or CH_2Cl_2. The explanation for these observations is that competitive interactive interactions of the vinyl ether monomer and the solvent with the living chain end exist. In experiments performed with DiCumOH as initiator, problems arise due to termination caused by indanyl ring formation. If the polymerization is made at a fixed temperature, it can be demonstrated that the polarity of the reaction media has a decisive influence on the relative ratio between the three potential structures[5]. From these considerations concerning the influence of solvents on different parameters in controlled / living cationic polymerization, it can be concluded that it is very important to choose the right solvent for each specific polymerization system.

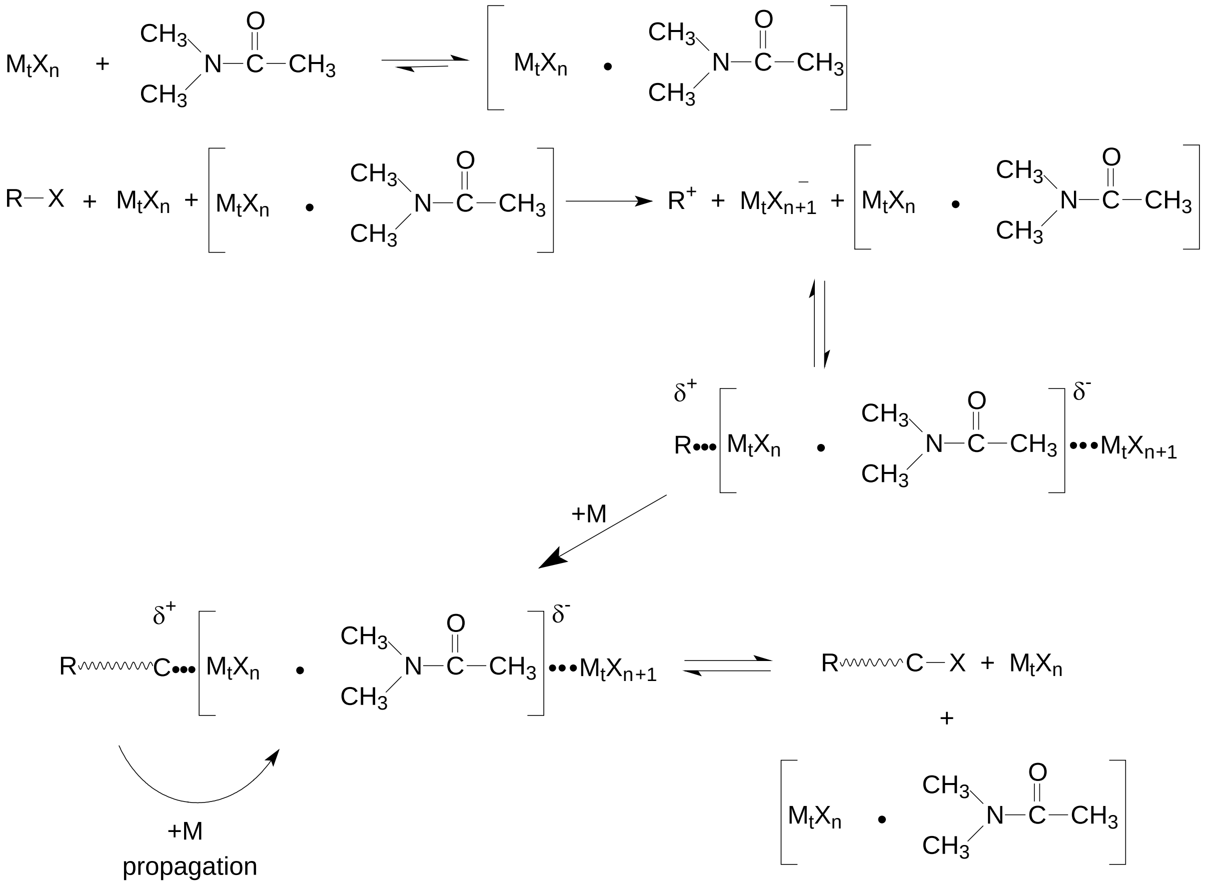
The limitations regarding cationic polymerization are first of all the restricted number of monomers which can be polymerized by this system. Secondly, the experimental setup used in our case is performed in a way where high vacuum-line technique is not necessary, and this caused a limit in regard to M_n ($M_n < 1000000$) due to potential impurities. However, a second problem which may arise at a very high molecular weight is detectable amount of transfer[28].

As discussed above, important features of controlled/living cationic polymerization are the possibility to obtain materials having a well-defined M_n, narrow MWD, and a versatile number of endgroups in quantitative yield which can be utilized for further reactions.

1. 1. 5. Additives

One type of additives are electron donors (EDs). The effect and propose of using EDs is to reduce the net positive charge of the propagating chain end and thereby reduce the rate of propagation and moreover the rate of transfer/termination. Different categories of EDs system exist depending on the way they are formed. The external ED system is made by adding the ED intentionally in order to obtain a Lewis acid/ED complex (see below). In the internal ED system the cation stabilization is achieved by EDs formed in situ during the initiation process due to initiators containing an oxygen atom e.g., an ether or alcohol group[2].

The most decisive objective using ED is the narrowing of the MWD and control of the chain ends. Polymerizations with our initiating system have been made with and without ED, N,N-dimethyl acetamide (DMA)[18,29]. The results clearly show the appreciable change in MWD. Without DMA, PDI = 2.0-3.0 while PDI < 1.4 with DMA. EDs suppress the indanyl ring formation, a potential side reaction when DiCumOH/DiCumCl are used, and chain transfer, just to mention the most important beneficial effects of EDs on MWD[2]. When DMA or other external EDs are used, one shall have in mind the relative proportion between coinitiator and ED. If ED is added in excess [ED]/[coinitiator] > 1 the conversion of monomer is equal to zero, whereas [ED]/[coinitiator] < 1 gives 100% conversion (normally $[I]:[ED]:[M_tCl_n] = 1:1:8\text{-}20$)[30]. DMA and DMSO are strong EDs[31] which means that the electron-pair donating tendency of these compounds is relatively high. The exact nature of the cation modulating effect is still obscure, but the concept of living polymerization with reversible termination (scheme 1) in the presence of EDs, such as DMA or pyridine, is supposed to take place via a complex between the Friedel-Craft acid and the ED[2,20,30,32]. The following scheme illustrates the key events when DMA is used as ED.



Scheme 1. 4.: Polymerization of isobutylene in the presence of an electron donor, e.g. DMA (R: initiator fragment).

In the case of DMA (scheme 1. 4.) coordination/complexation to the Lewis acid can take place with lone-pair electrons either from the oxygen or the nitrogen atom. However, the exact complex structure is not known yet.

Proton traps are a second type of additives added to the cationic polymerization system in order to improve the control of the polymerization. Contrary to EDs, the effect is not attributed to stabilization of the propagating species but to scavenging of protons[30,32-34]. They are strong bases (pyridine derivatives, especially 2,6-di-tert-butyl pyridine (DtBP)) which under ideal circumstances (e.g. homogeneous system) are able only to react with protons and not with other electrophiles. Quantitative results concerning this topic have been published[35]. The conclusion is that the alkyl groups in the 2- and 6-position have to be tert-butyl if the rate constant of reaction with other electrophiles shall be suppressed to an acceptable level. DtBP, a sterically hindered pyridine derivative is used in the same concentration which must be expected in regard to adventitious moisture in CH_2Cl_2 ($\approx 10^{-3}$ M)[36]. A simple way to prove whether or not DtBP abstracts a proton from the propagating end (causing a vinylic endgroup) is the use of ^1H NMR (detection of vinyl proton) and SEC. In the SEC trace a shoulder toward high molecular weight (doubled $M_{w,theo}$) is a direct prove for the interaction between DtBP and the chain end, since the vinyl-capped PIB reacts as a macromonomer with the living chain ends. In the literature the action of proton traps is regard to coupling has been discussed, and there is a pronounced reaction in some cases[37] when DtBP is used in the ratio 1:1 to initiator.

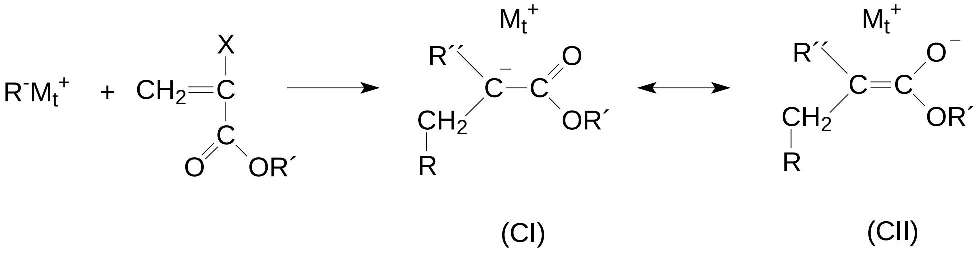
Addition of salts (common ion effect) is the third way to modulate the propagating chain end giving products with narrow MWD, but the concentration has to be in a certain range, or else bimodal MWD is obtained[38]. The effect of salts is realted to shifts in the Winstein spectrum toward the left side, meaning the equilibrium between inactive and active species is shifted to the inactive one lowering the rate of polymerization and the rates of side-reactions[2,38,39].

1. 2. Controlled / living anionic polymerization

1. 2. 1. General concepts of controlled/living anionic polymerization

In contrast to controlled/living cationic polymerization, controlled/living anionic polymerization has to be performed with high vacuum technique because of the sensibility toward, e.g., moisture and oxygen. Due to the use of such a technique, high molecular weight materials (> 100000) are attained. Controlled/living anionic polymerization can be carried out with many different systems. However, as in controlled/living cationic polymerization one has to choose the right conditions: initiator (counterion), solvent(s), additives, etc. for each monomer in order to reach ideal conditions.

In scheme 1. 5. the polymerization of a polar monomer containing an electron-withdrawing side-group is shown. The polar side-group makes the monomer highly reactive and stabilizes at the same time the living carbanion by the formation of an ester enolate.



Scheme 1. 5. The mesomeric structures CI/CII present in controlled/living anionic polymerization of (meth)acrylates (R´´ = CH_3 or H).

Scheme 1. 5. represents the two extreme cases (structures (CI) and (CII), since the actual structure is in between with delocalization of the π-electrons. In a similar way as described in scheme 1. 3., the Winstein spectrum, equilibria between ion pair, solvated ion pairs, free anions, and associated ion pairs exist. Since sometimes more than one of these species are present (in equilibrium) it is crucial that a fast exchange takes place compared to the rate of propagation[40]. If this is not the case, different propagating species would be smultaneously present leading to a broadening of the MWD. Besides, through the addition of additives (e.g. salts, and ligands) the direction of these equilibria can be affected[41]. At this point it is decisive what kind of systems we are dealing with, i.e. he type of solvent, polar (e.g., THF, DME, THP) or non-polar (e.g., toluene, benzene, hexane) and type of monomer, polar (e.g., (meth)acrylates) or non-polar (e.g., styrene). The choice of solvent has dramatic influence on the stereochemistry of the polymerization, and therefore on the Tg of the resulting material[42]. In this project the experiments are carried out with polar monomers, e.g., MMA, DMAA, EO etc. (see below) and mainly in THF. For such a system free anions, contact ion-pairs, and aggregates can exist[43]. The rate of propaation is here much higher for the free anions than for the other two chain ends ($k_p^{(-)} >> k_p^{(\pm)} >> k_p^{agg}$). In case of aggregation, the reaction order regarding the initiator can vary from 1 to 0.5, the latter value corresponding to high extent of dimer aggregation.

1. 2. 2. Monomers

Several classes of monomers can be polymerized by controlled/living anionic polymerization[44]. Non-polar monomers like styrenes and conjugated dienes and polar monomers, e.g., acrylates, methacrylates, vinyl ketones, and vinyl pyridines. Heterocyclic monomers, for example epoxides, lactams etc can be polymerized by ring opening polymerization. Since controlled/living anionic polymerization cannot be performed with monomers having labile protons (e.g., alcohols, acids, and amines) protected monomers are often utilized for the synthesis of hydrophilic or amphiphilic polymers. The requirement for these protecting groups, e.g., acetals, silyl derivatives, and tert-butyl esters[45,46], is that they are stabile in alkaline solution and easy to hydrolyze/remove in acid solution without destroying the polymer itself. In this work the hydrophilic monomers illustrated in figure 2 are of special interest since they are frequently used in the preparation of biomaterials[47-50] and the resulting PIB-based block copolymers are expected to be soluble (micelles) or at least swellable in water. By the polymerization of these monomers, one has to be aware of the possible complications, i.e. the presence of termination (see below). Therefore, careful selection of conditions, e.g., size of counterion is necessary in order to have a polymerization which proceeds in a controlled manner. For instance, the polymerization of N,N-dimethyl acrylamide (DMAA) (structure (II), figure 1. 2.) with Li^+ is heterogeneous since the resulting polymer is insoluble in THF (because of the large isotactic content), with K^+ it is nearly homogeneous and PDI = 1.2-1.3, whereas with Cs^+ it is completely homogeneous and leads to perfect controlled/living anionic polymerization with PDI < 1.1[51]. On the other hand, the best control of the polymerization of MMA and silyl protected HEMAs is obtained with Li^+.

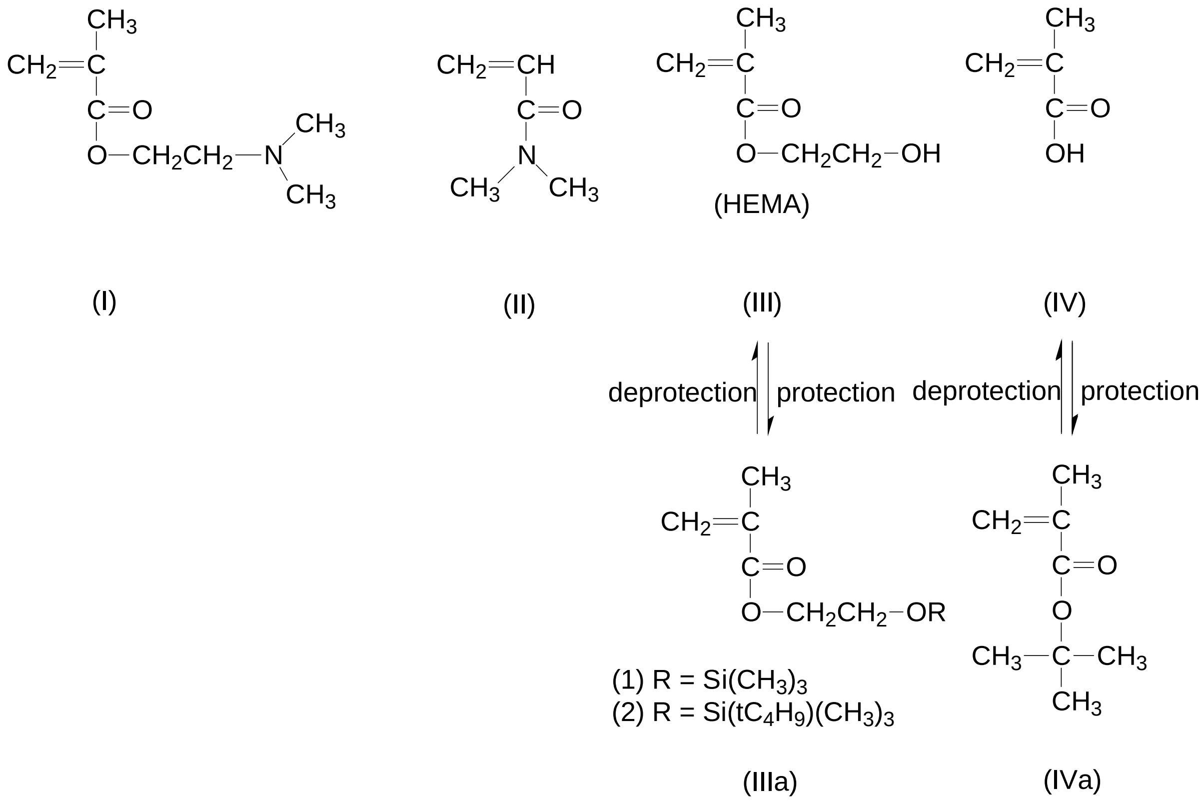
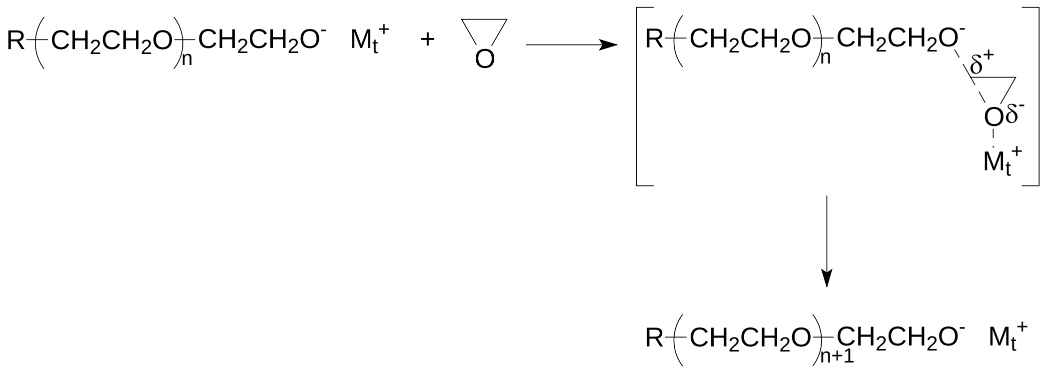


Figure 1. 2. Hydrophilic (meth)acrylic monomers which can be used for the synthesis of amphiphilic PIB-based block copolymers or networks.

For the synthesis of thermoplastic elastomer, monomers like MMA or isobornyl methacrylate[52] are interesting since the heat resistance, i.e. service temperature of the resulting polymer segment, is mainly related to the high T_g.

In polymerization of polar monomers, especially in the case of (meth)acrylates, a few potential termination reactions exist depending on the chosen conditions[53]. Nucleophilic attack at the carbonyl group either on the monomer or the polymer chain is one problem. However, it can be more or less eliminated by careful selection of initiators as discussed below, since attack by the ester enolate anions, i.e. living chain end, has been proved not to be important (and mainly in THF. For such a system free anions, contact ion-pairs, and aggregates can exist[43,54]. Backbiting on the other hand can be a result of several factors, e.g., size of counterion, the polarity of the solvent, monomer concentration, and reaction temperature. Again this side-reaction can be suppressed when the right conditions (e.g. low temperature and large counterion) are found. The consequences of termination, as mentioned before, is poor control of the molecular weight, broad MWD (PDI ≤ 2), difficulties in synthesizing block copolymers by sequential monomer addition, and less than quantitative end-functionalization.

A somewhat different, however, important hydrophilic monomer is EO which is often used for biomedical applications[55]. The controlled/living anionic polymerization of EO can be initiated by many different types of initiators: hydroxides, alkoxides, alkali alkyls etc.[56]. However, one has to be aware of the fact that the polymerization of EO only works with large counterion like potassium or cesium[57]. With lithium, polymerization is not possible, only mono-addition is reached due to the strong bonding between lthium and the alkoxide[58]. The explanatiom for thi difference between the alkali metals is described in the following scheme 6. It takes into account that the ring-opening reaction passes through an intermediate where an electrophilic activation of the epoxide ring is postulated to take place by the counterion[59].

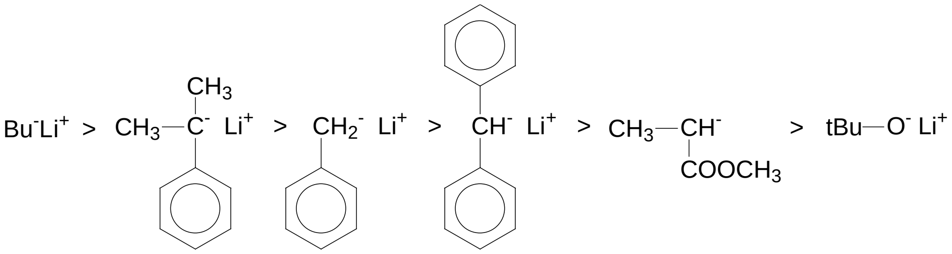


Scheme 1. 6.: Insertion mechanism proposed for the polymerization of ethylene oxide.

With potassium as counterion and a concentration of active chain ends in the range 5.10^{-3} M in THF at room temperature a deviation from the expected first order kinetics regarding initiator, i.e. potassium alkoxide, has been noticed[60]. A reaction order of 0.33 was found. This observation is assumed to be related to aggregation, where an equilibrium between an active unimer and an inactive trimer exists analogous to BuLi in THF[61]. With sodium a reaction order of 0.25, i.e. an association number of 4 was found[60]. The counterion is fixed by the negative charge on the alkoxide, but it also interacts with the solvent, monomer, ligands like crown ethers and cryptands, similar to that descripted above for the (meth)acrylates. By the use of ligands, aggregation can be eliminated leading to straightforward first order kinetics regarding the initiator[56]. The dilution of the active chain ends to below 10^{-4} M also decreases aggregation[56]. In the polymerization of EO, problems regarding termination are not important like for the (meth)acrylates.

1. 2. 3. Initiating system

The reactivity of an initiator depends on the nucleophilicity of the anion, which roughly correlates with the pK_A value of the non-metallated compound. In figure 1. 3. some initiators are shown starting with BuLi which is the most nucleophilic one and some counterions where Li^+ is the smallest and most strongly bonded one.

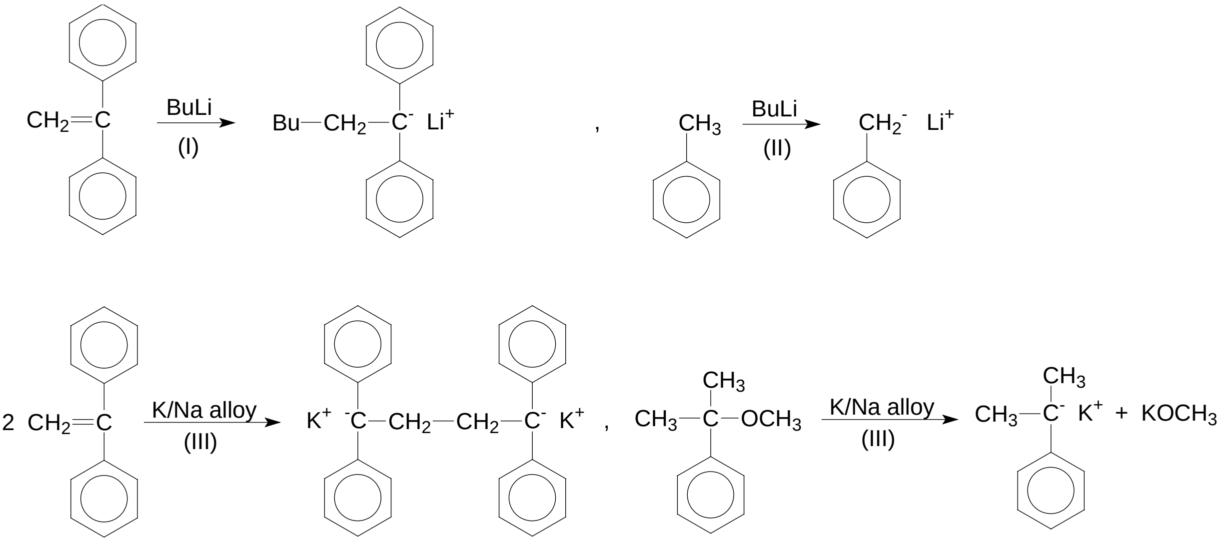


$NR_4^+ > Cs^+ > K^+ > Na^+ > Li^+$

Figure 1. 3. Typical initiators and counterions used in controlled/living anionic polymerization.

The initiators used in this work are all alkali metal based initiators, and since most of the investigated monomers are (meth)acrylates, they have to be sterically hindered (di)phenyl-substituzed carbanions in order to avoid the nucleophilic attack of the initiator on the ester group of the monomer (see above). In case of a non-polar monomer like styrene, BuLi can be used as initiator.

Initiators can be prepared in three different ways (scheme 1. 7.). Either by an addition reaction where, e.g. BuLi reacts with a double bond of DPE, by proton abstraction, by electron transfer reactions, e.g. to the double bond in DPE which leads to coupling of two radical anions[62] or cleavage of an ether bond[63-65].



Scheme 1. 7. Preparation of anionic initiators by different methods.

1. 2. 4. Additives

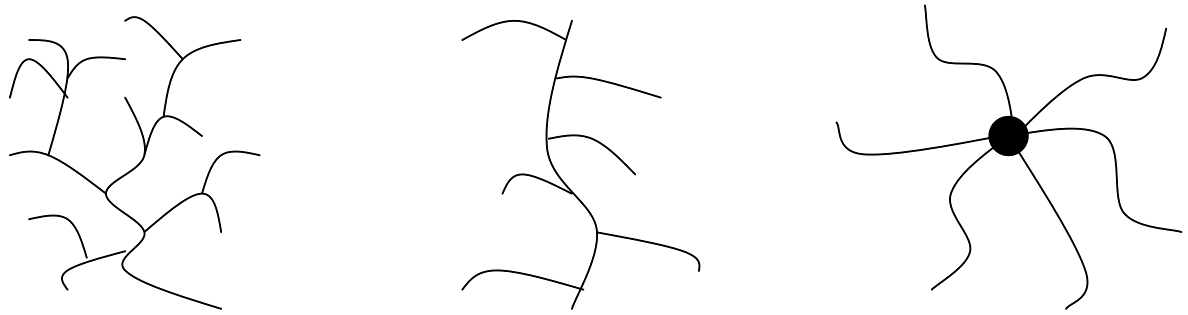
The living chain end can be modified in order to adjust ist reactivity (e.g. controllable rate of propagation) by the addition of additives, like LiCl, TMEDA, crown ethers, lithium alkoxides etc.[66-69]. Based on recent improvements gained by adding LiCl to the polymerization system[41,70-72], it is used as additive and for counterion exchange in the polymerization of different methacrylates in this project. LiCl affects the polymerization in different respects. In exerts a significant effect on both kinetics and MWD, mainly due to depletion of associated ion pairs[72]. Different adducts of living chain ends and living chain ends and LiCl can be formed. The 1:1 complex ($[LiCl]/[I] \leq 1$) has a rate constant comparable to that of the ion pair and the 2:1 complex ($[LiCl]/[I] > 1$) a lower one. Concerning the LiCl to initiator ratio it has been shown that with $[LiCl]/[I] > 10$ no changes, e.g. in MWD, could be detected[73,74]. Therefore, in this project 10 times excess LiCl is used in all experiments. Regarding the tacticity and rate of termination (back-bitting), no influence was observed in THF[74]. However, in a non-polar solvent, toluene/THF (9:1), the syndiotactic placements increase by the addition of LiCl[75].

1. 3. Star polymers

1. 3. 1. General concept of star polymers

Anionic polymerization methods have been used to synthesize a wide variety of macromolecules including linear[76] and cyclic[77] homopolymers, linear copolymers[76], and functional polymers such as macromonomers[78]. These macromolecules are well defined with predetermined molar masses, sharp molar mass distributions, and low compositional heterogeneity. They serve as ideal compounds to establish the relation between structure, properties, and theory.

Branched macromolecules (figure 1. 4.) are more compact than linear homologous ones because of their higher segment densities. The increased segment density results in a decreased tendency for these macromolecules to interpenetrate in solution as well as in bulk. In order to investigate this influence of structure (number of branches, length of branches) on macromolecular properties, well-defined star-shaped macromolecules are required. Statistically, branched polymers are not easily accessible by anionic polymerization. Comb-shaped polymers (figure 1. 1.), constituted of a polymeric backbone carrying a number of side chains usually of the same length and identical chemical nature as the backbone (although this may not always be the case) can be synthesized. Among the various means to access these structures, the copolymerization of macromonomers has proved to be one of the most efficient methods[79,80].



Statistical branching Comb-shaped Star-shaped

Figure 1. 4. Various branched structures.

Star polymers (figure 1. 4.) are characterized as the simplest case of branched species where all chains of a given macromolecule are connected to a single nodulus referred to as the core. The preparation methods and properties of star-branched polymers were examined in detail several years ago by Bywater[81] and more recently by others[82-86].

Star-shaped polymers have gained increasing interest because of their compact structure and high segment density, and because very efficient synthetic methods have made possible the functionalization of the outer branch ends. Until recently, anionic polymerization was one of the best methods to obtain well-defined star-shaped polymers of predetermined branched molar mass. This technique provided the long lifetime for the active sites necessary to allow the formation of star-shaped macromolecules. Anionic polymerization also limited the polymolecularity of the samples. Given the appropriate reaction conditions, the functionality of the core can be controlled in advance.

The various approaches to access star-shaped polymers via anionic polymerization will be presented and discussed in the following sections. Once these star-shaped materials have been characterized, they serve as ideal model compounds, and have been studied extensively with respect to theoritical predictions concerning their solution properties (dilute or semidilute regime) or their solid state properties[87-94].

In the first method, referred to as the "arm-first" method, monofunctional living chains are used as initiator for the polymerization of bifunctional monomers to generate the star core. The "arm-first" method produces homopolymeric or copolymeric star-shaped polymers. The use of a plurifunctional low-molar-mass deactivating agent represents an interesting alternative method for preparing well-defined star-shaped polymers. Recently, the "arm-first" method has been extended to the preparation of star-shaped polymers where polymer chains of different chemical nature are connected to the same nodulus (heteroarm stars).

The second method, the "core-first" method, a polyfunctional core is used to initiate the polymerization of the branches of the star. This method allows for easy access to chain end functionalization by simple deactivation of the active sites. The extension of the "core-first" method to the preparation of functional star-shaped polymers in nonpolar solvents will be discussed.

Star polymers generated using the "core-first" method have a large distribution in functionalities. To minimize the distribution in functionalities of the stars, the "in-out" technique was developed. The "in-out" method is a combination of the two techniques mentioned above and first generates a small "arm-first" star with living active sites, then uses this core to initiate the polymerization of the star branches. The resulting stars can be functionalized, and the control over the distribution in functionalities is greatly improved.

These different star-shaped macromolecules were extensively characterized to confirm the expected structure. Briefly, star-shaped macromolecules exhibit a smaller hydrodynamic volume than linear homologous ones, as is expected from the high segment densities, which lead to higher elution volumes. Size exclusion chromatography (SEC) techniques based on calibration with linear samples were not applicable, but light-scattering methods and SEC with light-scattering detection on-line can be employed. Standard SEC is necessary to qualify unreacted linear branches present in the star molecule. In order to establish the average molar mass of the star-shaped macromolecule, the exact functionality must be known. In the case of star-shaped polymers based on copolymeric branches, the chemical composition of the branches must also be determined using the available classic methods. Star-shaped polymers are also characterized by a decreased radius of gyration, decreased viscosity, and higher translational diffusion coefficients relative to linear homologous macromolecules.

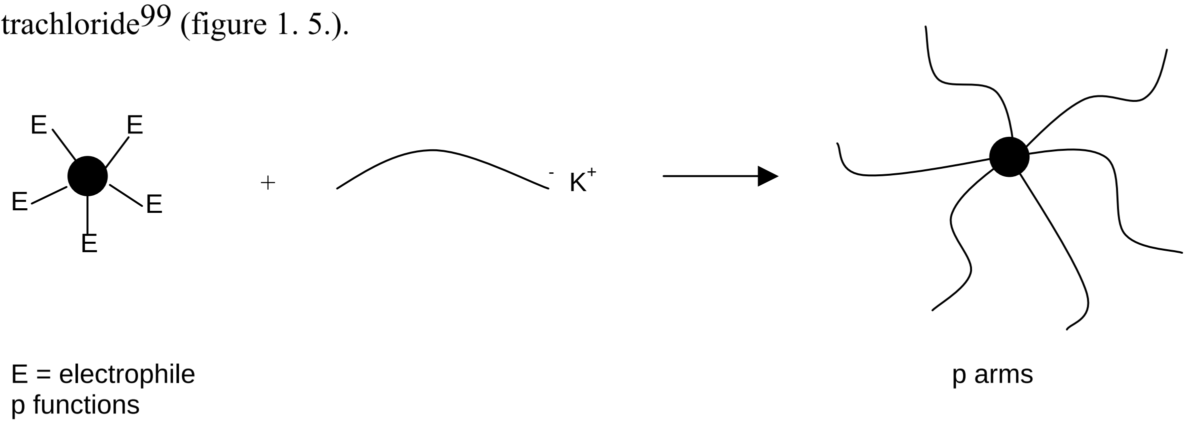
1. 3. 2. Star-shaped polymers via "arm-first" methods

In all "arm-first" methods a living monofunctional polymer of known length and low polymolecularity serves as a precursor. Subsequently, the active sites located at chain end can be used in one of two different ways: either they are reacted with a compound carrying a number of appropriate reactive functions, whereupon chemical links are formed, or they are used to initiate the polymerization of a small amount of an appropriate bisunsaturated monomer, whereupon small crosslinked cores are formed.

1. 3. 3. “Arm-first” methods by deactivation

The living polymer precursor can be reacted stoichiometrically with a plurifunctional deactivator (an electrophilic compound if the sites are anionic), and chemical links are formed between the precursor chains and the deactivator.

The precursor chains become the star branches, and the deactivator becomes the core (scheme 8).The difficulty is identifying compounds carrying a number of equally reactive and equally accessible electrophilic functions needed to control the average number of branches of the stars. The induced deactivation must be fast, quantitative, and free of any side reactions. The limitations encountered include the low functionality of the substances used as deactivators such as chloromethylated benzenes[95,96], trisallyloxytriazines[97,98], and silicon tetrachloride[99] (figure 1. 5.).



Scheme 1. 8. Synthesis of star-shaped polymers via deactivation reaction.

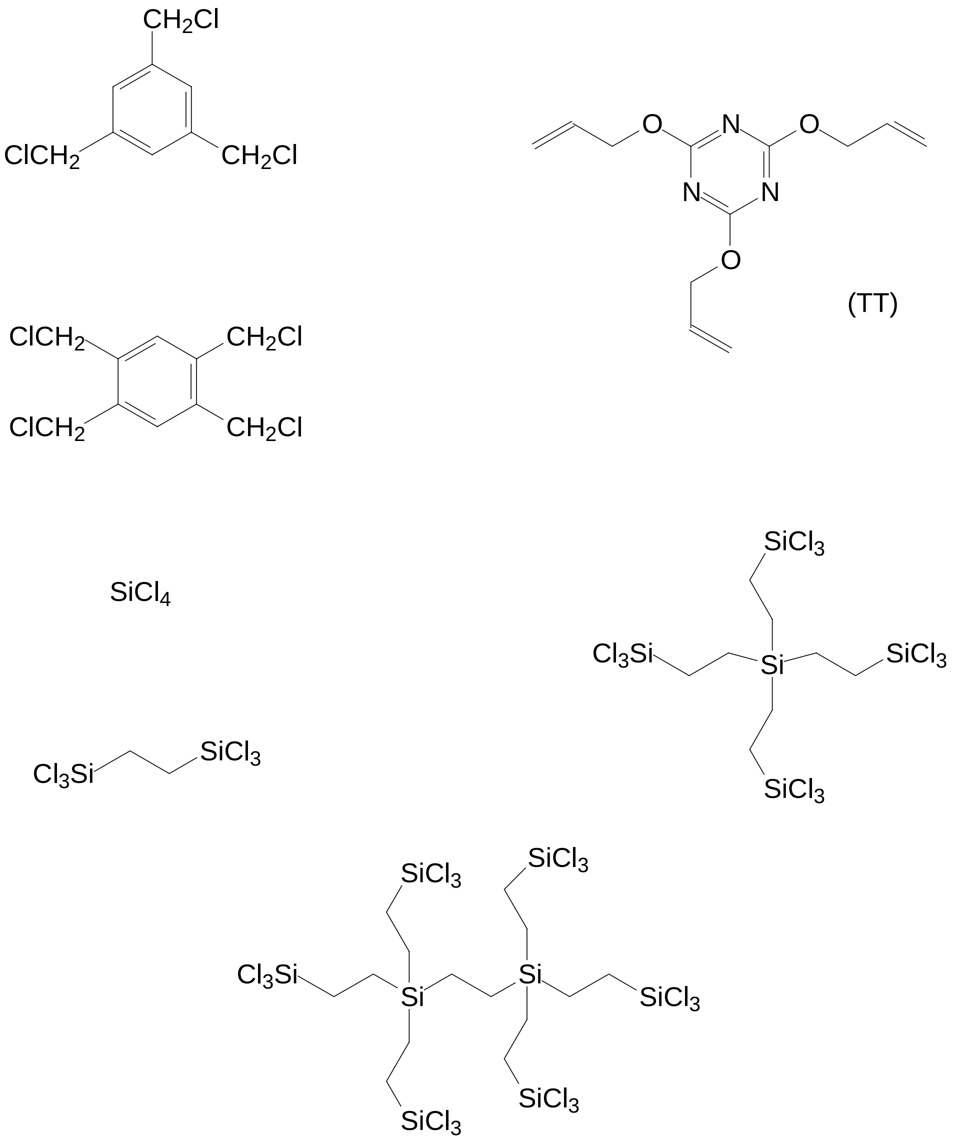


Figure 1. 5. Structures of deactivating agents.

The rate of electrophilic substitution also depends upon the carbanionic chain end: under identical conditions, living polyisoprene (PI) is much more reactive than living polystyrene (PS). As mentioned later in this discussion, Hadjicristidis has taken advantage of this to prepare a new type of star-shaped polymer where the same nodulus carries arms of different chemical nature.

In order to improve the functionalization yields and/or to increase the average functionality of these star-shaped polymers prepared with chlorosilane derivates, Fetters et al. [100,101] have synthesized and used a new generation of chlorosilane compounds of high functionality where the number of chlorine functions is limited to 2 or 3 per silicon and the silicon units are separated by ethylene spacers (figure 1. 2.). In that case, silicon halides react quantitatively, by addition, with carbanions derived from styrene, dienes, and other living polymers. Well-defined star-shaped polymers with up to 128 arms have been obtained[102]. The solution properties of these star-shaped polymers were studied to confirm the expected structure. They have also been used as a model for semidilute and solid state behavior. The properties of these star-shaped polymers would not be affected even if several Si-Cl functions remained unreacted. The number of arms per star molecule is determined by the functionality of the electrophilic compound used provided the yield of the coupling reaction is close to quantitative. Since the fluctuations in length of the branches are averaged, the molar mass distribution in such star polymer samples is expected to be rather narrow. The accurate characterization of star-shaped polymer samples demonstrates the efficiency of the method: the molar mass of the star molecules is very close to the expected value. Therefore, the linking reaction attains high yields despite the bulkiness of these star molecules toward the end of the coupling process.

Similarly, tetrakis[4-(1-phenylvinyl)phenylplumbane] (figure 1. 6.) was also used efficiently as a linking agent: well-defined tetrafunctional PS star-shaped polymers could be obtained in good yields. The procedure was extended to the synthesis of star-shaped polymers containing PS and poly(methylmethacrylate) (PMMA) branches and to the preparation of model networks exhibiting tetrafunctional crosslinking points[103].

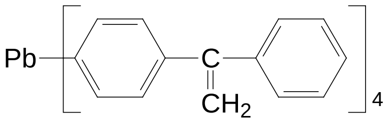
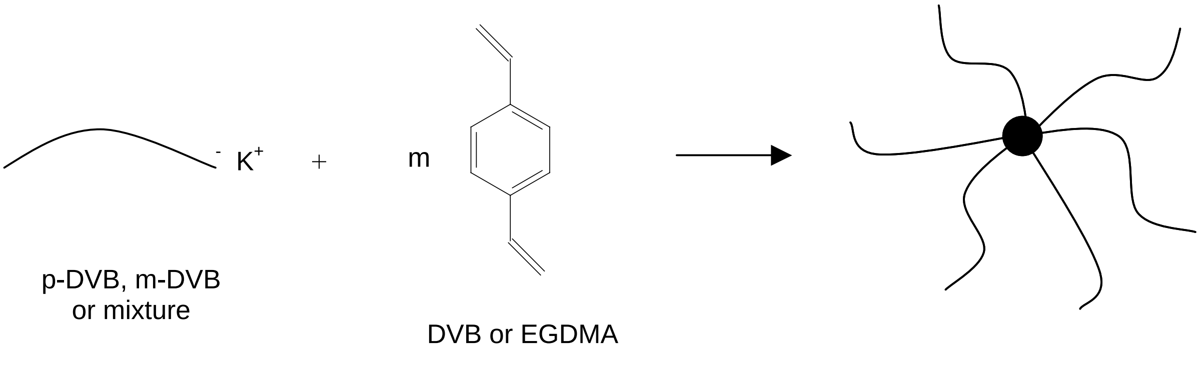


Figure 1. 6. Tetrakis[4-(1-phenylvinyl)phenylplumbane]

Anionic “deactivation” methods have proved their efficiency in the synthesis of star-branched oligomers where the central core is obtained upon reaction of oligobutadienyllithium with diesters and epoxidized soybean oil[104].

1. 3. 4. Star-shaped polymers via difunctional monomers

The monocarbanionic precursor chains can also serve as a efficient initiator for the polymerization of a small amount of a bis-unsaturated monomer, such as divinylbenzene (DVB) or ethylene glycol dimethacrylate (EGDMA) (scheme 1. 9.).



Scheme 1. 9. Star-shaped polymers by anionic block copolymerization.

That procedure was mentioned first by Milkovich[105], developed extensively by Rempp and coworkers[106-109], and later extended by Fetters[110], McGrath[111], Teyssié[112,113], and Hadjichristidis[114]. Upon polymerization of DVB (or EGDMA), small, tighly crosslinked nodules are formed, each of them being connected with the precursor chains that have contributed to its initiation. The branches shield the crosslinked cores to prevent crosslinking between individual star molecules.

In the case of DVB, no gelation has ever been observed in the reaction medium during the formation of the star molecules unless the cores grow very large and constitute more than 40 wt% of the star molecules[115]. The average length of the branches is given by the molar mass of the precursor chains. Although the average functionality of the crosslinked cores is not directly accessible, it can be determined from the ratio of the molar mass of the stars to the precursor polymer (taking into account the weight fraction of the cores). The formation of star polymers by the reaction of monocarbanionic chains with bifunctional polymerizable compounds is a kinetically and mechanistically complex reaction implying the participation of several simultaneous and competitive steps. Some aspects of that point have been discussed by Worsfold[116].

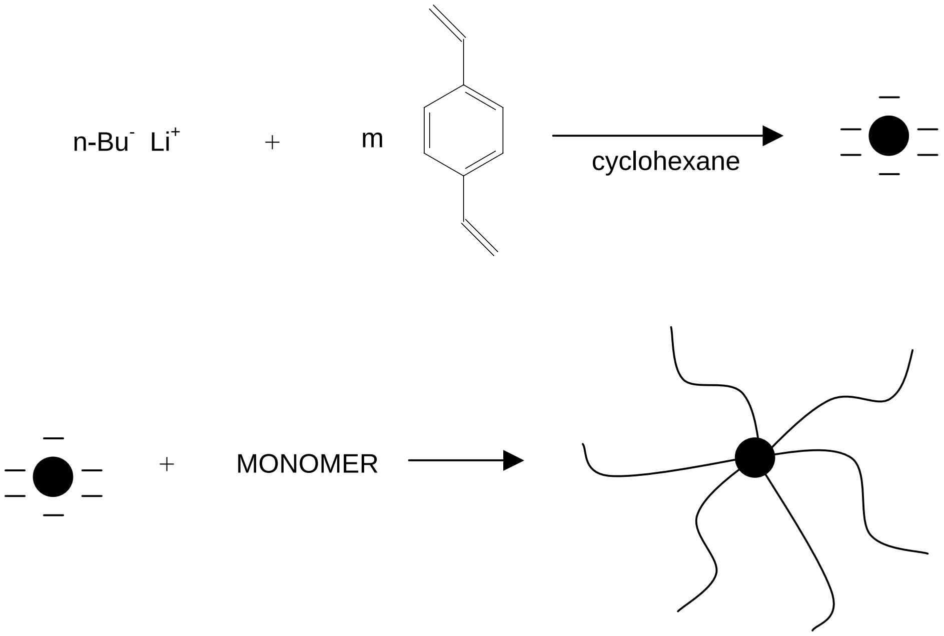
These methods were also applied successfully to the preparation of star polymers exhibiting elastomeric branches (polybutadienyl, polyisoprenyl chains). The crossover copolymerization reactions between the poly(isoprenyllithium) chain ends and DVB and correlatively the homopolymerization of different isomers of DVB were studied in great detal[110]. It was confirmed that the extent of branching increases with reaction time, and that the maximum extent of branching is not reached until the later stage of the reaction. That result was confirmed recently by other methods on the same type of samples[117].

As mentioned by Teyssié and Hadjichristidis, star-branched polymers have been prepared from the reaction of a living poly(methyl metahcrylate) chain prepared by anionic polymerization with ethylene glycol dimethacrylate (EGDMA). The active PMMA chain end initiates the polymerization of the two double bonds within EGDMA. Since no macroscopic gelation of the reaction medium was observed, the structure can be compared to a star-shaped macromolecule exhibiting a small crosslinked microgel in its center. A systematic investigation of that reaction is now under progress in different groups.

Quirk has recently applied that "arm-first" procedure to prepare functionalized star-branched PMMA using a protected hydroxy-functionalized alkyllithium initiator[118].

1. 3. 5. Star-shaped polymers via "core-first" methods

The "arm-first" methods are efficient at synthesizing well-defined star-shaped macromolecules. Difficulty arises, however, in the functionalization of the outer chain ends, which is only possible through the use of functional initiators to generate the precursor chains[118]. "Core-first" methods were developed extensively in polar solvents to access star-shaped macromolecules exhibiting functional groups at the outer chain ends. Once such species are obtained, they can serve as valuable intermediates in the elaboration of a large scope of macromolecular architectures. Attempts to prepare polyfunctional initiators have been descripted by Nagasawa and co-workers[119], who synthesized "core-first" star polymers starting from 1,3,5-tri(α-methoxystyrene), and more recently by Tung and Lo[120] in nonpolar solvents. Popov and Gehrke have worked on the same subject[121]. The most commonly used "core-first" method is actually derived from Burchard´s method[122,123] and requires an efficient soluble polyunctional initiator that can be used in polar solvents (scheme 1. 10.).



Scheme 1. 10. “Core-first” method based on *sec*-butyl lithium and divinylbenzene.

1. 4. Ring-opening polymerization

Aliphatic polyesters are an attractive class of polymer that can be used in biomedical and pharmaceutical applications. One reason for the growing interest in this type of degradable polymer is that their physical and chemical properties can be varied over a wide range by, e.g., copolymerization and advanced macromolecular architecture. The synthesis of novel polymer structures through ring-opening polymerization has been studied for a number of years[124-128]. The development of macromolecules with strictly defined structures and properties, aimed at biomedical applications, leads to complex and advanced architecture and a diversification of the hydrolyzable polymers.

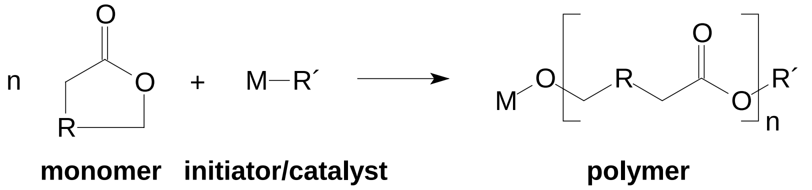
Degradable materials with new mechanical properties and modified degradation profiles have been produced and characterized. The increasing demands of a larger number of biomedical applications have resulted in an increasing interest in producing macromolecules through controlled polymerization.

1. 4. 1. General concepts of ring-opening polymerization

Polylactones and polylactides can be prepared by two different approaches, by the polycondensation of hydroxycarboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique is less expensive than ring-opening polymerization, but it is difficult to obtain high molecular weight polymers, to achieve specific end groups, and to prepare well-defined copolyesters. The ring-opening polymerization of lactones and lactides has been thoroughly investigated during the last 40 years, due to its versatility in producing a variety of biomedical polymers in a controlled manner. Carothers and coworkers first extensively explored the ring-opening polymerization technique for lactones, anhydrides, and carbonates[129-132]. Since then the method has been applied to a diversity of monomers to produce all types of polymers, and a number of initiator and catalyst systems have been developed. In many cases, the resulting polymers exhibit useful properties as engineering materials.

There are several reasons for studying the polymerization of cyclic esters. First, to exploit the potential of synthetic polymer chemistry to prepare a variety of polymers with control of the major variables affecting polymer properties. Experimental conditions have to be optimized in order to find the best polymerization system for a desired technological or industrial process. Factors such as economy, toxicology, and technical apparatus development are important. A second reason for studying ring-opening polymerization is to enable various advanced macromolecules, including homopolymers with well-defined structures and end groups, to be prepared, as well as copolymers with different architectures, e.g., block, graft, or star copolymers. The physical, mechanical, and degradation properties of these various macromolecules are studied to determine the structure-to-property relationship. The third reason for studying these kinds of systems is that they are valuable models for the examination of the kinetics[133] and mechanisms[134] of elementary reactions in polymerization.

Polylactones and polylactides of high molecular weight are exclusively produced by ring-opening polymerization of the corresponding cyclic monomers. A polyester is formed when cyclic esters are reacted with an initiator. Scheme 1. 11. presents the reaction pathway for the ring-opening polymerization of a cyclic ester.



Scheme 1. 11. Schematic representation of the ring-opening polymerization of a cyclic ester (R = $(CH_2)_{0\text{-}3}$ and/or (CHR´´)

Each macromolecule formed generally contains one chain end terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. By altering the catalyst or initiator and the termination reaction, the nature of the functional groups can be varied to fit the application of the polymer. The types of initiator and end group play important roles in determining both the thermal stability and hydrolytic stability of the resulting polyester[135-137]. Functional groups accessible to post-polymerization reactions can also be introduced into the polymer structure in this way.

The ring-opening reaction can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion[138,139]. Under rather mild conditions, high-molecular weight aliphatic polyesters of low polydispersity can be prepared in short periods of time. Problems associated with condensation polymerization, such as the need for exact stoichiometry, high reaction temperatures, and the removal of low molecular weght by-products (e.g., water) are excluded in ring-opening polymerization[140].

Depending on the initiator, the polymerization proceeds according the three different major reaction mechanisms[141], viz. cationic, anionic, or "coordination-insertion" mechanisms[142-144]. In addition, radical, zwitterionic[145], or active hydrogen[141] initiation is possible, although such techniques are not used to any great extent.

1. 4. 2. Monomers

Biodegradable polymers are receiving increasing attention for their use in a wide variety of surgical and pharmaceutical applications[146] as well as in disposable package[147]. Novel synthetic polymer materials may provide considerable improvement in medical applications due to their tailored thermal and mechanical properties and their decomposition to non-toxic products. Among various families of biodegradable polymers, aliphatic polyesters have a leading position since hydrolytic and/or enzymatic chain cleavage yields hydroxy carboxylic acids, which in most cases are ultimately metabolized[146,148,149]. Typical examples of synthetic, biodegradable polymers used in medical applications are polylactide[148], polyglycolide[150], and poly(ε-CL) [151]. The key properties, e.g., the rate of degradation, tensile properties, and surface chemical composition, can be optimized by copolymerization[152] or blending of homo- and/or copolymers.

1. 4. 2. 1. Lactide (LA)

Due to the presence of two chiral centers, there are three forms of the lactide monomer (figure 1. 7.). Repeating units with different configurations have been used to produce stereocopolymers where the physical and mechanical properties and the rate of degradation are easily adjusted.

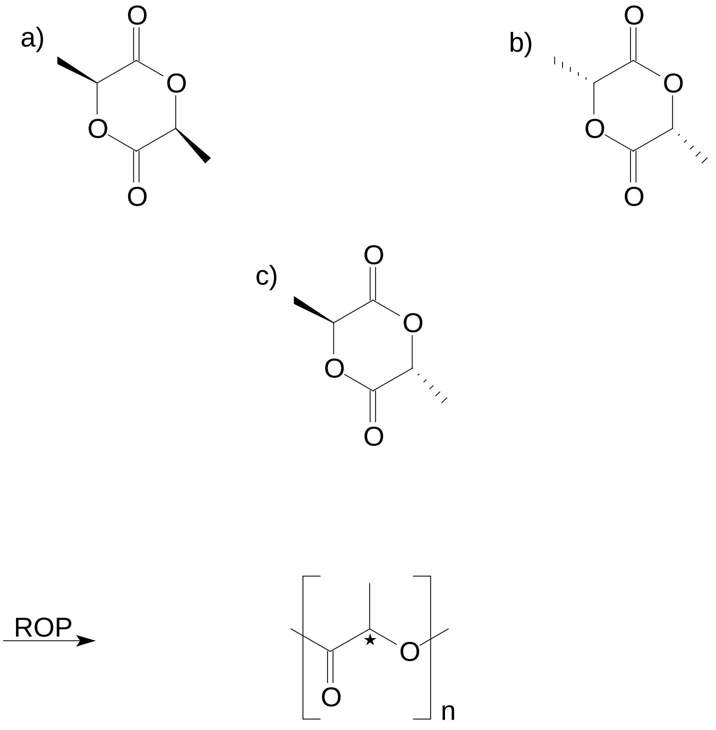


Figure 1. 7. Structure of the different stereoforms of the lactide monomer and the resulting repeating unit, the chiral center marked with *. a) L,L-LA, D,D-LA, and c) meso-lactide.

The most efficient way of preparing polylactides is ring-opening polymerization by coordination initiators[153]. This method usually allows a controlled synthesis leading to quite a narrow MWD. Polymerization of the different stereoforms results in materials with different properties. The polymers derived from the pure L-LA or D-LA monomers are semi-crystalline, relatively hard materials with melting temperatures around 184 °C[154] and glass transition temperatures of about 55 °C[155]. The L,L-lactide and D,D-lactide are normally termed L-lactide and D-lactide, respectively. Polymerization of the *rac*-(D,L)-lactide and meso-lactide results in an amorphous material with a glass transition similar to that of the semi-crystalline counterparts[154]. Polylactides are highly sensitive to heat, especially temperatures higher than 190°C. Heating these materials above this temperature results in a noticeable decrease in the weight-average molecular weight[154].

Poly(L-lactide) is biocompatible and when it is implanted in the body, it will in the course of time undergo hydrolytic scission to lactic acid, which is a natural intermediate in carbohydrate metabolism[148]. The in vitro degradation of poly(L-LA) is generally rather slow compared to the degradation of poly(D,L-LA). The higher degradability is probably due to the greater water absorption in the amorphous domains. Copolymers of L-lactide with several types of monomers, e.g., glycolide, or ε-CL, have been investigated[156]. Copolymerization is an important tool to modify the properties of the resulting copolymers and adjust them to the needs of a given application.

The crystallinity, brittleness, and melting point of poly(L-LA) can be decreased by incorporation of comonomer units such as 1,5-dioxepan-2-one (DXO). The large difference in reactivity ratio between the DXO and the lactides leads to a microstructure with a more block-like nature than is expected from a random copolymerization[157]. The copolymers have properties very different from those of the homopolymers. They show a low stiffness and high elasticity compared to poly(L-LA). The DXO/LA copolymers are interesting materials with possible applications in, e.g, the biomedical field[158]. The in vitro/in vivo degradation has been studied and it was found that the copolymer was hydrolysed mainly by ester bond cleavage[159,160].

1. 4. 2. 2. ε-Caprolactone (ε-CL)

Poly(ε-CL) has been investigated thoroughly because of the possibility of blending this aliphatic polyester with a number of commercial polymers such as PVC and bisphenol A polycarbonate[140]. It is of interest as a packaging material and in biomedical applications since it is degradable and its degradation products are non-toxic. Figure 1. 8. shows the monomer structure and the resulting repeating unit.

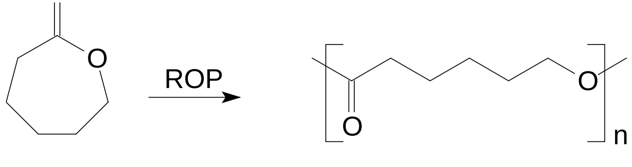


Figure 1. 8. The chemical structure of ε-CL and the resulting repeating unit

The poly(ε-CL) material has a long degradation time, which is usually a disadvantage in medical applications. The in vivo degradation of poly(D-LA) was 2.8 times faster than that of the poly(ε-CL) chain cleavage under the same conditions[152]. Different approaches have been used to copolymerize ε-CL to increase the degradation rate. Copolymers of ε-CL and D-LA of all compositions degraded much more rapidly than their component homopolymers[152]. This observation has been attributed to morphological differences, specifically a reduction in crystallinity and a lowering of the glass transition temperature.

Random copolymers of ε-CL with 1,5-dioxepan-2-one (DXO) have been investigated[161-163]. The copolymers were crystalline up to a DXO content of 40%, and it was concluded that the DXO units were incorporated into the poly(ε-CL) crystals. The block copolymerization has also been investigated and the resulting material was shown to exhibit thermoplastic elastomeric properties[164].

1. 4. 3. Initiating system

The synthesis of novel initiators and the ring-opening polymerization of existing or new monomers and macromonomers substituted with functional groups provide a very interesting and promising strategy for producing structurally advanced macromolecules.

A large variety of organometallic compounds, e.g., metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis[165]. Many reactions catalysed by metal complexes are highly specific and, by careful selection of metal and ligands, reactions can be generated to form a desired polymer structure[166,167]. The covalent metal alkoxides with free *p* or *d* orbitals react as anionic or cationic initiator[168]. Figure 1. 9. summarizes some of the most frequently used initiators and catalyst.

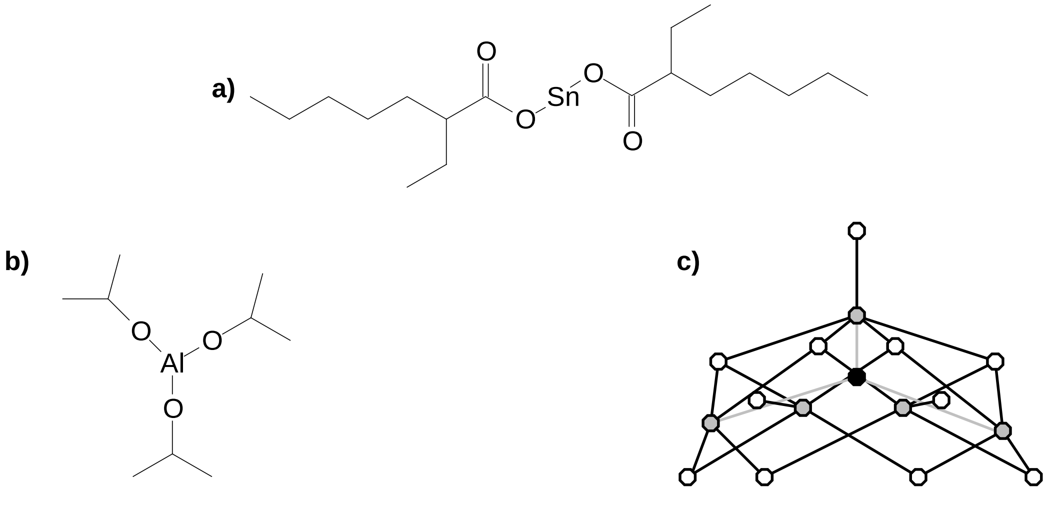
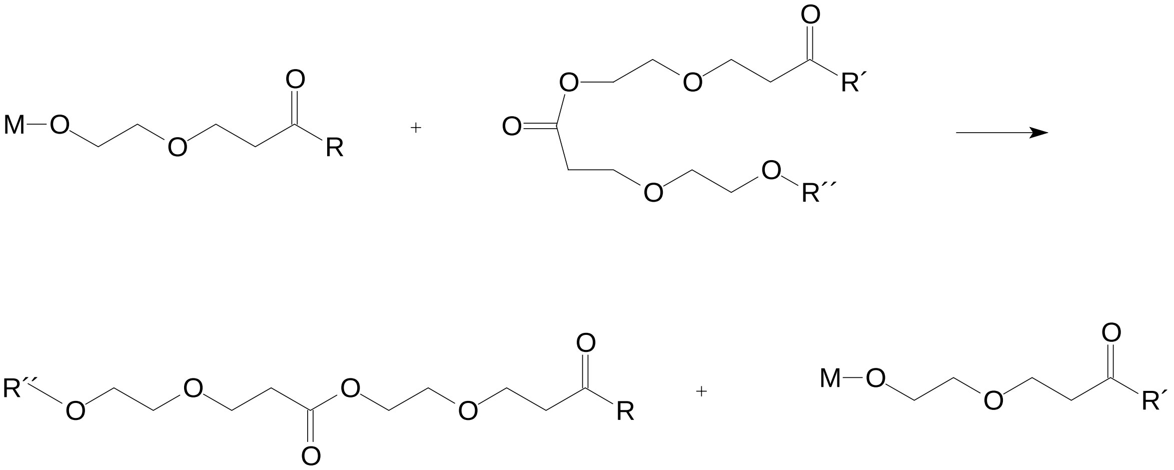


Figure 1. 9. Chemical structure of initiators used in ring-opening polymerization of lactones and lactides. a) stannous octoate, b) aluminium isopropoxide, c) lanthanide isopropoxide. Lanthanum atoms are represented by grey circles and oxygen atoms by white cirles. The black circle represented the bridging oxygen atom connecting all lanthanum atoms. Alkyl groups are omitted for clarity.

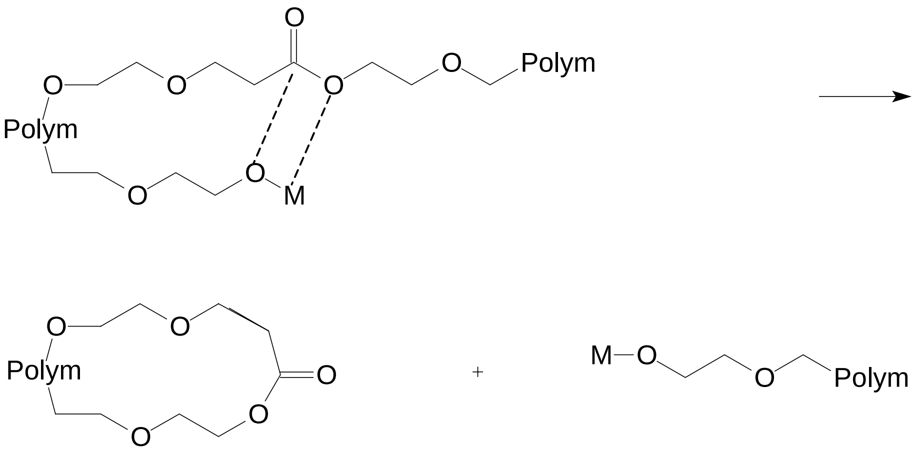
1. 4. 3. 1. Transesterification reactions

It is well known from the ring-opening polymerization of lactones and lactides that transesterification reactions occurs at elevated temperatures[169], or at long reaction times (scheme 12) [170]. Intermolecular transesterification reactions modify the sequences of polylactones and prevent the formation of block copolymers. Intramolecular transesterification reactions, i.e., back-biting, cause degradation of the polymer chain and the formation of cyclic oligomers[171]. Both types of transesterification reaction broaden the molecular weight distribution (MWD).

Intermolecular transesterification



Intramolecular transesterification



Scheme 1. 12. Reaction schemes for intermolecular and intramolecular transesterification reactions.

As displayed in the proposed scheme, each intramolecular transesterification randomly breaks the polymer chain. In this way, an attack on the polymer chain leads to a free residual polymer and a new randomized, modified polymer. Consequently, an original copolymer with a block-like structure would be converted to a randomized copolymer after undergoing n transesterifications[172,173].

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator[174]. Depending on the metal used, the initiator is more or less active towards side-reactions such as transesterification reactions[168,174]. The relative reactivity of different metal alkoxide initiators towards chains already formed has been reported to be: $Bu_2Sn(OR)_2 > Bu_3SnOR > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$[174].

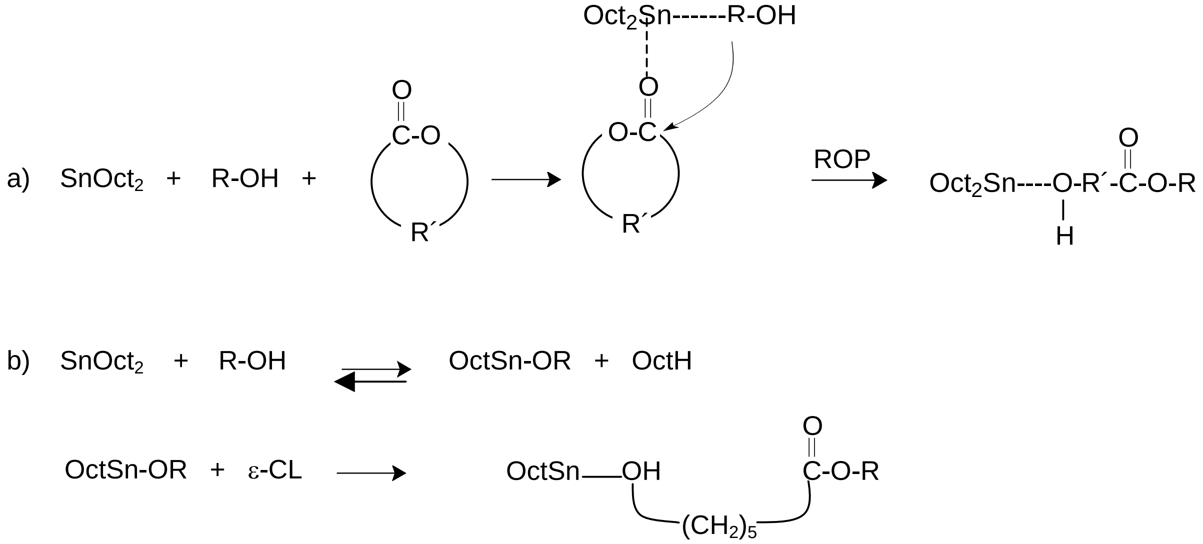
The lactide configuration influences the extent of the transesterification reactions taking place during polymerization[175]. The contribution of transesterification processes in the case of D,L-lactide (D-LA) was found to be considerably higher than that observed when L,L-lactide (L-LA) was polymerized. The difference in the number of side-reactions was attributed partly to the polymer chain stiffness. The poly(D-LA) is more flexible than the poly(L-LA) due to the atactic lactide blocks.

When ε-CL and L-LA are block copolymerized, the monomer addition sequence is very important. AB block copolymers can be prepared by ring-opening polymerization with $SnOct_2$ as catalyst and ethanol as initiator provided that ε-CL is polymerized first[176]. If the L-LA block is synthesized first and the hydroxy-terminated macroinitiator formed is used to initiate polymerization of ε-CL, the polymer formed is totally randomized.

1. 4. 3. 2. Tin(II) 2-ethylhexanoate

Tin(II) 2-ethylhexanoate, commonly referred to as stannous octoate ($Sn(Oct)_2$), is a frequently used catalyst in the ring-opening polymerization of lactones and lactides[157,161,172,177-179]. $Sn(Oct)_2$ has been approved as a food additive by the American Food and Drug Administration (FDA). The mechanism of polymerization has been widely discussed. Despite several proposals[134,176,180,181] over a long period of time, it is not until now that the ring-opening polymerization mechanism is about to be elucidated[182-185]. The $Sn(Oct)_2$ is not thought to be the actual initiator since the molecular weight does not depend on the monomer-to-$Sn(Oct)_2$ molar ratio. The true mechanism is a coordination-insertion mechanism where a hydroxy functional group is thought to coordinate to $Sn(Oct)_2$, forming the initiating tin alkoxide complex.

Investigations of the coordination-insertion mechanism have resulted in two slightly different reaction pathways. Kricheldorf and coworkers have proposed a mechanism[134,184] where the co-initiatiing alcohol functionality and the monomer are both coordinated to the $Sn(Oct)_2$ complex during propagation. Penczek and coworkers have presented a mechanism[180] where the $Sn(Oct)_2$ complex is converted into a tin alkoxide before complexing and ring-opening of the monomer. Direct observation of this tin alkoxide complex has been reported by using MALDI-TOF spectroscopy for both lactide[183] and ε-caprolactone[182] polymerization. Scheme 13 shows the two different proposals.



Scheme 1. 13. The main ring-opening polymerization mechanism proposals with Sn(Oct)$_2$ as catalyst, a) complexation of a monomer and alcohol prior to ring-opening polymerization and b) formation of a tin-alkoxide before ring-opening polymerization of ε-caprolactone (ε–CL).

SnOct$_2$ catalyst is a strong transesterification agent, and the resulting copolymers normally have a randomized microstructure[170]. An increase in reaction temperature or reaction time increases the amount of transesterification reactions.

The ring-opening polymerization of lactide with SnOct$_2$ is fairly slow and it is desirable for economic and commercial reasons to increase the rate of polymerization. The addition of an equimolar amount of triphenylphosphine increases the rate and, as an additional advantage, this compound delays the occurrence of the undesirable backbiting reactions[186].

1. 4. 3. 3. Aluminium tri-isopropoxide

Ring-opening polymerization initiated with aluminium tri-isopropoxide has been extensively investigated by several research groups[164,171,174,187-190] since it yields well-defined polymers through living polymerization[191].

Polymerization with aluminium tri-isopropoxide is assumed to proceed through a coordination-insertion mechanism, which consists of monomer complexation to the active species and insertion by rearrangement of the covalent bonds. The mechanism leads to cleavage of the acyl-oxygen bond of the monomer and of the metal-oxygen bond of the propagating species. The propagation is characterized by the almost total absence of side-reactions such as transesterification reactions, at least until complete monomer conversion has occurred[169,188,192]. Some results indicate that transesterification reactions may take place during the polymerization of L-LA[192]. However, the main rearrangement of the polymer occurs when the monomers are completely consumed. The initiator is active at low temperatures (reaction temperatures of 0-25 °C are often reported) and the initiator is preferentially used in solution polymerization.

Most metal alkoxides are aggregated in solution and, as a result, an induction period during which the initiator is rearranged to form the active species often characterizes the polymerization. Only a few of the M-OR bonds are not involved in coordination to the metal atom and can consequently behave as initiation centers. The type and size of the aggregates depend on the solvent polarity, the nature of the substituents, and the presence of coordinative ligands such as amines[193] and alcohols[194,195]. The groups involved in coordinative aggregation are not active in propagation. Significant advances in the understanding of the "coordination-insertion" ring-opening polymerization mechanism have been made through the kinetic studies of Duda and Penczek[133,171,193,194].

Recently, systems have been developed where the aluminium alkoxide is covalently bound to solid porous silica[196]. This system takes advantage of the exchange reaction between the alkoxide and the hydroxy-terminated free molecules to produce a catalyic process, i.e., to produce a larger number of polymer chains than aluminium complexes present. The initiator/catalyst used can easily be recovered by filtration and recycled. In addition, the polymers obtained are free from metal residues.

1. 4. 3. 4. Tin(IV) alkoxides

Monotin alkoxides, tin dialkoxides and cyclic tin alkoxides have been utilized as initiators in the ring-opening polymerization of cyclic esters. The tin alkoxides are known to form cyclic species during synthesis and the dibutyltin alkoxides are known to exist as monomers and dimers[197]. The cyclic tin alkoxides were originally studied because of their resistance towards hydrolysis[198]. The tin alkoxides have been reported to be effective transesterification catalysts initiating polymerization at moderate temperatures[199].

The tributyl derivatives have been thoroughly studied since they are easily synthesized by nucleophilic substitution of commercial tributyltin chloride, they are easy to handle due their moisture resistance, and they are relatively soluble in lactones[200].

The polymerization of lactones with tin alkoxides is thought to follow the coordination-insertion mechanism. The ring-opening of the monomer proceeds through acyl-oxygen cleavage with retention of the configuration. Tin (IV) complexes have been used to produce predominantly syndiotactic poly(β-hydroxybutyrate) [201,202], macrocyclic poly(β-hydroxybutyrate) [203], poly(ε-CL), and polylactide[199,200,204].

The cyclic tin alkoxides have the additional advantage of offering a convenient synthetic pathway for the synthesis of macromonomers, triblock, and multiblock copolymers[204,205]. Macromonomers from L-LA, ε-CL[206], and 1,5-dioxepan-2-one (DXO)[Stridsberg, 1999 #222 have been synthesized as well as triblock poly(L-LA-b-DXO-b- L-LA) [207] and multiblock copoly(ether-ester) from poly(THF) and ε-CL[208]. The polymerization proceeds by ring expansion and the cyclic structure is preserved until the polymerization is quenched by precipitation.

1. 4. 3. 5. Tin(II) alkoxides

Recently, tin (II) butoxide was used in the polymerization of L-LA[209]. The initiation is fast and quantitative and no transesterification or back-biting reactions are observed. The reaction proceeds with acyl-oxygen bond scission with retention of the configuration, and can be used both in bulk and solution (THF, 20-80 °C) polymerization. It is possible to control the molecular weight in the range of 10^3 to 10^6 with a PDI of 1.15-1.85. The polymerization is very fast, $k_p=5.10^{-1}$ $mol^{-1}.L.s^{-1}$, with only the rare earth alkoxides being faster.

1. 4. 3. 6. Lanthanide alkoxides

Ring-opening polymerization of lactones and lactides using lanthanide alkoxide-based initiators is another discovery. The first example of lactone polymerization by lanthanide alkoxide complexes was reported in a DuPont patent written by McLain and Drysdale in 1991[210]. In general, the activity of these catalysts is much higher than that determined for aluminium alkoxides, especially in lactide polymerization[211-213]. Polymers of relatively high molecular weight and narrow MWD are formed. The negative side-reactions such as macrocycle formation, transesterification, and racemization are absent.

Yttrium isopropoxide and yttrium 3-oxapentoxide initiators were the first lanthanide alkoxides described in the literature for the ring-opening polymerization of ε-CL[214]. The discovery of lanthanide-based initiator systems allowed the block copolymerization of ε-CL with compounds such as ethylene[215], tetrahydrofuran[216], L-LA[217], trimethylene carbonate[218], and methyl methacrylate[219]. This type of initiator has also been used to prepare poly(β-butyrolactone)s[220,221].

1. 5. Polymerization of thiophene

1. 5. 1. General concepts of the polymerization of thiophene

In the late 1970s, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of electronic and optical devices. It now appears with the discoveries of, for example, organic light emitting diodes (OLEDs)[222] and organic transistors[223] that new technologies are eminent. Polythiophenes are an important representative class of conjugated polymers that form some of the most environmentally and thermally stable materials that can be used as electrical conductors, non-linear optical devices, polymer LEDs, transistors, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices[224,225]. Polythiophene and its derivatives work very well in some of the above applications and less impressively in other devices. Creative new design and development strategies of new polythiophenes has led to captivating new materials and enhanced performance in certain devices. The ability of molecular designers to begin to understand how to gain control over the structure, properties, and function in polythiophenes continues to make the synthesis of polythiophenes a critical subject in the development of new advanced materials. Here we attempt to review the synthesis of polythiophenes comprehensively. Due to the enormous literature on the synthesis of polythiophenes, we are sure that excellent work in this area will be inadvertently overlooked. However, we will highlight both the pioneering work and the frontier in the synthesis of polythiophenes.

It is important to realize that, as it as become clear that structure plays a dominant role in determining the physical properties of conducting polymers, more research has focused on directing structure and function of these materials with synthesis. Synthesis can help to determine the magnitude of π overlap along the backbone and eliminate structural defects. Materials assembly (and/or processing) determines interchain overlap and dimensionality. Planarization of the backbone and assembly of the backbone in the form of π stacks lead to better materials and enhanced device performance in almost every category ranging from electrical conductivity to stability. Therefore, both remarkable enhancements in the electronic and photonic properties of the resultant materials and the creation of new functions, such as new sensory materials, critically depends on the synthesis of the polythiophene. This of course leads to the exciting prospect that the properties of the polythiophenes can be selectively engineered through synthesis and assembly. A large portion of both the pioneering and future work in conjugated polymers strongly depends on synthetic chemists creating new polymers that can be fabricated into new devices and whose physics and chemistry can be deeply understood.

Polythiophene is environmentally stable and highly resistant to heat. Usually, conjugated molecules and polymers are labile to oxygen. β-Carotene and polyacetylene are easily attacked by oxygen and their conjugated systems are interrupted by sp^3 carbon atoms. Due to the stability of neutral polythiophene, great progress in the chemistry of polythiophene has been made in the last decade. Many polythiophene derivatives have been prepared and their properties clarified. Now we know how to give desirable properties to polythiophenes to some extent. Improvements in polymerization procedures have produced polymers with a highly regular structure, which has significantly enhanced the performance of polythiophenes. The chemistry of polythiophene is developing rapidly and many industrially useful materials will be discovered.

Polythiophene has been prepared first by electrochemical polymerization. Since a film is produced on the anode during polymerization, this method is suitable for the preparation of polymers such as polythiophene and poly(3-methylthiophene), which are not processable after polymers are formed. However, in electrochemical polymerization, the yield of polymers is low and the polymers often do not have a well-defined structure. On the other hand, since facile oxidative polymerization with iron (III) chloride produces polythiophene in a high yield, this method is suitable for processing polythiophenes such as poly(3-alkylthiophene). The molecular weight of polymer obtained by this method is sufficiently high for a film to be cast. The method has contributed much to advances in the science of polythiophenes.

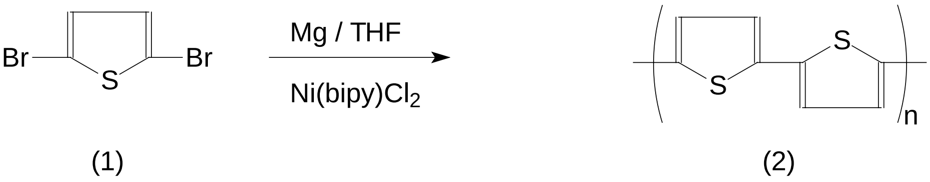
Grignard coupling is also an important route to polythiophenes. Polymers produced by this method often show lower conductivity than those obtained by other methods. This technique is still important for the preparation of polymers with a well-defined structure, since no migration of substituents takes place during the coupling reaction.

NMR studies of poly(3-alkylthiophenes) have indicated that this polymer has a number of irregular couplings about the position of the alkyl groups. These are referred as head-to-head and tail-to-tail couplings. Regioregular poly(3-alkylhiophenes) have longer π-electron conjugation along the polymer backbone and show higher conductivity. In addition, it has a higher stability in the doped state and self-organizing properties. McMullough *et al.* [226] prepared the regioregular polymer by Grignard coupling and Rieke *et al.* [227-231] by the coupling of 2-bromo-5-bromozincio-3-alkylthiophene.

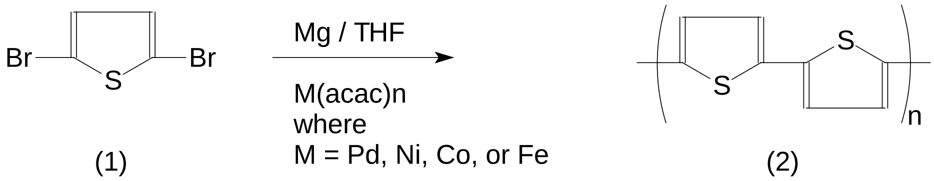
1. 5. 2. Chemical synthesis of unsubstituted polythiophene (PT)

One of the first chemical preparations of unsubstituted polythiophene was reported in 1980 by two groups[232,233]. Both synthesized polythiophene by a metal catalyzed polycondensation polymerization of 2,5-dibromothiophene (scheme 1. 14.). Yamamoto´s synthesis treats 2,5-dibromothiophene (1) with Mg in THF in the presence of nickel(bipyridine) dichloride. The Mg reacts with either bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromo-thiophene, which is self-coupled with the Ni(II) catalyst to form a thiophene dimer carrying a MgBr unit at one end and a Br at the other. This condensation reaction is propagated and eventually low molecular weight polythiophene is formed. The polymerization is the extension of Kumada coupling of Grignard reagents to aryl halides[234]. Since polythiophene, even at low molecular weights, is insoluble in THF, the precipitation of the polymer under the above reaction conditions limits the formation of higher molecular weights. The polythiophene synthesized by this method leads to 78% insoluble polymer that does not melt. The soluble fraction is lower molecular weight oligomers. Polythiophene of molecular weight greater than 3000 is not soluble in hot chloroform[235]. The elemental analysis of this polymer indicated that 1-3% Mg remains in the polymer sample. Similar results were found by Lin and Dudek. Polymerization of 2,5-dibromothiophene in the presence of Mg in THF using either palladium(acac)$_2$ (acac = acetylacetonate) or Ni(acac)$_2$ or Co(acac)$_2$ or Fe(acac)$_3$ catalyst yields low molecular weight polythiophene containing at 3% impurities as determined by elemental analysis.

Yamamoto Route

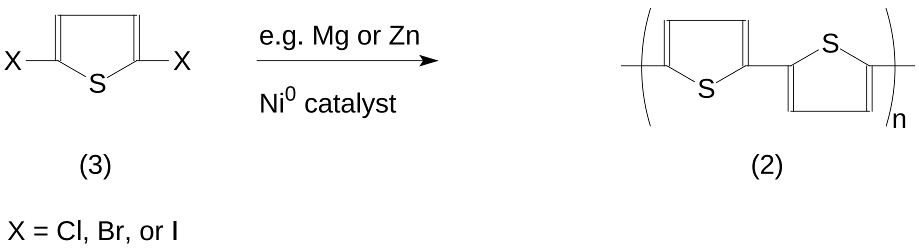


Lin and Dudek Route



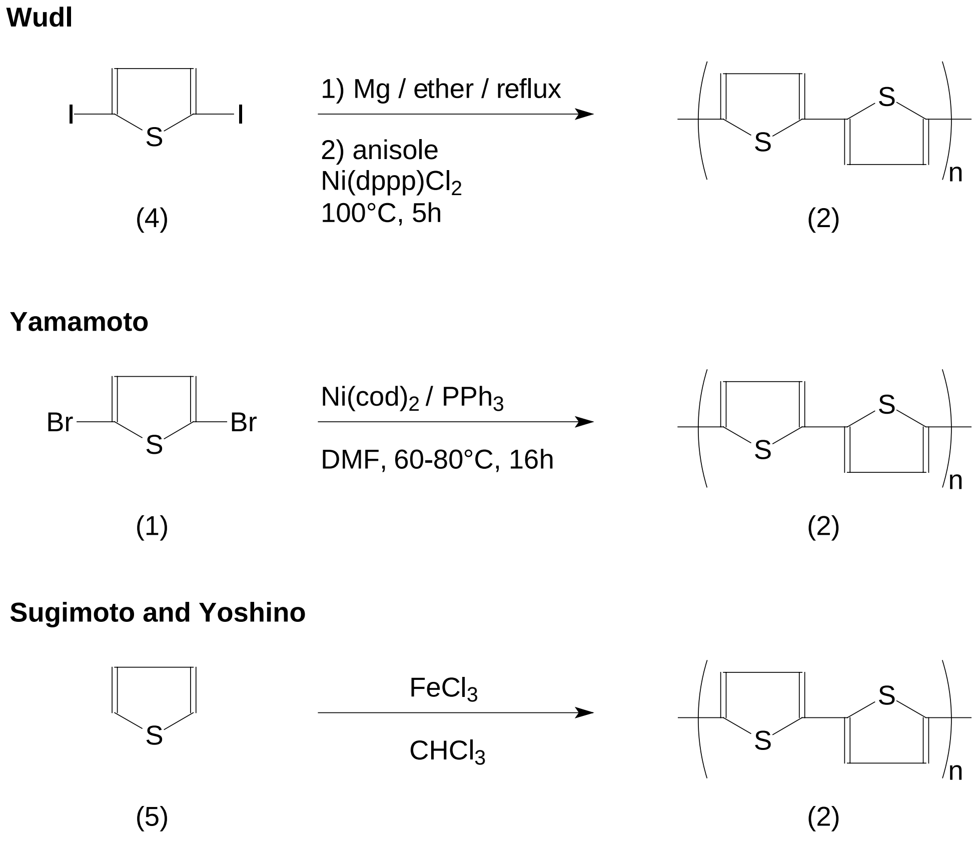
Scheme 1. 14. The first chemical syntheses of polythiophene.

Polymerization of 2,5-dihalothiophene can be accomplished by reacting the generated bromo-Grignard of thiophene with Ni(II) catalyst such as Ni(dppp)Cl$_2$ (dppp = 1,3-diphenylphosphinopropane) or the 2,5-dihalothiophene can be polymerized by a polycondensation dehalogenation reaction with Ni(0) (scheme 1. 15.). Systematic studies of the polymerization of 2,5-dihalothiophene (3) have subsequently have been done by primarily Yamamoto[47,235-238] and others[239-241]. Varying the amounts of Mg[239], the solvent[237,240,241], the type of metal (i.e. Mg, Zn, etc.) [237], concentration of monomer[239], the type of halogen on the monomer[47,235,239-241], the temperature[47,235,236], reaction time[235], and the type of catalyst used[47,235-239] has led to some good chemical methods for the synthesis of polythiophene.



Scheme 1. 15. Polycondensation dehalogenation route to polythiophene.

It is seen in a paper by Wudl[240] that very good sample of polythiophene can be prepared by the polymerization of highly purified 2,5-diiodothiophene (scheme 1. 16.). First 2,5-diiodothiophene (4) is reacted with Mg in ether at reflux. The preformed iodomagnesioiodothiophene is isolated as a residue and redissolved in hot anisole, whereupon Ni(dppp)Cl_2 is added and the mixture heated at 100 °C for 5h to induce polymerization. Extensive washing of the isolated polythiophene with methanol, chloroform, THF, and chlorobenzene leads to the isolation of polythiophene with elemental analysis within 0.3% of the calculated values for $C_{188}H_{97}IS_{46}$ (molecular weight ≈ 4000 or 46 thiophene rings and 1 butadiene unit). This high purity polythiophene sample contains barely 50ppm of Mg and Ni. However, it is proposed that the one butadiene unit arises from a desulfurization reaction promoted by Ni (0) intermediates[234]. Polymerization of the 2,5-dibromothiophene yielded polythiophene that analyzed 2-3% low in sulfur, apparently due to said desulfurization. The Wudl sample of polythiophene was characterized by IR, ESR, conductivity and thermopower measurements. The conductivity of the AsF_5-doped material was about 10 $S.cm^{-1}$.



Scheme 1. 16. Specific examples of the synthesis of polythiophene.

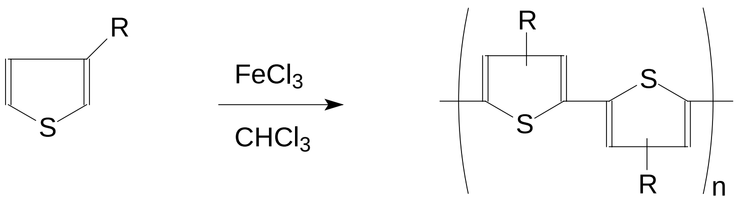
Work on the polycondensation polymerization of 2,5-dihalothiophenes by Yamamoto has shown that essentially a quantitative yield of polythiophene can be made from 2,5-dibromothiophene, Ni(cod)$_2$ (cod = cyclooctadiene), and PPh$_3$ at 60-80 °C in DMF (scheme 1. 16.) [235]. It is also reported that the percentage of Br end groups decreases as reaction times are increased from 8 to 16 h, indicating that perhaps some seemingly insoluble polythiophene continues to grow. Both less active catalysts such as Ni(PPh$_3$)$_4$ and less active monomers such as 2,5-dichlorothiophene lead to lower yields of polythiophene. The polythiophene synthesized is exclusively coupled at the 2,5-carbons as indicated by solid state ^{13}C NMR which exhibits peaks at 136 and 125 ppm only. Other synthetic methods can produce the conjugation disrupting 2,4-coupled polythiophene structure. While the elemental analyses for carbon and hydrogen are within 0.3%, the sulfur content of the polythiophene is off by 3%. Vacuum deposition of polythiophene (estimated molecular weight of 1.5-2 K) onto carbon, gold, KBr, or aluminum at 250-300 °C at 10^{-4} Pa can be accomplished. Electron diffraction patterns of polythiophene on carbon indicates the formation of crystalline polythiophene with the polythiophene chains arranged perpendicular to the carbon substrate – similar to oligothiophene films. Vacuum deposition of polythiophene on rubbed polyimide films gave polythiophene chains oriented parallel to the polyimide substrate with a dichroic ratio 1.5. The polythiophene films are further characterized by IR, X-ray, and conductivity measurements. Powder conductivity measurements on iodine doped samples gave a maximum conductivity of 50 S.cm^{-1}.

Although the above methods have been generally used to prepare high quality polythiophene, other methods have been reported. An early report by Sugimoto reported the synthesis of polythiophene by treating thiophene (5) with FeCl$_3$ (scheme 1. 16.). The treatment of thiophene with butyl lithium provides 2,5-dilithiothiophene that can be polymerized with CuCl$_2$[242]. Thiophene can also be polymerized by trifluoroacetic acid in the presence of thallium(III) trifluoroacetate[243]. The acid-induced polymerization of thiophene was reported as early as 1883, yet produced tetrahydrothiophene units[244]. A novel polymerization of thiophene vapor can produce encapsulated polythiophene in transition metal-containing zeolites[245].

Despite the lack of processability, the expected high temperature stability[240] and potential for very high electrical conductivity of polythiophene *films* (if made) still make it a highly desirable material. Perhaps precursor routes to polythiophene will eventually lead to processable polythiophene films.

1. 5. 3. FeCl$_3$ method for the synthesis of polyalkylthiophenes (PATs)

Yoshino and Sugimoto[246] reported in 1986 a very simple method to prepare polyalkylthiophenes (scheme 1. 17.). The monomer, 3-alkylthiophene (6), is dissolved in chloroform and oxidatively polymerized with FeCl$_3$[246], MoCl$_5$, or RuCl$_3$[247]. Generally the "FeCl$_3$ method" has been used to prepare polyalkylthiophenes[248-253]. Materials prepared by the FeCl$_3$ method produce a polyalkylthiophene with molecular weight ranging from M_n = 30-300K with polydispersity ranging from 1.3-5[252,253]. The FeCl$_3$ method does not appear to generate 2,4-couplings in polyalkylthiophenes.



(6) (7)

Scheme 1. 17. Synthesis of poly(3-alkylthiophene).

One very good paper on the synthesis of polyalkylthiophenes via the $FeCl_3$ method has been reported by Leclerc and Wegner[252]. This paper provides a detailed synthesis, molecular weight data, ^1H and ^{13}C NMR spectra, X-ray, electrochemistry, UV-Vis, and electrical conductivity data on polyalkylthiophenes synthesized chemically with $FeCl_3$ and electrochemically. In this paper, alkylthiophenes in dry $CHCl_3$ (0.15 M) were treated dropwise with $FeCl_3$ in chloroform (0.4 M). The mixture was stirred for 24h under a gentle argon stream (to help to remove generated HCl(g)). The polymer was then precipitated into methanol, filtered, redissolved in $CHCl_3$, and the $CHCl_3$ slowly evaporated to give a free-standing film. The film was washed by Soxhlet extraction using methanol and acetone which yields a dedoped polymer containing <0.10% Fe. The yields ranged from 75-80% with molecular weights of M_n = 30-50K with PDIs around 5. The regioregularity, measured by the head-to-tail content ranges from 70-80% by this method. This paper reports that the polyalkylthiophenes synthsized with $FeCl_3$ are more crystalline and regular than electrochemically prepared polymers.

Very high molecular weights have been reported in the synthesis of polyalkylthiophenes using the $FeCl_3$ method by bubbling dry air through the reaction mixture during the polymerization[253]. After isolation and dedoping of the polymer with concentrated ammonia solutions, and washing of the polyalkylthiophenes, the molecular weights are determined by GPC using UV-Vis, refractive index (RI), and light scattering detectors.

One of the major problems with the $FeCl_3$ method is that the method gives variable results. The reproducibility of the reaction has been examinated, for example by Pomerantz and Reynolds[253]. The polymerization of 3-octylthiophene with $FeCl_3$ was repeated under identical reaction conditions five times. Investigations of the molecular weights of the five samples of poly(3-octylthiophene) revealed molecular weights that ranged from 54K to 122K (UV-Vis) with PDIs ranging from 1.6-2.7. Holdcroft[254] has reported that three identical preparations yielded three polymer samples containing three different levels of Fe impurities. The %Fe impurities found in the three samples were 9.6 mol%, 4.15 mol%, and 0.15 mol%. The Fe impurity affects device performance of polythiophene in field effect transistors[254] and in LEDs[255].

The Finnish company Neste Oy has been working on cost effective methods to synthesized polyalkylthiophenes they reported on the mechanism of the $FeCl_3$ synthesis of polyalkylthiophenes[256]. $FeCl_3$ initiates an oxidation of the alkylthiophene to produce radical centers predominantly at the 2- and 5-position of thiophene that propagate to form polymer. Systematic studies on the optimization of the reaction conditions leading to polyalkylthiophenes[257] and improvements in the method[258] have been reported. A new synthesis of octylthiophene, followed by $FeCl_3$ polymerization led to a poly(3-octylthiophene)(POT) containing 84% head-to-tail couplings in a 70% yield. The molecular weight was reported as M_w = 70K (PDI = 2.6). The iron content was only 0.008% and the chlorine content was 0.5%, compared with 1% observed in conventional POT[259]. The electrical conductivity of $FeCl_3$ doped POT was 47 S.cm^{-1}.

The $FeCl_3$ method is a well-established method to polymerize thiophenes[247-263] and even polydeuterated polyalkylthiophenes[264] and continues to be the most widely used and straightforward method to prepare polythiophene and its derivatives, despite the limitations and drawbacks to the method.

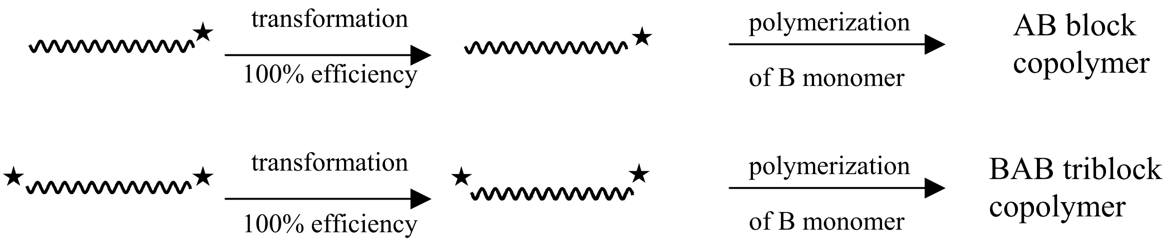
1. 6. Synthesis of block copolymers by a combination of different polymerization methods

1. 6. 1. General concepts of combination of polymerizations

The well-documented fact that not all monomers can be polymerized by every available polymerization mechanism limits the possible combinations of monomers that can be employed in a block copolymer chain, if only one polymerization method is used. However, synthetic schemes have been devised that allow the polymerization mechanism to be changed appropriately in order to suit the monomers that are going to be incorporated in the same macromolecule. These polymerization processes widen considerably the variety of block copolymers that can be produced.

Active center transformation reactions usually involve the efficient end functionalization of a polymer chain that is going to comprise one of the blocks of the final copolymer. This concept can be also described as the use of a suitable macromolecular initiator for the polymerization of the second monomer. Transformation of the chain-end followed by the polymerization of the second monomer produces a diblock copolymer, whereas the transformation of both ends of a linear polymer chain results in the formation of an ABA triblock copolymer (Scheme 1. 18). Transformation reactions must be 100% efficient because any unfunctionalized macromolecular chains will not initiate the polymerization of the second monomer and will be present in the final product as a homopolymer impurity. Transformation of chain-ends may involve several steps. The preparation of well-defined block copolymers requires that every individual step, including the separate polymerization reactions, must be highly efficient and finely controlled. It is obvious that these synthetic strategies involve special care in the design and the application of the chosen synthetic methodology.

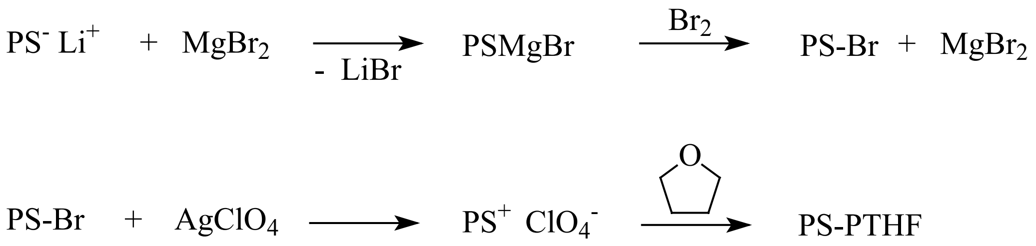
Several transformation mechanisms have been employed so far for the preparation of block copolymers. Some of them are outlined in this chapter.



Scheme 1. 18.

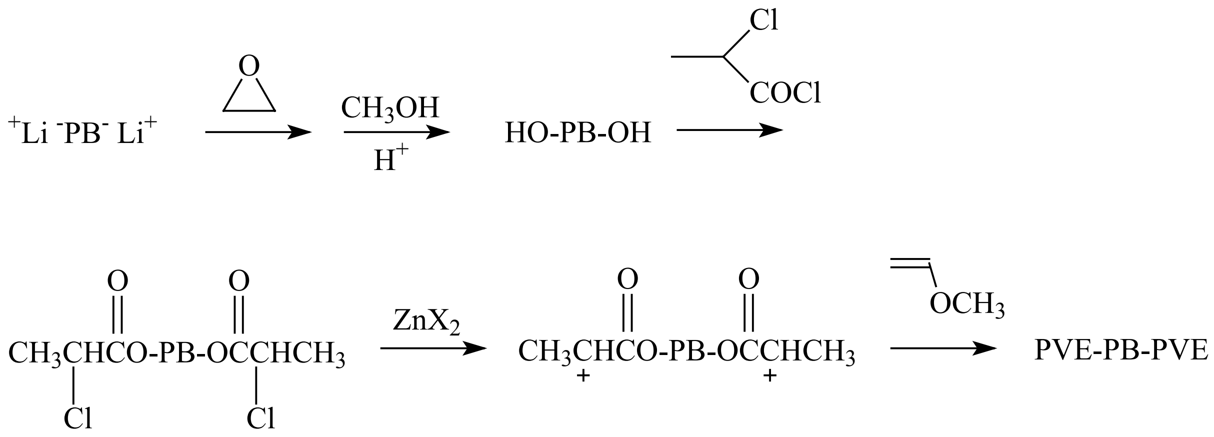
1. 6. 2. Synthesis of block copolymers by anionic to cationic mechanism transformation

The synthesis of polystyrene-b-polytetrahydrofuran block copolymers is a typical example of transformation of active anionic centers to cationic ones. Living polystyryl-Li (PSLi) is transformed to ω-bromopolystyrene. The best way to produce this functional polymer is intermediate formation of the macromolecular Grignard reagent and subsequent reaction with Br_2, according to Scheme 1. 19.[265]. An alternative route is functionalization of PSLi with excess phosgene[266]. The terminal halogen atom can be activated using silver salts, e.g., $AgSbF_6$, $AgClO_4$, $AgPF_6$, generating a carbocation. This cationic active center is used for the polymerization of THF, forming the poly(tetramethylene oxide) block.



Scheme 1. 19.

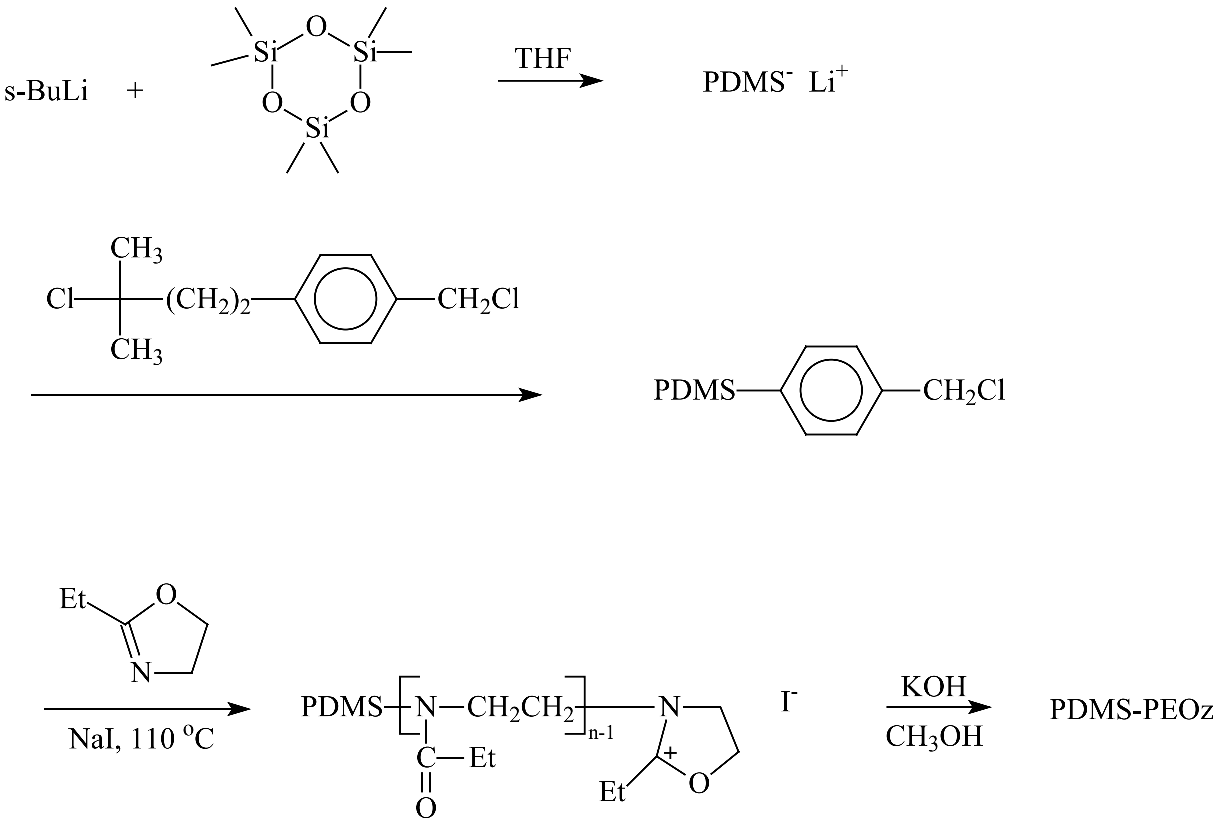
In another case, difunctional living polybutadiene, produced by the use of a difunctional initiator, is reacted with excess EO giving an α,ω-polybutadiene diol (wich is now commercially available (Scheme 1. 20). The OH groups are converted to haloether groups, and the new difunctional polymer is used as a macromolecular initiator for the cationic polymerization of vinyl ethers in the presence of ZnX_2[267].



Scheme 1. 20.

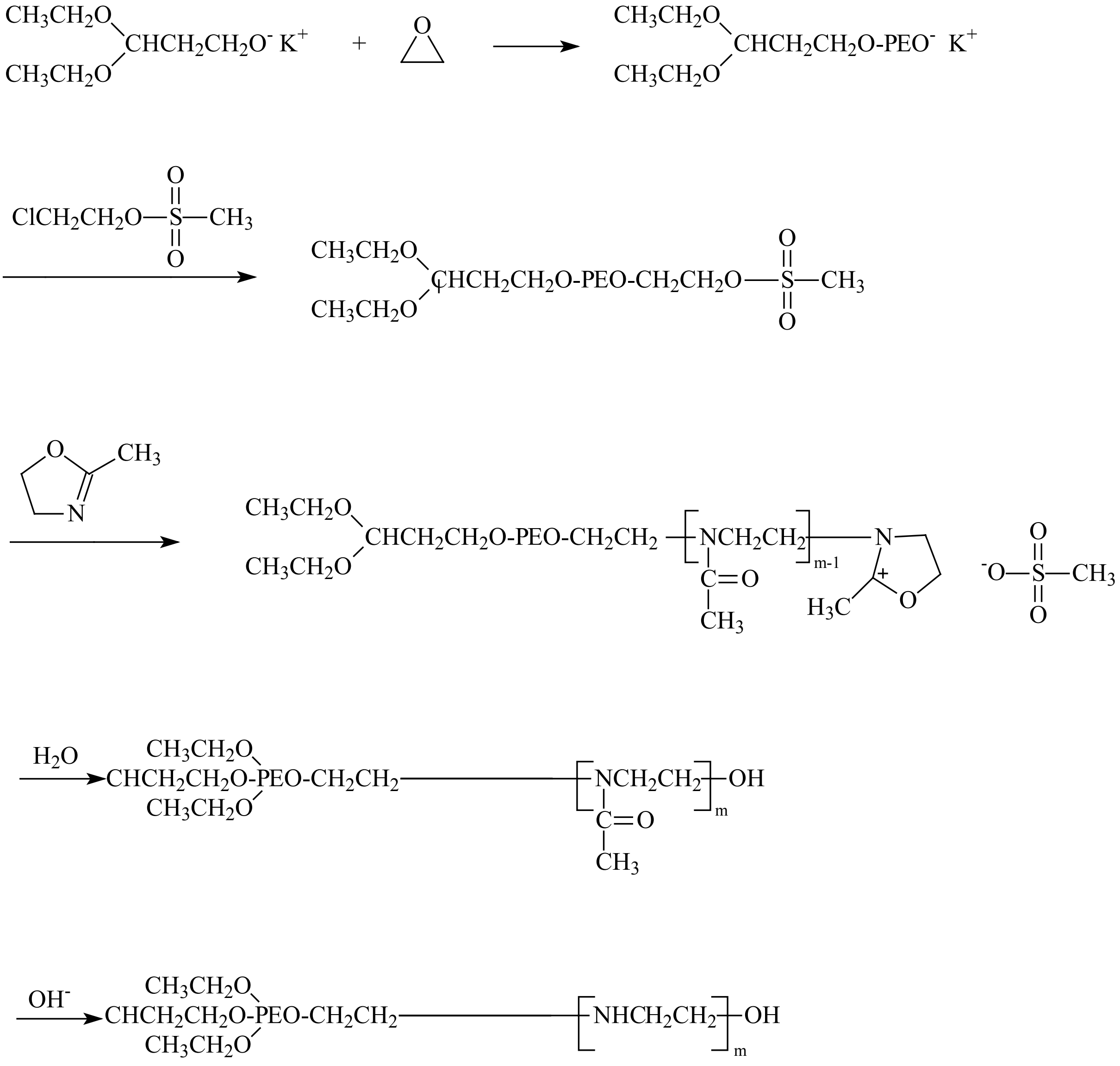
In another case, polydimethylsiloxane-b-poly(2-ethyl-2-oxazoline) block copolymer was synthesized in two steps[268,269] (Scheme 1. 21). The first step involved the ring opening anionic polymerization of dimethylsiloxane in THF with s-BuLi as the initiator. The living PDMS was subsequently reacted with a benzyl chloride containing chlorosilane-terminating agent, giving the monofunctional-benzylchloride-terminated PDMS. After purification, the end-functionalized PDMS was used as the macroinitiator for the ring-opening-cationic polymerization of 2-ethyl-2-oxaline (EOz) in the presence of NaI in chlorobenzene at 110 °C.

A number of copolymers having narrow molecular weight distributions and a range of compositions were synthesized.



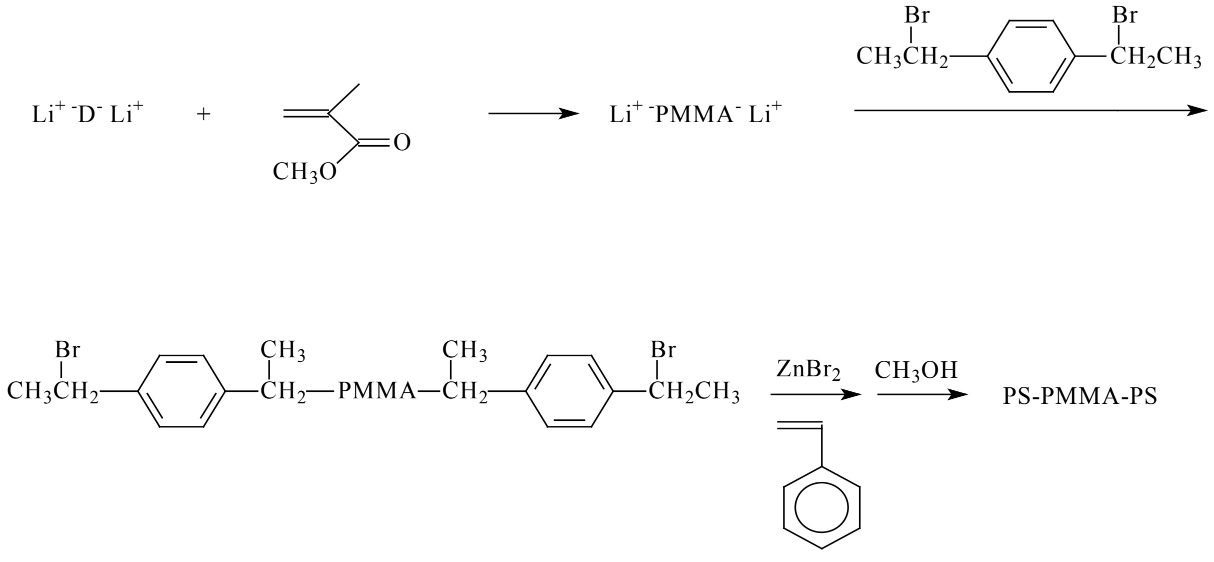
Scheme 1. 21.

Poly(ethylene oxide)-b-polyethyleneimine) copolymers were prepared by anionic ring-opening polymerization of ethylene oxide in THF with potassium 3,3-diethoxypropanolate[270]. The living chains were end-capped with methanesulfonyl chloride, giving the heterotelechelic acetal-PEO-SO_2CH_3. This was used as a macroinitiator for the cationic ring-opening polymerization of 2-methyl-2-oxazoline in nitromethane at 60 °C. Alkaline hydrolysis of the amide group in the POZ block to a secondary amino group, by addition of NaOH, resulted in the desired block copolymers (Scheme 1. 22).



Scheme 1. 22.

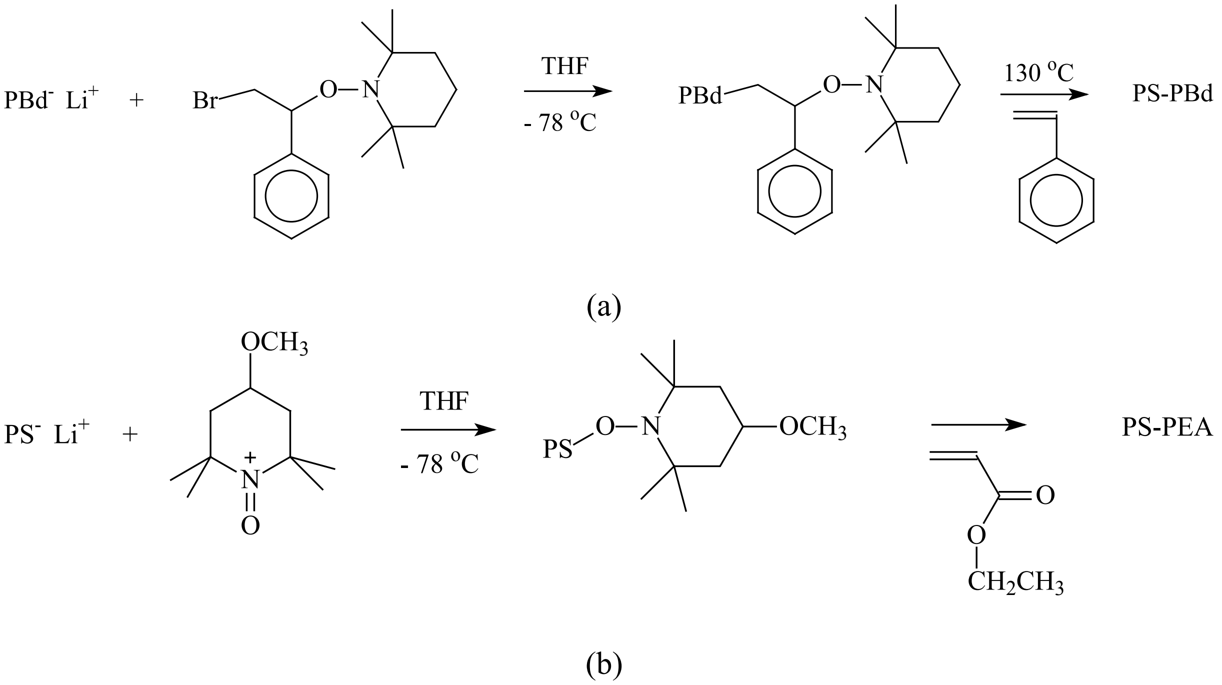
PS-PMMA-PS triblock copolymers were synthesized by transformation of polymerization mechanism from anionic to cationic[271]. MMA was polymerized first using a difunctional initiator. The anionic sites were converted to cationic by reaction with 1,4-bis-(1-bromoethyl)benzene, and the PS blocks were formed by cationic polymerization of styrene (Scheme 1. 23.). In an alternative way, a PS-PMMA diblock copolymer was synthesized first by anionic polymerization, the living ends were transformed to cationic using the same functionalization reaction as above, followed by the cationic polymerization of styrene.



Scheme 1. 23.

1. 6. 3. Synthesis of block copolymers by anionic to living free radical mechanism transformation

Recently, the transformation of a living anionic center to a functional group containing TEMPO was reported[272,273]. The reaction scheme involved the reaction of a suitable modified TEMPO derivative with a living polymer prepared by anionic polymerization. The functionalization reaction has been shown to be highly efficient, and the formation of block copolymers was accomplished by controlled free radical polymerization of styrene in the second step (Scheme 1.24.(a)). In a similar way[274], PSLi was reacted with 1-oxo-4-methoxy-2,2,6,6-tetramethylpiperidine at –78 °C in THF in order to produce a TEMPO-terminated PPS macroinitiator, which was used for the polymerization of methyl, ethyl, and butyl acrylates to give the corresponding block copolymers (Scheme 1. 24.)

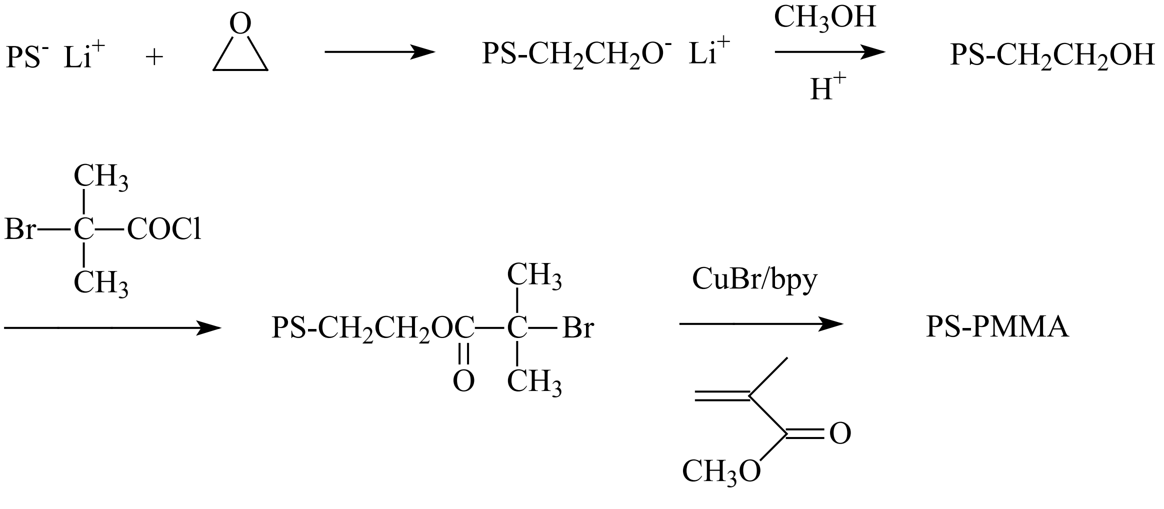


(a)

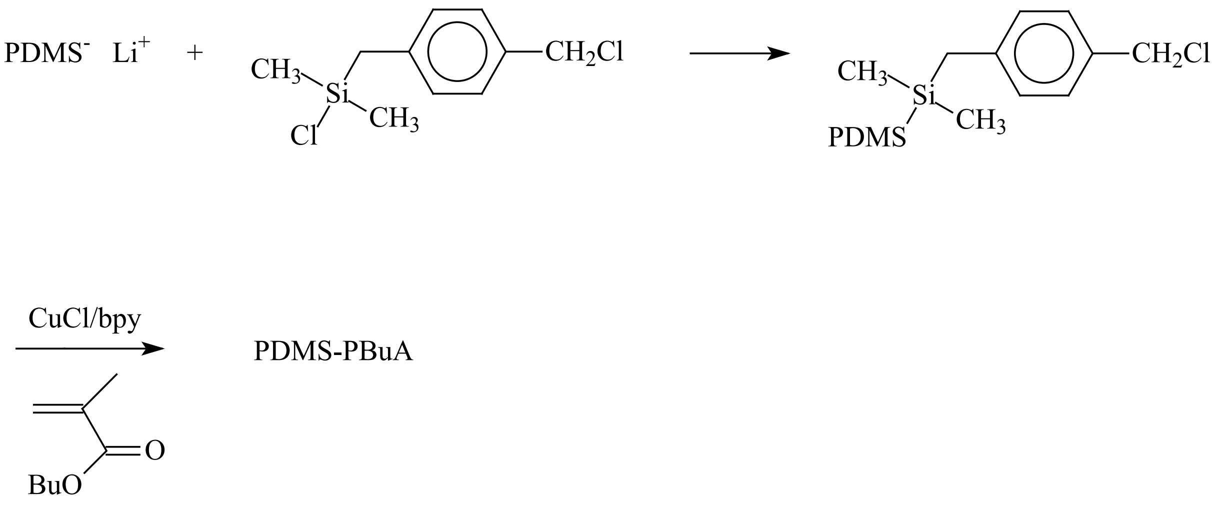
(b)

Scheme 1. 24.

Anionically polymerized styrene- and diene-based living polymers were terminated with ethylene oxide, giving hydroxyl end-functionalized homopolymers. The terminal OH groups were converted to 2-bromoisobutyroxy groups, which were subsequently used as initiating sites for the ATRP polymerization of (meth)acrylates (Scheme 1. 25.). In another case living poly(dimethyl siloxane) prepared by anionic polymerization was terminated with ClSiMe2CH2PhCH2Cl, producing the chlorobenzyl-terminated analogue. The terminal group was used for the polymerization of styrene and acrylate monomers, resulting in well-defined block copolymers (Scheme 1. 26.) [275].



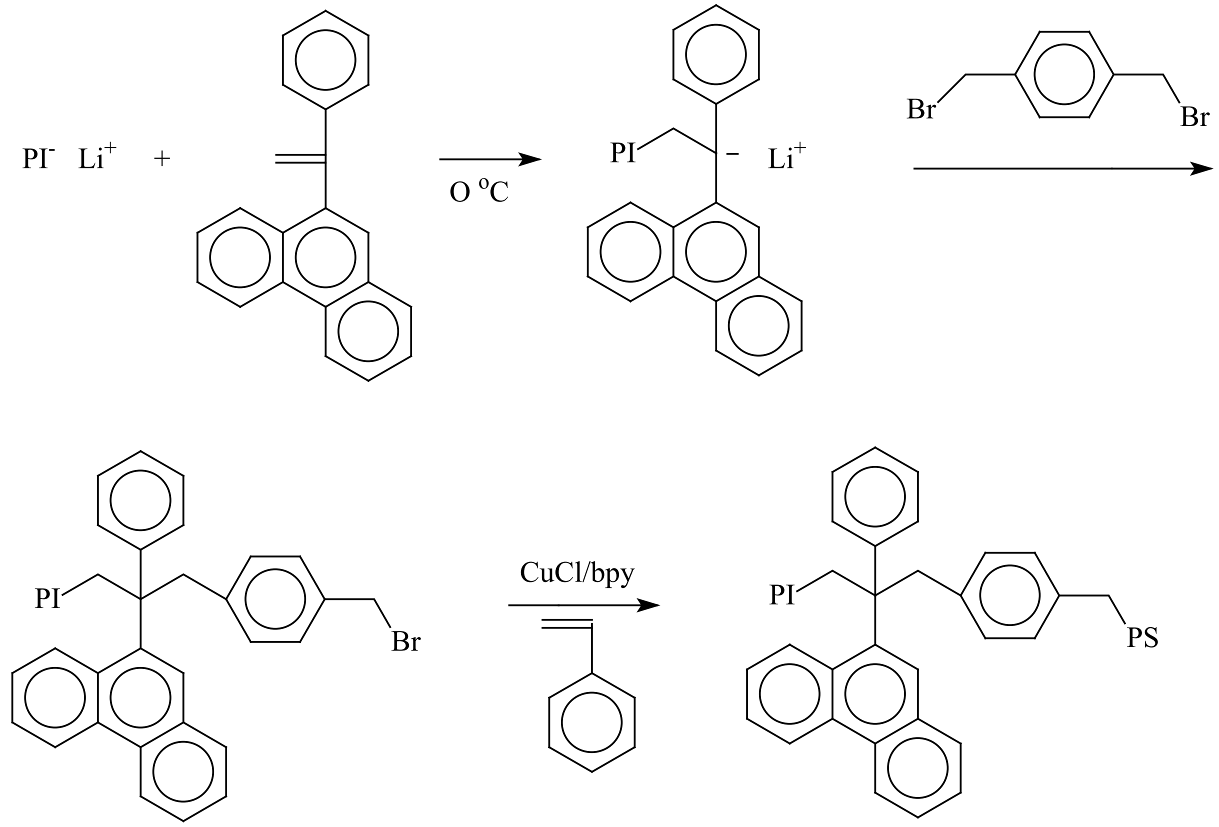
Scheme 1. 25.



Scheme 1. 26.

Block copolymers of isoprene and styrene bearing a fluorescent probe at the junction point were synthesized by an anionic-to-living free radical polymerization mechanism transformation[276]. First, the polymerization of isoprene was realized anionically in cyclohexane using s-BuLi as the initiator. Reaction of the living chain with the dye derivative 1(9-phenanthryl)-1-phenylethylene resulted in the dye end functionalized PI block, which was subsequently reacted with excess dibromo-p-xylene to afford a Br terminated PI chain.

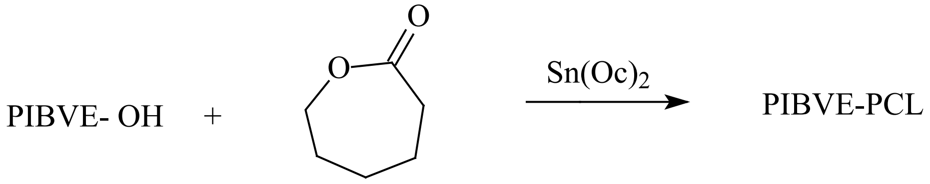
This end-functionalized polymer was used, in conjunction with CuBr/bpy, to give the second PS block through atom transfer radical polymerization (Scheme 1. 27.).



Scheme 1. 27.

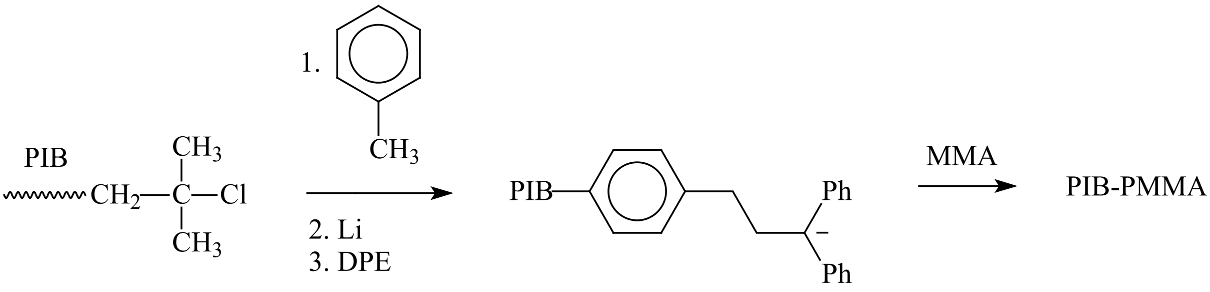
1. 6. 4. Synthesis of block copolymers by cationic to anionic mechanism transformation

Hydroxyl terminated poly(isobutyl vinyl ether) (PIBVE) prepared by terminating the living cations with K_2CO_3/H_2O followedby $NaBH_4$ was used as an anionic macromolecular initiator, in the presence of stannous octanoate as the catalyst, for the polymerization of ε-caprolactone[277]. In this way well-defined block copolymers of poly(vinyl ether)-b-poly(ε-caprolactone) were synthesized (Scheme 1. 28.).



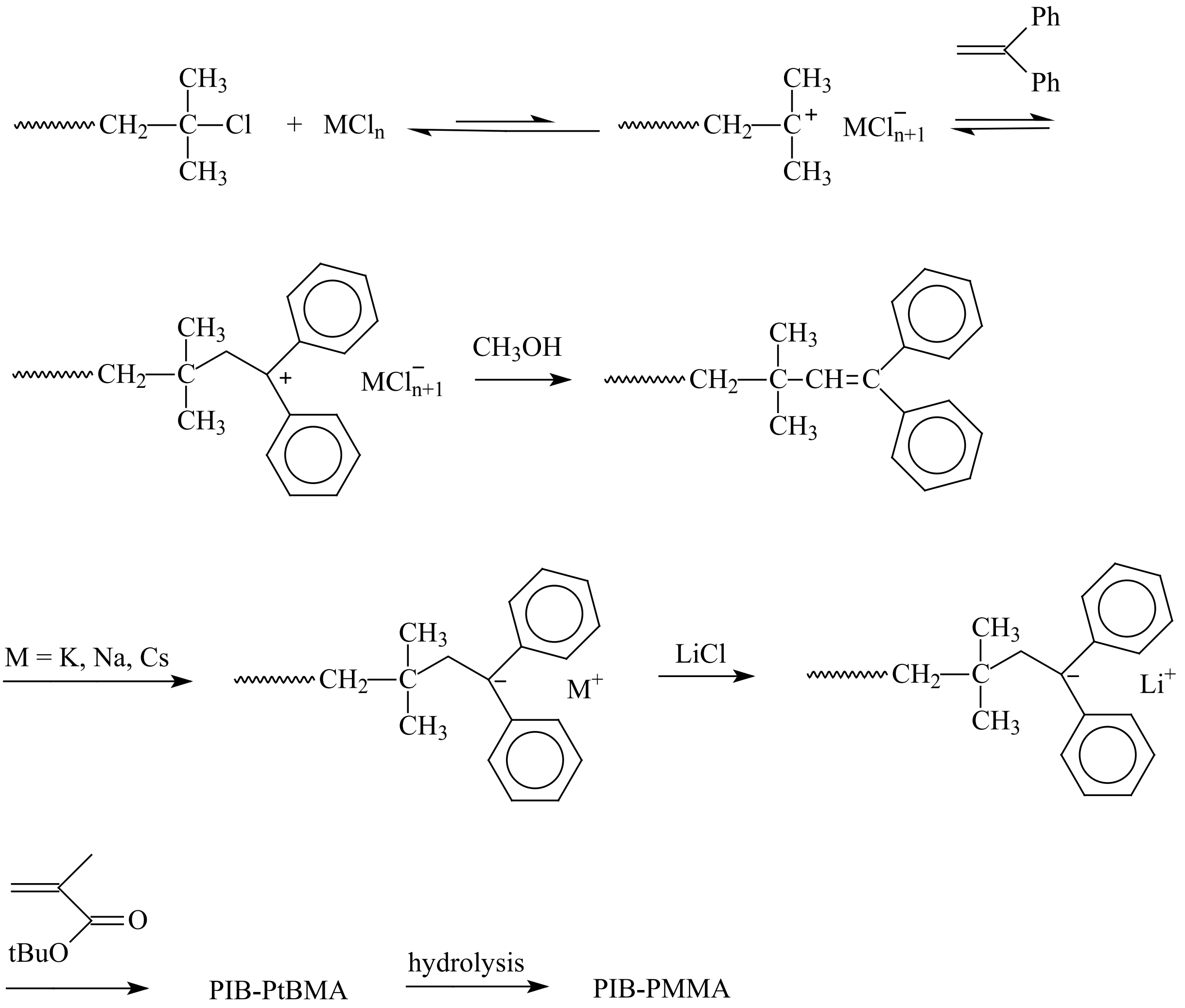
Scheme 1. 28.

In another example the terminal chlorine atom of a polyisobutylene chain, prepared by a typical cationic polymerization procedure, was converted to the benzyl anion, which, in turn, was able to polymerize methyl methacrylate anionically[278]. Thus, polyisobutylene-b-poly(methyl methacrylate) diblock copolymers were produced. The living cationic polymerization of isobutylene results, even after quenching with methanol, in chlorine-terminated polymers. Therefore, no special end-functionalization reactions are needed in order to produce the terminal Cl functionality (Scheme 1. 29.).



Scheme 1. 29.

Living PIB chains, produced by cationic polymerization of isobutylene, were end-capped with 1,1-diphenyl-1-methoxy (DPOMe) or 2,2-diphenylvinyl (DPV) terminal groups[279]. These end groups were metallated quantitatively with K/Na alloy in THF. The resulting macroanionic initiators were used for the polymerization of tert-butyl methacrylate, producing well-defined block copolymers. Metallation of the DPOMe or DPV termini with Li dispersion and subsequent polymerization of MMA gave PIB-b-PMMA block copolymers. The use of difunctional linear PIB macroinitiators resulted in the formation of PMMA-b-PIB-b-PMMA triblock copolymers (Scheme 1. 30.)

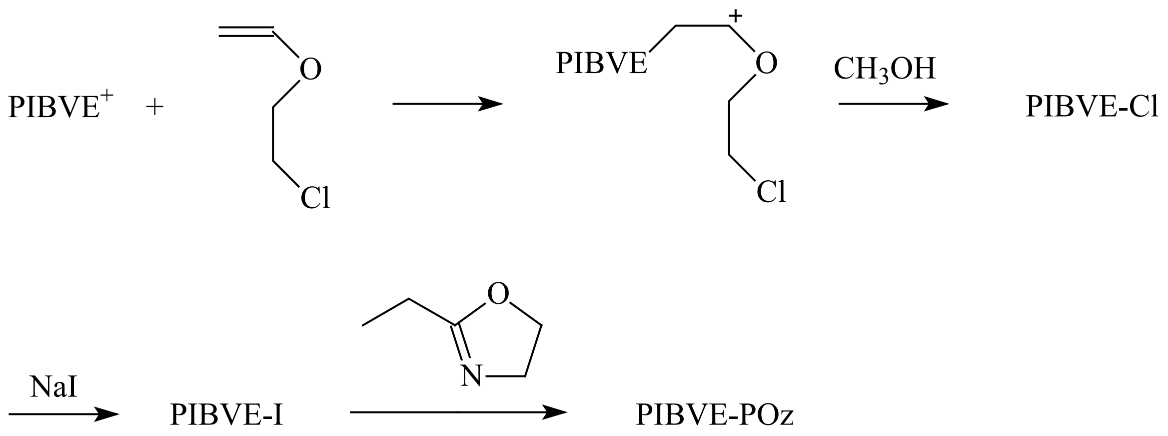


Scheme 1. 30.

1. 6. 5. Synthesis of block copolymers by cationic to onium mechanism transformation

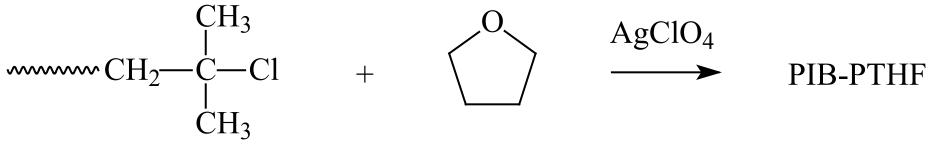
The cationic-ring-opening polymerization of heterocyclic monomers is a well-established polymerization process. Direct sequential polymerization of vinyl and cyclic monomers is not possible due to the different initiating systems required in the two cases. However, block copolymers containing blocks composed of vinyl and cyclic monomers can be produced by cationic to onium transformation processes.

Poly(isobutyl vinyl ether), produced by cationic polymerization, can be end-functionalized with a chlorine atom by end-capping with 2-chloroethyl vinyl ether segment. The Cl can be converted into the more reactive iodine by reaction with sodium iodide. The terminal iodide can be appropriately activated to initiate the ring-opening cationic polymerization of 2-ethyl-2-oxazoline, giving PIBVE-b-poly(oxazoline) block copolymers[268,269] (Scheme 1. 31).



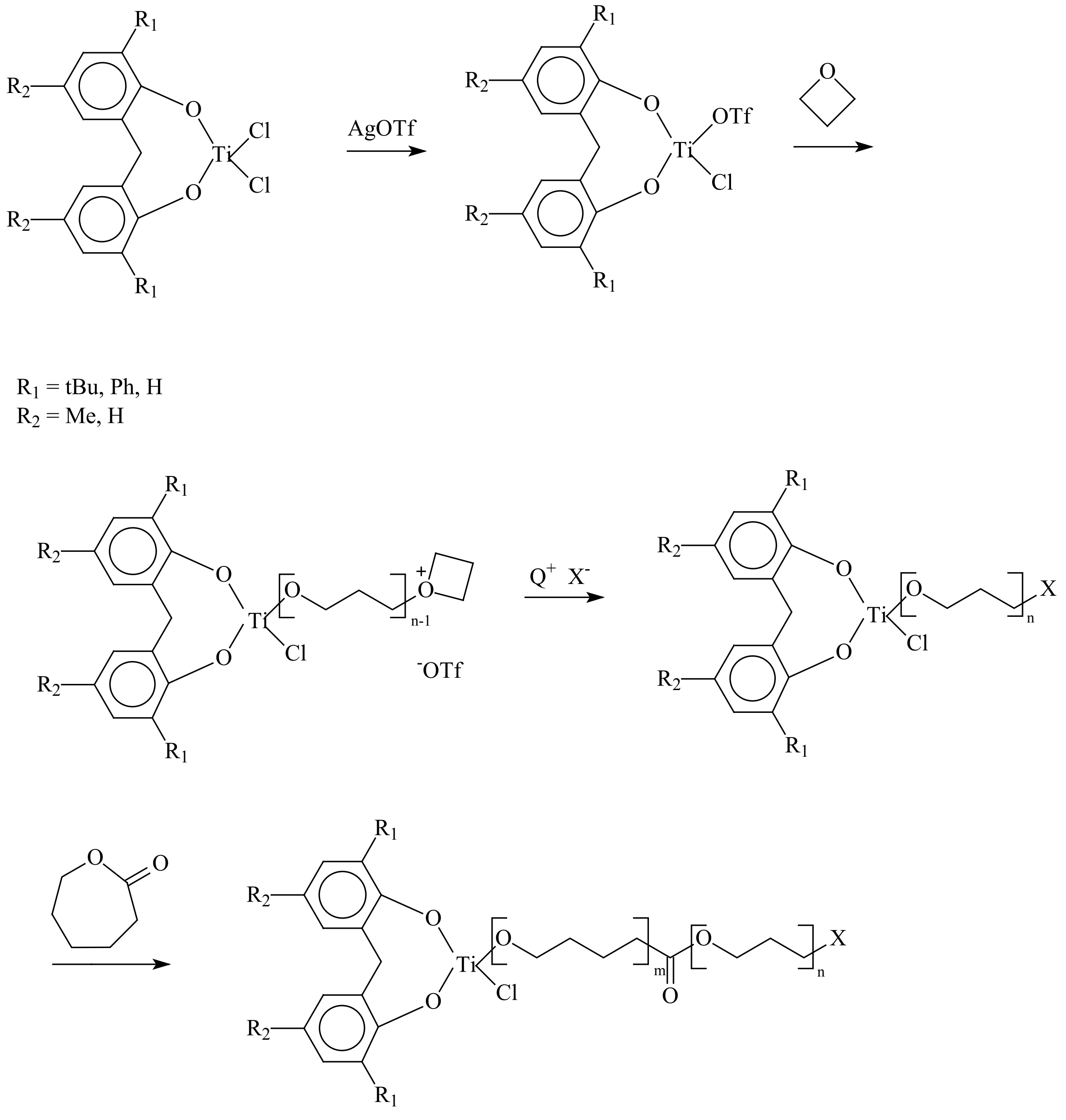
Scheme 1. 31.

The tertiary or benzylic-terminal chlorine atoms of polyisobutylene or poly(p-chlorostyrene), respectively, synthesized by cationic polymerization, using tertiary alkyl chlorides as the initiators, can be activated by silver salts in order to polymerize THF by a ring-opening cationic mechanism (Scheme 1. 32.). Thus, PIB-PTHF[280] and PpMeS-PTHF[281] block copolymers were prepared.



Scheme 1. 32.

The preparation of polyoxetane-b-poly(ε-caprolactone) via a cationic to anionic polymerization mechanism transformation has also been reported[282]. The methodology involved the use of triflate complexes of bulky titanium bisphenolates as moieties for initiating polymerization (Scheme 1. 33.).

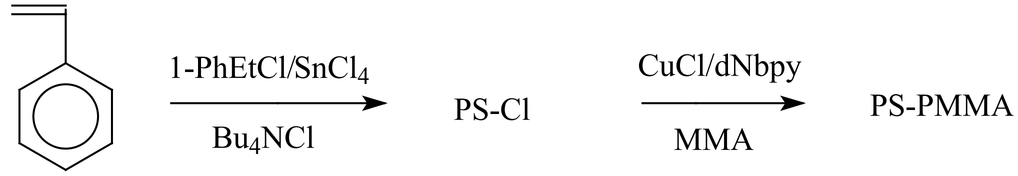


R_1 = tBu, Ph, H
R_2 = Me, H

Scheme 1. 33.

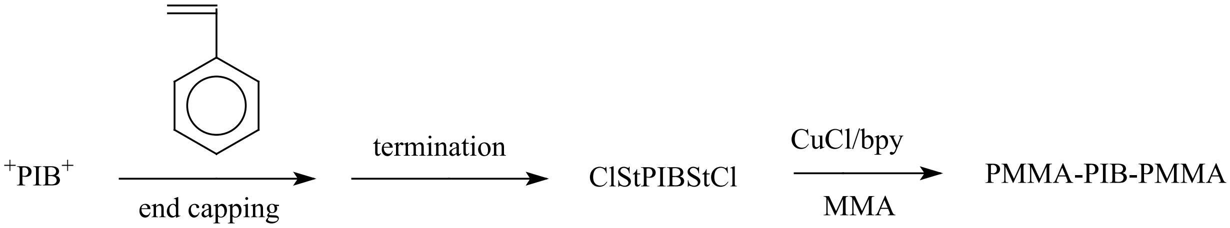
1. 6. 6. Synthesis of block copolymers by cationic to living free radical mechanism transformation

Polystyrene prepared by the 1-PhEtCl/$SnCl_4$ system in the presence of n-Bu_4NCl possesses a Cl-terminal atom. This end-functionalized polymer can be used directly for the atom transfer radical polymerization of methyl acrylate and methyl methacrylate in the presence of the catalytic complex CuCl/4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) [283]. Well-defined PS-PMA and PS-PMMA block copolymers were obtained (Scheme 1. 34.).



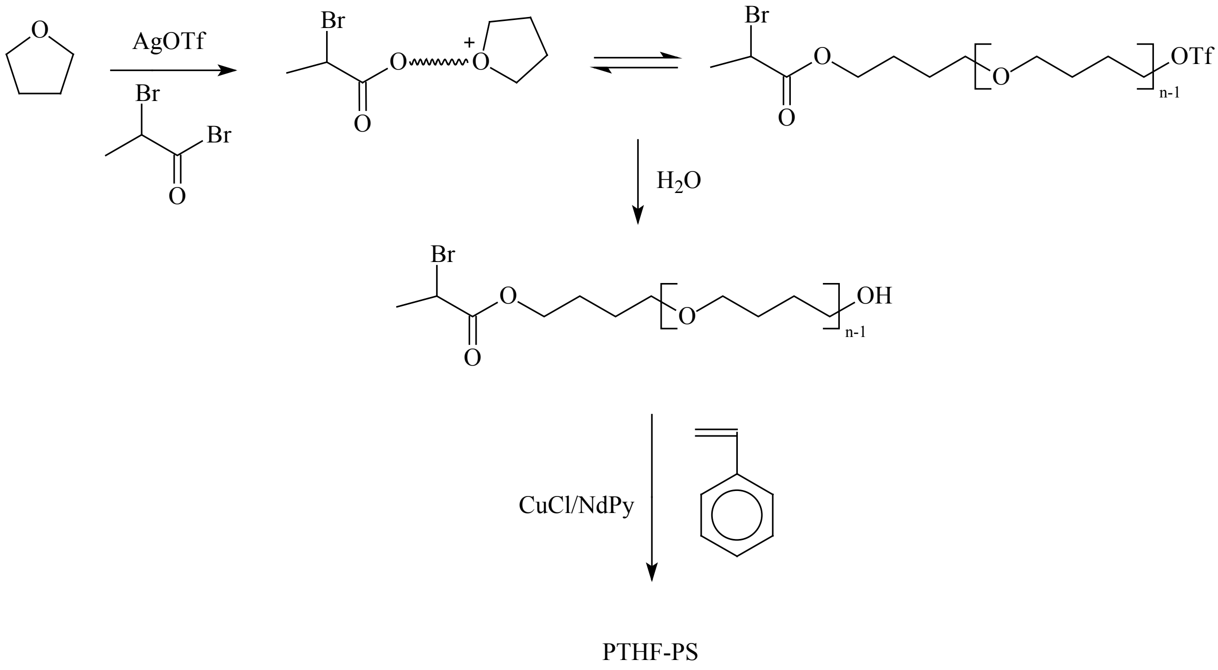
Scheme 1. 34.

Polyisobutylene prepared by cationic polymerization, using a difunctional initiator, was end-capped with a few units of styrene. The resulting macromolecule had two terminal chlorine atoms that were used as initiating sites for the polymerization of styrene, methyl acrylate, isobornyl acrylate, and methyl methacrylate by an ATRP mechanism[284]. Symmetrical ABA triblock copolymers of the the types PS-PIB-PS, PMA-PIB-PMA, PIBA-PIB-PIBA, and PMMA-PIB-PMMA were, thus, synthesized, in the presence of a CuCl/bipyridyl complex (Scheme 1. 35.). Molecular weight distributions were unimodal and narrow. The final triblock contained no homopolymer impurities from the starting macromolecular initiator, indicating high functionalization and polymerization efficiency.



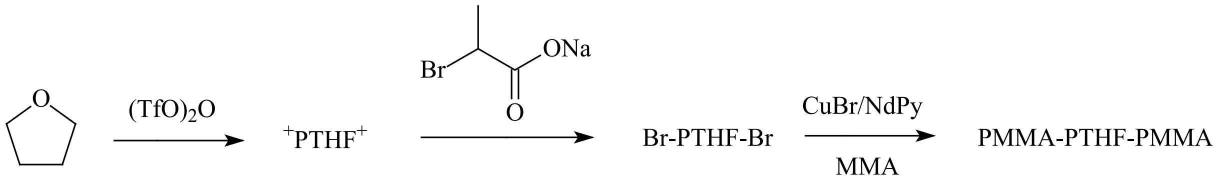
Scheme 1. 35.

Living cationic ring-opening polymerization of THF with bromopropionyl/silver triflate system, leads, after termination of the polymerization with H_2O, to the formation of a bifunctional polytetrahydrofuran chain having bromo and hydroxyl end groups. The terminal bromine atom of this macromolecule was used for the ATRP of styrene and methyl methacrylate to give PS-PTHF and PMMA-PTHF diblock copolymers with a hydroxyl end group[275] (Scheme 1. 36.).



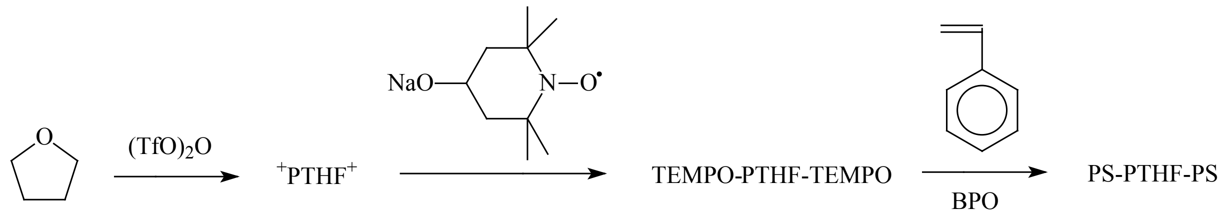
Scheme 1. 36.

When THF polymerization was carried out with the difunctional initator $(Tf)_2O$, a difunctional PTHF was formed. The living ends were reacted with sodium bromopropionate in order to generate a bromodifunctional chain. These functions served as initiating sites for the ATRP polymerization of MMA, giving PMMA-PTHF-PMMA triblock copolymers (Scheme 1. 37.). Similar attempts were made for the ATRP of styrene and methyl acrylate with less satisfactory results.



Scheme 1. 37.

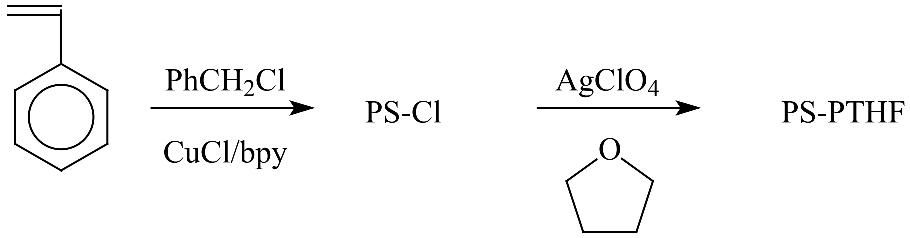
PS-b-PTHF-b-PS triblock (and diblock) copolymers were also synthesized by a cationic to nitroxide-mediated radical polymerization transformation[285,286]. Difunctional living PTHF chains, prepared by cationic polymerization using $(Tf)_2O$ as initiator, were reacted with sodium 4-oxy-TEMPO giving PTHF chains with two terminal TEMPO groups quantitatively. These groups served as initiating sites, in the presence of BPO, for the radical polymerization of styrene, resulting in the aforementioned triblock copolymers (Scheme 1. 38.). Molecular weight distributions were rather broad, but consumption of the second monomer was nearly quantitative.



Scheme 1. 38.

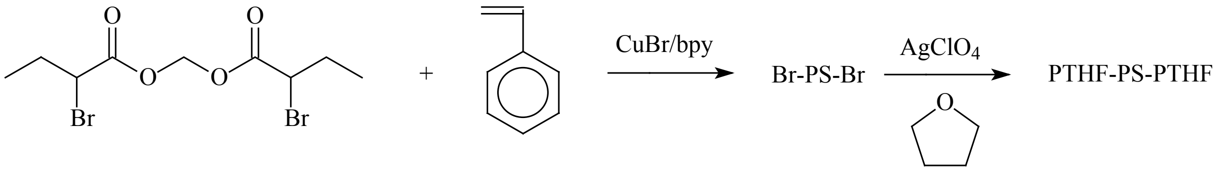
1. 6. 7. Synthesis of block copolymers by living free radical to cationic mechanism transformation

Linear PS prepared by ATRP using $PhCH_2X/CuX/bpy$ initiatior/catalyst systems possess terminal halogen atoms that can be activated by $AgClO_4$ in order to initiate the cationic ring-opening pomerization of THF, giving PS-PTHF copolymers (Scheme 1. 39.).



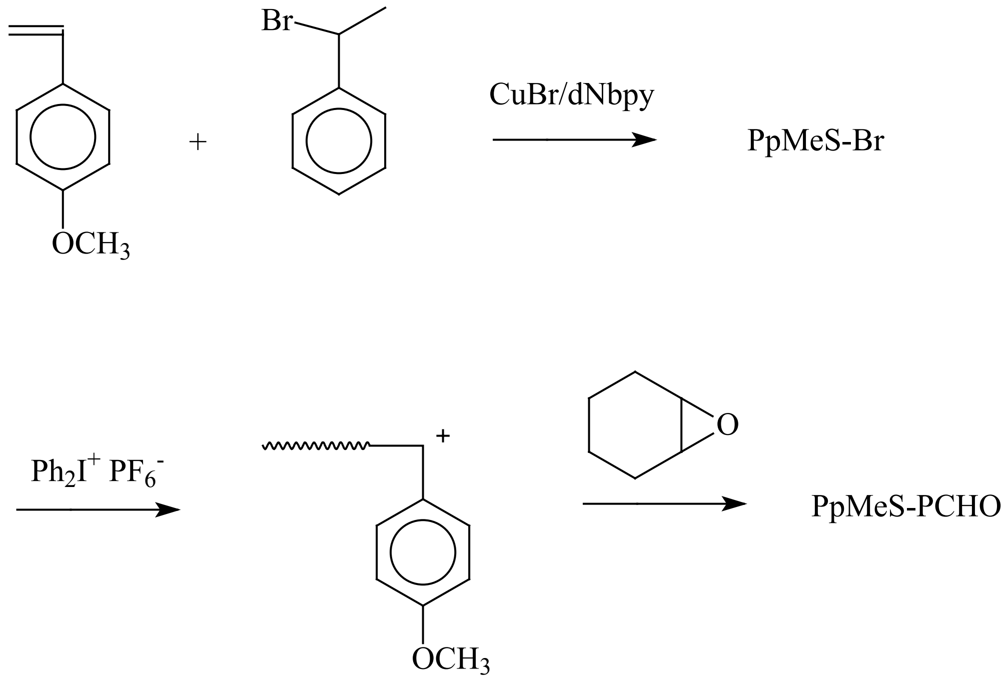
Scheme 1. 39.

Difunctional PS terminated by bromine atoms at both ends was synthesized by ATRP using the difunctional initiator 1,2-bis(2'-bromobutyryloxy)ethane in the presence of CuBr/bipyridine[287]. Reaction of the terminal bromine atoms with silver perchlorate resulted in a macromolecular initiator that was subsequently used in the cationic ring-opening polymerization of THF, giving PTHF-b-PS-b-PTHF triblock copolymers (Scheme 1. 40.).



Scheme 1. 40.

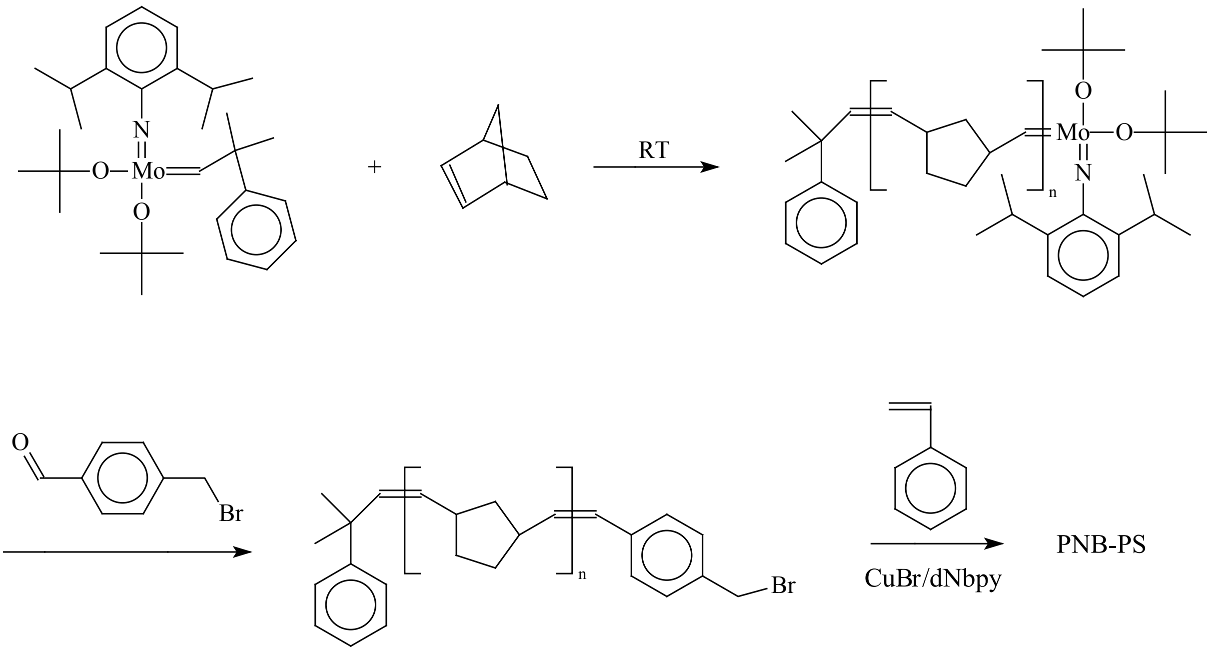
Diblock copolymers of p-methoxystyrene and styrene with cyclohexene oxide (CHO) were synthesized by a combination of ATRP and cationic polymerization[288]. First, the poly(p-methoxy styrene) and PS, bromine-terminated, blocks were prepared by ATRP using (1-bromoethyl)benzene as the initiator in the presence of CuBr as the catalyst and 4,4'-di-(5-nonyl)-2,2'-bipyridine as the complexing agent. The terminal Br atoms were activated by $Ph_2I^+ PF_6^-$, and CHO was polymerized cationically to give the desired block copolymers (Scheme 1. 41.).



Scheme 1. 41.

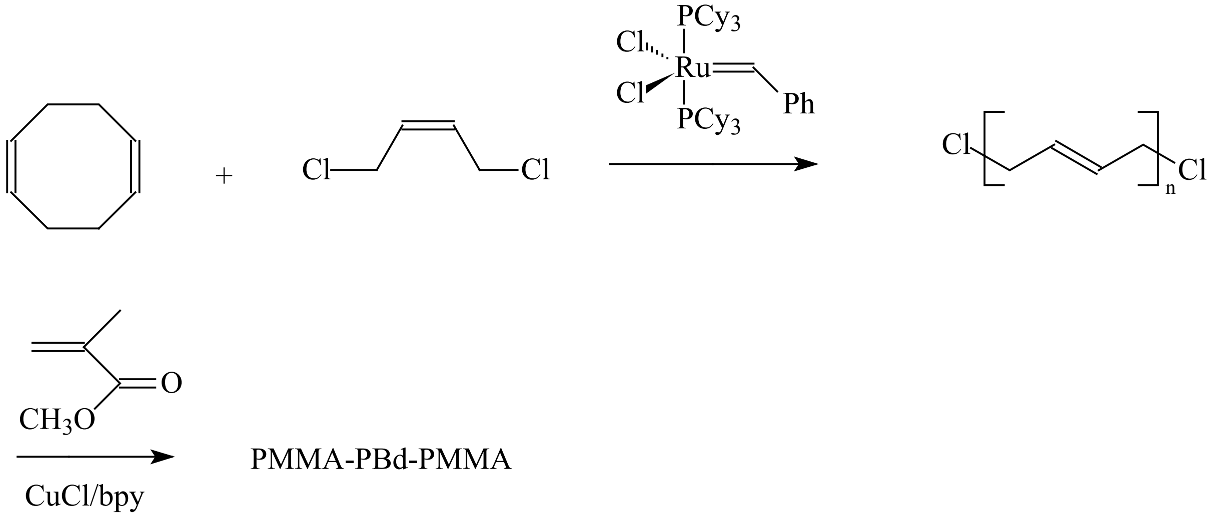
1. 6. 8. Synthesis of block copolymers by ring opening metathesis to living free radical mechanism transformation

Living polynorbornene chains prepared using molybdenum or tungsten complexes were reacted with an excess of 4-formylbenzyl bromide in a Witting type reaction, giving a polynorbornene chain with a terminal benzylic bromide function[289]. This chain-end was used to initiate ATRP of styrene and methyl acrylate. The resulting polynorbornene-b-PS and polynorbornene-b-PMA diblock copolymers showed unimodal molecular weight distributions. No homopolymer impurity coming from the macromolecular initiator was detected by SEC (Scheme 1. 42.). In a similar reaction scheme, polydicyclopentadiene (PDCPD) benzylic bromide end-functionalized chains were used as macroinitiators for styrene and methylacrylate atom transfer radical polymerization, resulting in well-defined PDCPD-b-PS and PDCPD-b-PMA diblock copolymers.



Scheme 1. 42.

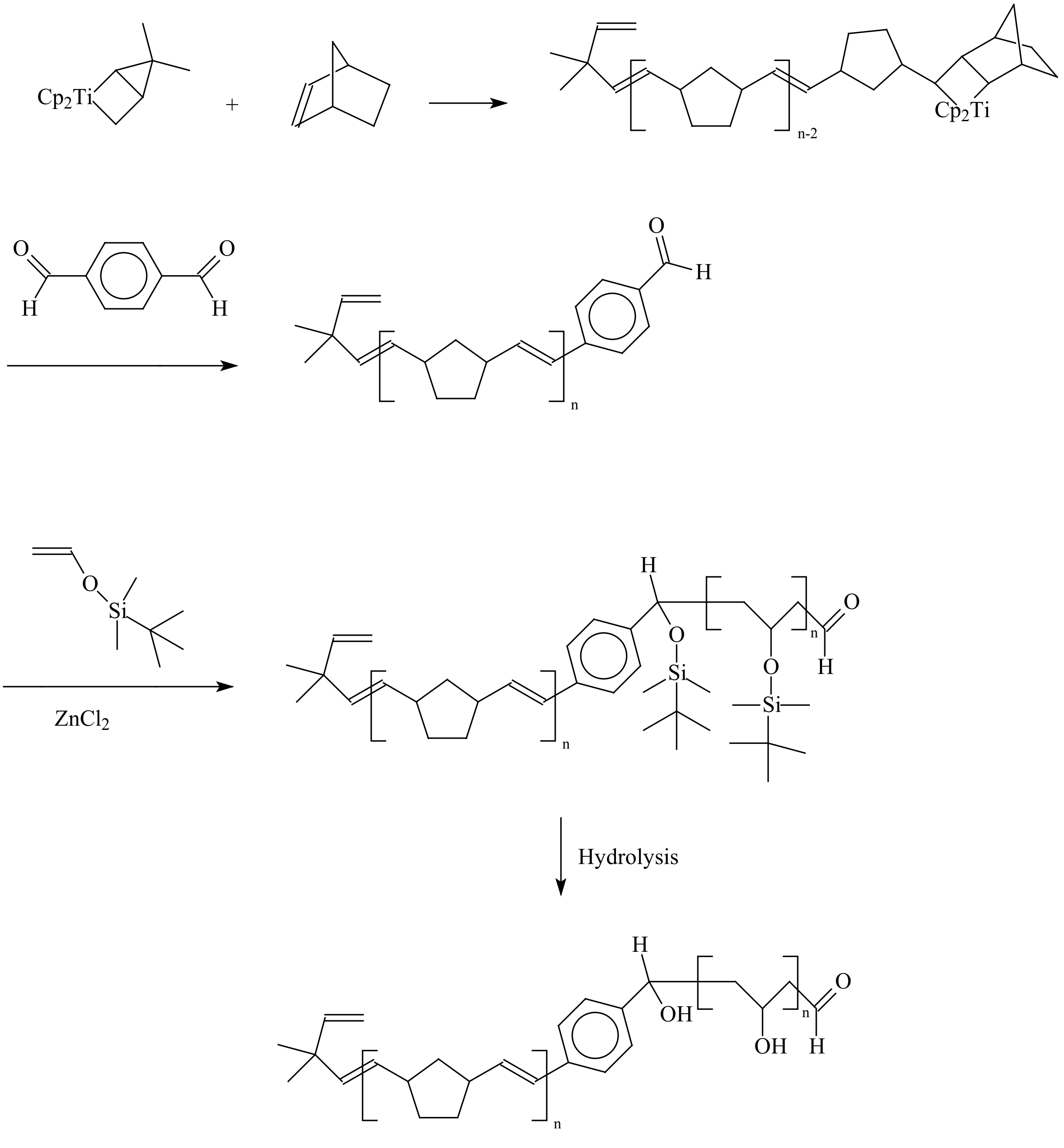
Triblock copolymers with polybutadiene middle blocks and polystyrene or poly(methyl methacrylate) end blocks were synthesized by a combination of ROMP and ATRP[290]. The middle blocks were prepared by ROMP polymerization of cyclooctadiene in the presence of 1,4-chloro-2-butene or cis-2-butene-1,4-diol bis(2-bromo)propionate using an Ru complex as catalyst. The resulting polymers were end-capped at the both ends with allyl chloride or 2-bromopropionyl ester groups. These end groups were subsequently used for the polyrization of styrene or methyl methacrylate under ATRP conditions, using CuX/bipyridine catalyst systems (X = Cl or Br) (Scheme 43). The final block copolymers had relatively narrow monomodal molecular weight distributions.



Scheme 1.43.

1. 6. 9. Synthesis of block copolymers by ring opening metathesis to aldol group transfer mechanism transformation

Living polynorbornene was synthesized by ring-opening metathesis polymerization and was terminated using p-$CHOC_6H_4CHO$. Thus, an aldehyde group was introduced at the chain terminus. This group was used as the initiating site for the aldol group transfer polymerization of t-butyldimethylsilyl vinyl ether, producing a polynorbornene-b-poly(silyl vinyl ether) diblock copolymer[291]. The final copolymers had the predetermined molecular weights and compositions. Hydrolysis of the silyl groups in the presence of tetrabutylammonium fluoride and methanol resulted in amphiphilic block copolymers of poly(vinyl alcohol) and polynorbornene (Scheme 1. 44.).



Scheme 1. 44.

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2. Strategy

Based on the results from the literature, it really seems necessary to start from the beginning concerning considerations about the transformation from living/controlled cationic polymerization (LC$^+$Pzn) to living/controlled anionic polymerization (LA$^-$Pzn). The other way around first LA$^-$Pzn and then LC$^+$Pzn is not feasible, since oxygen atoms (e.g. in (meth)acrylates) may disturb the polymerization of isobutylene (IB), due to the complexation of the Lewis acid.

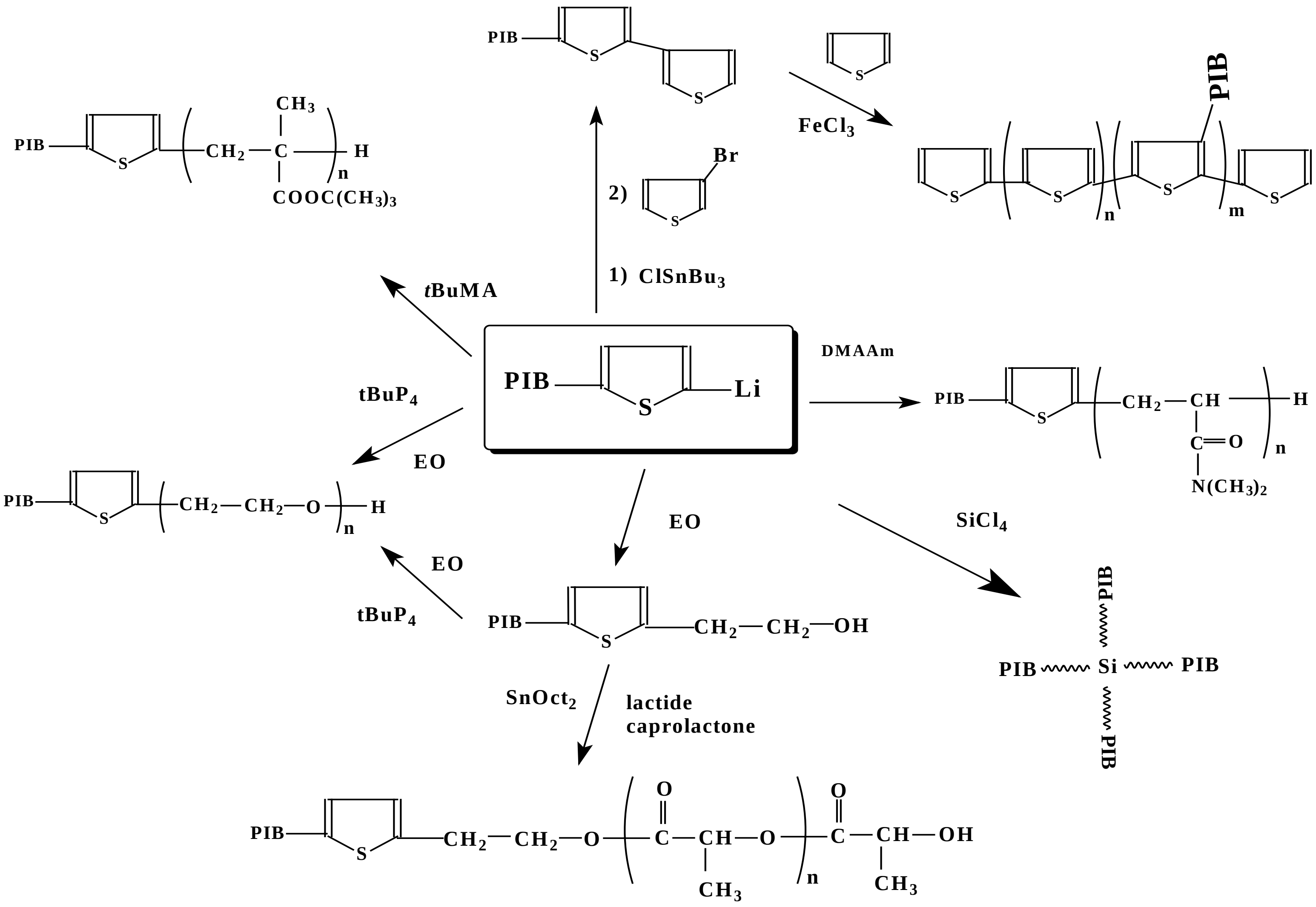
Therefore, the desired way to solve this problem, is to prepare PIB precursors which contain endgroups suitable for subsequent LA$^-$Pzn , primarily of (meth)acrylates. This means, that functional endgroups which can lead to not too reactive carbanions with a versatile number of counterions are wanted. One possible approach is the addition of thiophene to living PIB chains followed by lithiation with BuLi. In this case the resulting carbanion (PIBT-Li) is not similar to DPH-Li, a common initiator for LA$^-$Pzn of (meth)acrylates, but is interesting to see if the resulting carbanion is good initiator for *t*BuMA.

Most of the times the possibility to vary the counterion is essential, since many monomers can be polymerized optimally with one or two distinct counterions (MMA : Li and Cs; DMAA : Cs: **t**BuMA : Li, K, and Cs; EO : K and Cs), but in our case we will use the PIB-T$^-$ Li$^+$ the carry out the polymerization of different monomers.

The metalation with K/Na alloy is inconvenient, it is much easier to use BuLi, but that does not work with PIB-DPE.

The synthesis of polyisobutylene-b-polylactide and polyisobutylene-b-poly(ε-caprolactone) can be performed using hydroxyl-functionalized polyisobutylene (PIB-OH). PIB-OH can be obtained by end-capping of PIB-T$^-$ Li$^+$ with ethylene oxide. The resulting PIB-OH can be used as macroinitiator for the ring-opening polymerizations of L-lactide and ε-caprolactone catalyzed by stannous octoate.

The synthesis of conductive polymers comprising polythiophene or terthiophene can be carry out using the following strategy: terthiophene end-capped polyisobutylene (PIB-TT) can be prepared by monoaddition of terthiophene to living PIB chains. Polythiophene-g-polyisobutylene (PT-g-PIB) graft copolymer is obtained in several steps using bithiophene end-capped polyisobutylene (PIB-BT) as macromonomer : (a) the macromonomer can be prepared using either the use of a Stille coupling reaction or a Suzuki-Miyaura coupling reaction, yielding a polyisobutylene end capped with two units of thiophene in which the last unit of thiophene presented its positions 2 and 5 free allowing the chemical oxidative polymerization, (b) the polythiophene backbone of the polythiophene-g-polyisobutylene (PT-g-PIB) graft copolymer can be synthesized using the chemical oxidative polymerization with anhydrous iron (III) chloride ($FeCl_3$). The scheme 2. 1. shows the different strategies to use in order to synthesize the different polymer structures.



Scheme 2. 1. Synthetic approaches for synthesis of different polymer structures using PIB-T$^-$ Li$^+$.

3. Experimental part

3. 1. Polymerization methods

3. 1. 1. Anionic Polymerization

All the polymerization and functionalization reaction were performed in a sealed laboratory autoclave (Büchi, 1 L) equipped with a stirrer . The probe was fed through a port in the stainless steel top plate of the reactor and immersed into the reaction mixture.

Figure 3.1. Büchi reactor used for the anionic polymerization.

The whole setup together with the solvent distillation is a completely closed system that can be evacuated and held under dry inert atmosphere Figure **3. 2**.

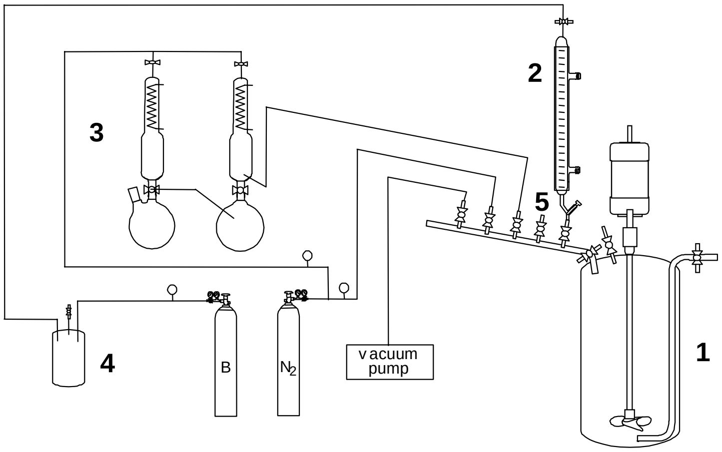


Figure 3. 2. **S**etup of upscaling reactor .1, autoclave ; 2, burette for condensation of gaseous monomers (e. g. butadiene, isobutylene); 3, solvent distillation setup; 4, reactor for purification of butadiene; 5, connector for monomer ampoules, e. g. ethylene oxide.

The procedures are demostrated herein for the anionic polymerization of N,N Dimethylacrylamide in tetrahydrofurane at -40 C. Anionic polymerization of N,N-Dimethylacrylamide using thienyllithium in presence and absence of additives (Et_3Al, Et_2Zn or Et_3B) as well as using TMEDA were carried out in 1 L stirred glass reactor (Büchi) with a thermostatted cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampoules via spherical joint or with dry syringe. Solution of thienyllithium (T-Li) was handled with syringes. In a typical procedure 0.11 mL (0.11 mmol) T-Li solution and 2 equiv mol of Et_2Zn were added to 400 mL purified THF . The reactor was cooled to – 40 °C and after few minutes of stirring the purified monomer (DMA) 9.3 ml (0.09 mol) was added to the mixture initiator / Et_3Al. After completion of the reaction, the reaction was terminated with methanol. The conversion estimated by gas chromatography detection of the residual monomer in the reaction mixture was 95 %. The reaction mixture was concentrated by evaporation and poured into a large excess amount of hexan to precipitate the polymer. Finally, the polymer was dried under vacuum at room temperature.

UV-visible spectroscopy study

The UV-VIS spectrum was recorded in a quartz cuvette (10 mm, equipped with a 9.8 mm spacer) attached to a glass reactor in which the reaction between thienyllithium and Lewis acid took place (see below). The UV-visible absorption spectra were obtained at desired aging intervals.

Figure 3. 3. Glass reactor used for the UV-visible spectroscopy study.

3. 1. 2. Cationic polymerization of isobutylene

All polymerization experiments are performed by a simple laboratory process, making it possible to work in a laboratory hood under inert atmosphere. This technique makes it possible to avoid the use of dry boxes. Before the polymerization is carried out all reagents in the system have to be purified and dry. The procedure is demostrated herein for the cationic polymerization of isobutylene in n-hexane/ CH_2Cl_2

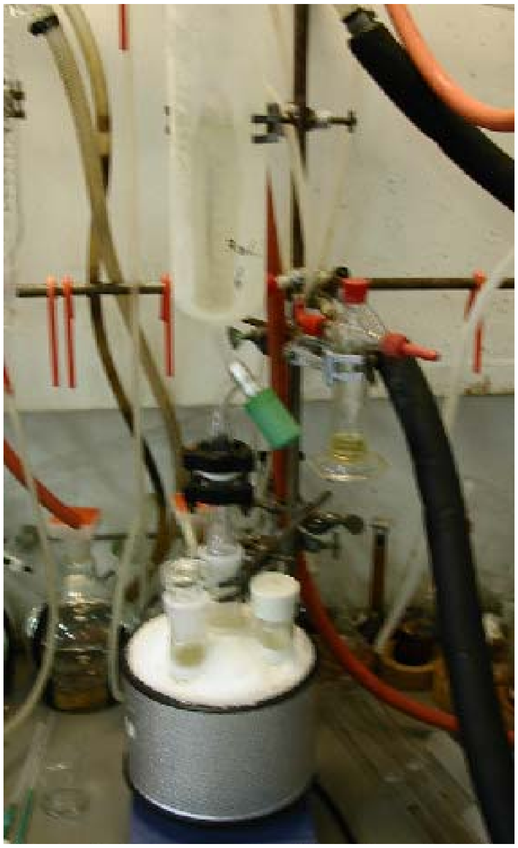


Figure 3. 4. Glass reactor used for the cationic polymerization.

Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added of 240 mL of CH_3Cl, 404 mL of n-hexane, and 0.355 mL (0.302 g, 1.58 mmol) of D*t*BP and then the mixture was cooled to -78 °C. 15 mL (10.57 g, 0.188 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring 0.6 mL (0.525 g, 3.53 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 1.5 mL (2.68 g, 0.014 mol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 28.3 mL (29.74 g, 0.353 mol) of T was added to the polymerization system; the color of the solution changed from slightly yellow to red. T was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude product was dissolved in n-hexane and the mixture was filtered in order to remove inorganic precipitates. Then, the hexanes phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was dissolved in a small amount of *n*- hexane and precipitated two or three times into acetone in order to remove excess T.

3. 1. 3. Ring Opening Polymerization

All operations except the polymerization were carried out in a glove box under nitrogen atmosphere. A representative polymerization procedure was as follows: L-Lactide (LA) (1.7511 g , 12.15 mmol) and 2-(2-thienyl)ethanol (0.1384 g , 1.079 mmol) were weighed into a round-bottom flask. The LA and 2-(2-thienyl)ethanol were dissolved in THF and after few minutes of stirring, dry $SnOct_2$ (0.43 g , 1.079 mmol) was added. The mixture was stirred until all the initiator, monomer and catalyst were dissolved completely. After few minutes of stirring the flask was sealed and the polymerization was started by immersing the flask in an oil bath at 120 °C for a certain time. The polymerization was stopped by cooling to room temperature and after removing the solvent, the monomer conversion was determined by ^1H NMR from monomer and polymer signals. Finally, the polymer was dissolved again and was precipitated into hexane and dried under vacuum at room temperature.

3. 2. Characterization

3. 2. 1. Scanning force microscopy (SFM)

SFM has become a versatile method for characterization of the microstructure of polymeric materials at the nanometer scale[1]. In addition to the topological resolution, SFM can distinguish surface areas differing in local mechanical properties and composition, respectively[2,3]. Mechanical properties, such as viscoelasticity, friction, and adhesion, as well as long-range electrostatic and steric forces can be characterized on the scale of a few nanometers.

The instrument used in this work is a Digital Instruments Dimension 3100 SFM with a Nanoscope III Controller. Of particular interest in determining topography and phase morphology of polymers is Tapping Mode SFM.

Tapping Mode measures topography by lightly tapping the surface with an oscillating probe tip. This technique eliminates lateral forces that can damage soft samples and reduce image resolution. Tapping Mode imaging is implemented in ambient air by oscillating the cantilever at or near its resonance frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a high amplitude (typically equal or greater than 20 nm) when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to slightly touch, or “tap” the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 250 - 350 kHz. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation amplitude is reduced due to energy loss caused by the tip contacting the surface. The oscillation amplitude of the tip is measured. A digital feedback loop then adjusts the tip-sample separation to maintain a constant amplitude. The reduction in oscillation amplitude is used to identify and measure surface features.

Two important types of images which are used in this work described in the following:

Height image: The vertical position of the probe tip is monitored by noting changes in the length of the z-axis on the xyz scanning piezo tube. The input voltage to the scanning piezo tube is proportional to the length of the tube. The change in the z-axis is plotted as a topographical map of the sample surface. Height data is a good measure of the height of surface features but does not show distinct edges of these features.

Phase image: This type of imaging monitors the change in phase offset, or phase angle, of the oscillating cantilever with respect to the phase offset of the input drive signal (to the drive piezo). The phase of the drive signal is compared to the phase of the cantilever response signal on the photo diode detector. The phase offset between the two signals is defined as zero for the cantilever oscillating freely in air. As the probe tip engages the sample surface, the phase offset of the oscillating cantilever changes by a certain angle with respect to the phase offset of the input drive signal. As regions of differing elasticity are encountered on the sample surface, the phase angle between the two signals changes. These changes in phase offset are due to differing amounts of damping experienced by the probe tip as it rasters across the sample surface. This phase shift is very sensitive to variations in material properties such as adhesion and viscoelasticity.

Applications include contaminant identification, mapping of components in composite materials, and differentiating regions of high and low surface adhesion or hardness.

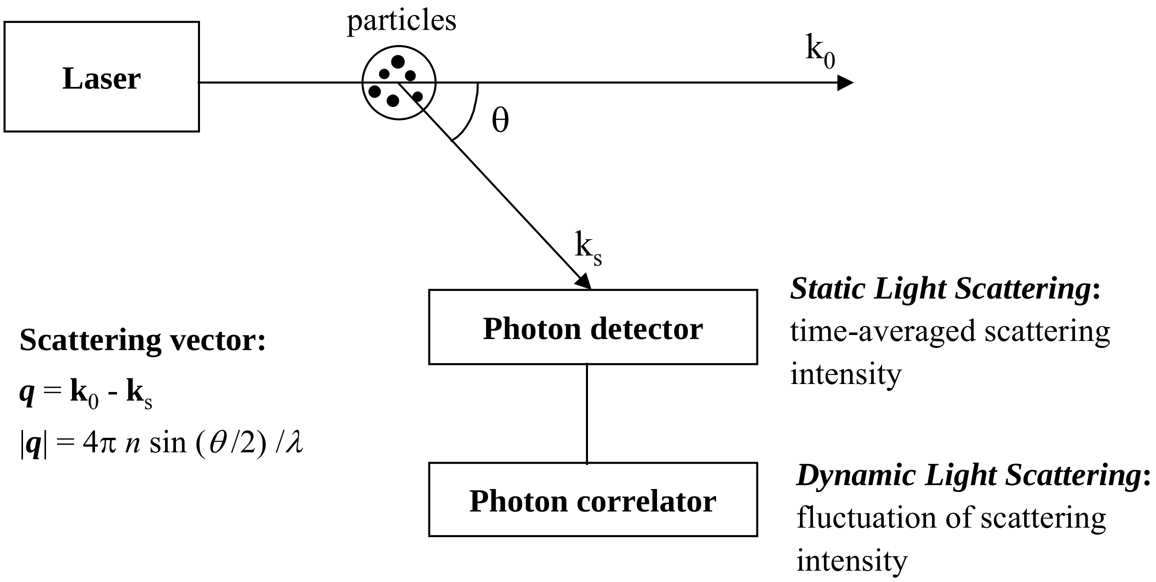
3. 2. 2. Light scattering

When an incident light of intensity I_0 penetrates a medium, a loss of intensity may happen due to the scattering and/or absorption:

$$I_0 = I_t + I_s + (I_a) \qquad \text{Eq. 3-1}$$

where I_t , I_s and I_a denote the intensities of the transmitted, scattered and absorbed light respectively.

Light scattering is very useful in determination of the molecular weight and the size of polymer. Generally, as an characterization method for polymer solutions, light scattering includes static light scattering (SLS) and dynamic light scattering (DLS), which study the equilibrium behavior and dynamic behavior of polymer solutions respectively (Scheme 2-7). In SLS, the time-averaged “excess” scattering intensity of polymer solution above that of pure solvent is measured, which is directly proportional to the dimension of polymer as well as concentration. On the other hand, In DLS method the detector monitors the dynamic behavior of the intensity of scattered light (scattering intensity fluctuation), which is related to the movements of scattering molecules, and therefore diffusion coefficient and the corresponding hydrodynamic radius of the molecule can be determined.



Scheme 3. 1**.** Schematic illustration of light scattering

Dynamic light scattering (DLS)

Polymer molecules in solution always undergo Brownian movements, which result in the fluctuation in scattering intensity. DLS is a technique to investigate the scattering intensity fluctuation and get the size information of molecule. Molecules in solution move in all directions with the same probability and they have a continuous rate distribution. Consequently, the frequency of the scattered light is shifted to higher or lower values depending on the velocity and moving direction of the molecules relative to the detector (Doppler effect). Thus, a broadening of the spectrum is observed with respect to the frequency line of the stimulating radiation (ν_0). Therefore, light scattering is rather quasi-elastic than elastic[4]. The spectral broadening is too small to be detected by conventional spectrometers working in the frequency domain (interferometers). For this reason, measurements are performed in the time domain, and fluctuation of the scattered light with time is measured. Generally, this is done according to the Homodyn method, i.e. the scattering light is directed to the photo detector. The detector's output signal is proportional to the intensity of light I(t) and, thus, also proportional to the mean square of the electric field $|E(t)|^2$. The output signal of the detector is auto-correlated with time according to the following equation[5,6]:

$$g_2(t) = \frac{\langle I(0)\cdot I(t)\rangle}{\langle I(0)\rangle^2} \qquad \text{Eq. 3-2}$$

where $g_2(t)$ is the normalized intensity autocorrelation function.

The field autocorrelation function $g_1(t)$, which describes the fluctuations of the electric field of the scattered light, can be deduced from $g_2(t)$ using the Siegert relation:[39]

$$g_1(t) = \frac{\langle E(0) \cdot E(t) \rangle}{\langle E(0) \rangle^2} = \sqrt{\frac{g_2(t) - A}{B}} \qquad \text{Eq. 3-3}$$

where A and B are usually equal to unity. A is determined by an experimental baseline, and B is a coherence factor accounting for deviation from ideal correlation.

For monodisperse hard spheres, $g_1(t)$ can be described by an exponential function:

$$g_1(t) = \exp(-\Gamma \cdot t) \qquad \text{Eq. 3-4}$$

where Γ is the fluctuation rate with $\Gamma = Dq^2$, and D is the translational diffusion coefficient, which can be used to calculate the hydrodynamic radius R_h via Stokes-Einstein equation[7].

$$R_h = \frac{kT}{6\pi\eta D} \qquad \text{Eq. 3-5}$$

where k is Boltzmann constant, T is the temperature Kelvin, and η is the solvent viscosity.

For a system of polydisperse spheres, the following equation holds:

$$g_1(q,t) = \sum_j a_j(q) \exp(-\Gamma_j t) \qquad \text{Eq. 3-6}$$

with $a_j(q)$ = relative amplitudes:

$$a_j(q) = \frac{c_j M_j P_j(q)}{\sum_j c_j M_j P_j(q)} \qquad \text{Eq. 3-7}$$

where M_j and $P_j(q)$ are the molecular weight and particle form factor, respectively, of particle j. In the case of large spheres (diameter > $\lambda/20$ and $P_j(q) < 1$), $g_1(t)$ becomes dependent on q. Change from hard spheres to polymer molecules in solution involves rotational diffusion and internal modes in addition to translational diffusion. Rotational diffusion is of particular importance in rod-like molecules, whereas internal modes are significant in large coil-like molecules[7]. From a mathematical point of view, these factors involve additional additive and multiplicative terms. The terms can be eliminated by angle-dependent measurements as the amplitudes approach zero for $q^2 \rightarrow 0$.

The determination of the mean diffusion coefficient and standard deviation for polydisperse systems is best accomplished by the CONTIN method[8,9]. The function $g_1(t)$ is described by a continuous distribution:

$$g_1(t) = \int_{\Gamma_{\min}}^{\Gamma_{\max}} G(\Gamma)\exp(-\Gamma \cdot t)d\Gamma \qquad \text{Eq. 3-8}$$

where $G(\Gamma)$ denotes the fluctuation rate distribution function. Equation 2-15 can be inverted by a Laplace transformation. This inversion is problematic as there is basically an unlimited number of solutions that describe the data within experimental error. In order to minimize these solutions, the CONTIN analysis uses the following regularization:

$$R_n(G(\Gamma)) = \int_{\Gamma_{\min}}^{\Gamma_{\max}} \left(\frac{\partial^n G(\Gamma)}{\partial \Gamma^n} \right) d\Gamma \qquad \text{Eq. 3-9}$$

where n is the order of regularization. Regularization of 0th order represents minimization of the integration area of function $G(\Gamma)$; regularization of 2nd order corresponds to smoothing of function $G(\Gamma)$. The original CONTIN routine calculates a rate distribution ($\log(\Gamma)$ scale), whereas the CONTIN routine of the ALV software calculates a time distribution ($\log(t)$ scale) that is proportional to the distribution of hydrodynamic radius.

The ALV software also enables a direct fit of $g_2(t)$-1 via a special algorithm. This usually yields a smoother distribution function with less artifacts as compared to $g_1(t)$.

$$g_2(t) - 1 = \left(\int_{t_{\min}}^{t_{\max}} e^{-t} G(t)dt \right)^2 \qquad \text{Eq. 3-10}$$

Care must be exerted on interpreting results so as to avoid artifacts, especially in the case of a low signal-to-noise ratio, an inappropriate baseline or inappropriate choice of $\Gamma_{\max}$ and $\Gamma_{\min}$. Thus, the signal-to-noise ratio should always be high. For evaluation of the results, it should be considered that two different distributions can only be distinguished with the CONTIN program if the respective hydrodynamic radii differ from each other by a minimal factor of two.

The mean radii or rather diffusion coefficients obtained by the CONTIN method are z values. In order to eliminate the influence of form factors for large molecules, the D and R_h values, respectively, measured at different angles have to be extrapolated for $q^2 \rightarrow 0$.

3. 2. 3. High Performance Liquid Chromatography (HPLC) under critical conditions

In HPLC the separation of polymers is achieved by adsorption on the pore material which corresponds to the thermodynamic quantity, enthalpy (ΔH) [10]. The critical point of adsorption is related to a chromatographic situation (through the choice of solvents and temperature), where the entropic and enthalpic interaction of the polymers and the column material compensate for each other. The free energy of the polymer does not change when entering the pores of the stationary phase ($\Delta G = 0$, $T\Delta S = \Delta H$). Based on this relation, the distribution coefficient $K_d = 1$ ($\Delta G = -RT\ln K_d$, where K_d is equal to the ratio of the analyte concentration in the stationary phase and in the mobile phase), meaning all polymers with chemically equal structure elute in one peak irrespective of the molar mass. Therefore, this analysis method can be used to separate homopolymers with different endgroups and homopolymers from block copolymers. In case of block copolymers the conditions are adjusted in a way where one of the segments is "invisible" at the critical point and the second in SEC mode and thereby, blocking efficiencies can be calculated[11]. Data related to the used HPLC apparatus: Temperature: 35 ^{o}C; Solvents: depend on the analyzed polymers; Pump: Thermo Separation products (TSP) P4000, flow-rate: 0.5 ml/min; UV-detector (TSP UV3000) with variable wave-lengths; Evaporating light scattering detector (Polymer Laboratories): analysis temperature: 40-60 ^{o}C and gas flow-rate: 3-4 l/min; columns: depend on the analyzed polymers. Software: Win-GPC4 from PSS. The conditions for critical HPLC analysis of PtBMA are: Column combination: Modified-YMC, S-5µm, 25 cm x 4 mm, RP18, 120 Å and 300 Å and solvent mixture: $THF:CH_3CN$ 53:47.

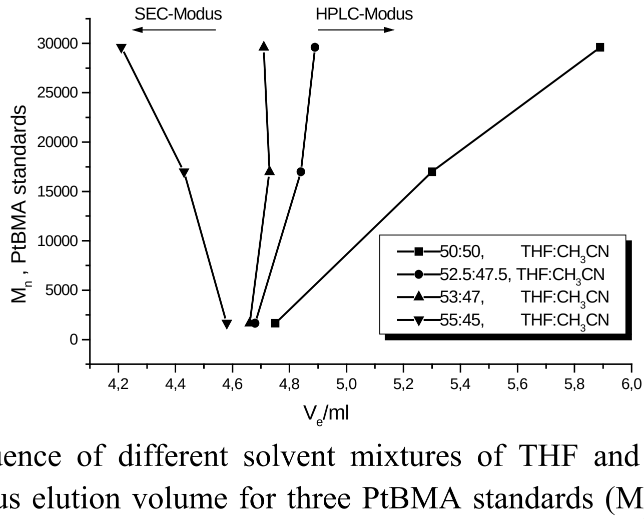


Figure 3. 5. The influence of different solvent mixtures of THF and CH_3CN on the molecular weight versus elution volume for three PtBMA standards (M_n: 1640, 17,000, and 29,600) is shown.

In Figure 4.3, the results related to different ratios of THF and CH_3CN are illustrated. It is easy to see that even small changes in the solvent composition shifts the chromatographic mode from SEC to HPLC and vice versa.

In a similar way it was found the critical conditions for PIB. The critical solvent composition for PIB is THF/Methanol 80.5/19.5 (wt/wt). LACCC was conducted on a TSP HPLC system at a flow rate of 0.5 mL/min. An Evaporative Light Scattering Detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow rate of 3.5 L/min was used for mass detection. 10 μL of ca. 0.5 wt% polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two Reversed Phase columns (YMC, 250 x 4 mm) with 5 μm average particle size, 100 Å and 300 Å pore diameter were used.

3. 2. 4. NMR spectroscopy

^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AC 250 at an operating frequency of 250 MHz and 62.5 MHz, respectively. Various deuterated solvents (Deutero GmbH) were used depending on the solubility of the samples. As an internal standard, either tetramethylsilane or the residual proton signal of the deuterated solvent was used.

3. 2. 5. UV/visible spectroscopy

UV spectra were recorded on a Perkin-Elmer Lambda15 UV-vis spectrophotometer in the wavelength range from 190 to 700 nm. Measurements were carried out in solution. The spectrum from a quartz cuvette containg pure solvent was subtracted from sample spectra.

3. 2. 6. Gel permeation chromatography (GPC)

SEC experiments were performed on a Waters instrument calibrated with narrowly distributed polystyrene standards at 30 °C. Four PSS-SDV columns (5µm, Polymer Standards Service, Mainz) with a porosity range from 10^2 to 10^5 Å were used together with a differential refractometer and a UV-detector at 254 nm. Measurements were performed in THF with a flow rate of 1 ml/min using toluene as internal standard.

3. 2. 7. Differential Scanning Calorimetry (DSC)

For thermal analysis a Perkin Elmer DSC 7 with a CCA 7 liquid nitrogen cooling device was used. For all measurements a two point calibration with n-decane and indium was applied. Measurements of polymers were carried out at a scanning rate of 10 °C/min. All displayed heating traces correspond to the second heating run in order to exclude effects resulting from any previous thermal history of the samples.

3. 2. 8. Fluorescence spectroscopy

The samples for fluorescence measurements were prepared according to a procedure described elsewhere[12-14]. Certain aliquots (60µl) of 2.5×10^{-5} M solution of pyrene in acetone were carefully dropped into empty dark vials by a 100 µl Hamilton microsyringe, acetone was afterwards evaporated by gentle heating. Then the sample solutions (3 ml) prepared by an appropriate dilution of the stock solutions of PIB-b-PEO were added. To equilibrate pyrene, the prepared samples were kept at 40-50°C for ca. 2 days under intensive stirring. The final concentration of the fluorescent probe in the prepared samples was kept constant at 5×10^{-7} M, that is, only slightly below the saturation concentration of pyrene in water at 22°C.

Steady-state fluorescence spectra of the air-equilibrated samples were recorded with a Hitachi F-4000 fluorescence spectrophotometer (right angle geometry, 1 cm × 1 cm quartz cell). The widths of slits were chosen to be 3 and 1.5 nm for excitation and emission, respectively.

3. 3. References

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4. Polyisobutylene stars and polyisobutylene-*block*-poly(*tert*-butyl methacrylate) block copolymers by site transformation of thiophene end-capped polyisobutylene chain ends.[1]

4. 1. Introduction

Living polymerizations provide the most versatile synthetic routes for the preparation of a wide variety of well-defined polymer structures, such as end-functionalized polymers, star-shaped polymers, or block copolymers. Since specific living polymerization methods (e.g., anionic and carbocationic polymerizations) are applicable only to a limited number of monomers, the combination of different living polymerization techniques is expected to lead to new and unique combination of blocks in block copolymers. Recent success in the synthesis of functionalized polyisobutylene (PIB) with quantitative functionality and of block copolymers with high structural integrity is based on the applications of non-(homo)polymerizable monomers such as 1,1-diphenylethylene (DPE) in cationic polymerization.[1] These processes involve the intermediate capping reaction of living PIB with DPE or its derivatives. The resulting stable and fully ionized carbenium ions have been successfully employed for the quantitative end-functionalization of living PIB with soft nucleophiles such as silyl ketene acetals[2] and the controlled initiation of the second monomers such as *p*-methyl styrene[3] and isobutyl vinyl ether.[4]

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[1] This chapter has already been published: N. Martínez-Castro, M. G. Lanzendörfer, A. H. E. Müller, J. C. Cho, M. H. Acar, R. Faust, *Macromolecules* **36,** 6985 (2003).

Block copolymers of isobutylene (IB) and polar monomers, such as methacrylates, acrylamides, polyethers, or polyesters combine the high environmental stability of elastomeric, non-polar PIB with the large variety of structures and properties of polar polymers. Since PIB can only be obtained by carbocationic polymerization, however, many attempts have been undertaken to transform living cationic PIB chain ends to radical[5] or anionic ones.[6]

Although many prior attempts were less successful, metalation of DPE end-capped PIB with Na/K alloy or cesium followed by anionic polymerization allowed to synthesize PIB-*b*-P*t*BMA diblock copolymers, PMMA-*b*-PIB-*b*-PMMA triblock copolymers, and (PMMA-*b*-PIB)$_3$ starblock copolymers with high blocking efficiency.[7,8] Metalation with alkali metals, however, is inconvenient and lithiation with butyllithium would be preferable. Unfortunately, lithiation of DPE end-capped PIB by alkyllithium does not proceed quantitatively. This led us to search for other capping agents which might be more easily lithiated. Recently, Faust et al. showed that furan (Fu) functional polyisobutylene (PIB-Fu) can be obtained by the quantitative reaction of living PIB and 2-tributylstannyl furan.[9] Using unsubstituted Fu, coupling of two living chain ends as a side reaction could not be avoided. PIB-Fu chain ends could be lithiated with *n*-BuLi, however, the polymerization of methacrylates using this macroinitiator was accompanied by side reactions. [10]

In place of PIB-Fu, thiophene (T) functional PIB (PIB-T) could also be used in the metalation reaction. An additional advantage is that unsubstituted T may be used to prepare PIB-T, since the reactivity of thiophene is about one tenth of Fu.[11] Iván et al. reported on attempts to use T as a coupling agent for living PIB, but under the conditions chosen (-80 °C, methylcyclohexane/dichloromethane 60/40 v/v, [$TiCl_4$]/[initiator]/[T] = 10/2/1) only 17% of coupling product was formed after 2 h and 36% after approx. 24 h when stirred at room temperature.[12] Obviously, they did not aim at mono-functionalization of PIB with T.

We wish to present a new route to anionic PIB macroinitiators by end-capping of living PIB with one T molecule and subsequent lithiation with *n*-BuLi. These macroinitiators efficiently initiate the anionic polymerization of *tert*-butyl methacrylate (*t*BMA) to produce block copolymers in nearly quantitative yield. Moreover, we will show that they can also be used for the synthesis of PIB stars by coupling with chlorosilanes,[13,14] a method well established for the coupling of anionic chain ends, e.g. living polybutadiene, to form star polymers.

4. 2. Experimental part

4. 2. 1. Materials

2,6-Di-*tert*-butylpyridine (D*t*BP, Aldrich, 97%) was purified by distillation from CaH_2. Isobutylene (IB, BASF) was passed through in-line gas purifier columns packed with $CaSO_4$ and no. 13 molecular sieves and condensed at -15 °C prior to polymerization. CH_3Cl was passed through in-line gas purifier columns packed with BaO/Drierite and condensed at -80 °C prior to polymerization. CH_2Cl_2 was purified by washing it with 10% aqueous NaOH and then with distilled water until neutral and dried over anhydrous $MgSO_4$ overnight. It was refluxed for 24 h and distilled from CaH_2, just before use. N-hexane was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with 10% aqueous NaOH and then with deionized water until neutral and stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled. Methylcyclohexane (MeCHX, Aldrich, 99%) and titanium (IV) chloride ($TiCl_4$, Aldrich, 99.9%) was used as received. Thiophene (T, Aldrich, 99%) was distilled the day before use and stored at 4 °C. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by hydrochlorination of 2,4,4-trimethyl-1-pentene (Fluka, 98 %) with hydrogen chloride gas in dry dichloromethane at 0 °C.[15] The product was dried over $CaCl_2$ and distilled under reduced pressure before use. 5-*tert*-Butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*BuDiCumCl) was synthesized following the procedure reported elsewhere.[16] Chlorotrimethylsilane (Me_3SiCl) and tetrachlorosilane ($SiCl_4$) (both Merck, 98 %) were stirred over freshly ground CaH_2 for at least 24 h, followed by distillation prior to use. Triethylaluminum ($AlEt_3$, Aldrich, 1.0 M in hexane) was used as received. *tert*-Butyl methacrylate (*t*BMA, BASF) was predried with CaH_2, carefully degassed by freeze-thaw cycles in high vacuum, mixed with $AlEt_3$ solution until a yellow color persisted and then condensed into ampoules. THF (Merck p.a) was purified first by distillation under nitrogen from CaH_2 and then by refluxing over potassium. *n*-Butyllithium (*n*-BuLi, 1.6 M in hexane) was purchased from Aldrich and its concentration was titrated by a standard method.[17]

4. 2. 2. Synthesis

Synthesis of Thiophene-Ended PIB (PIB-T)

The synthesis of PIB-T was carried out under a dry nitrogen atmosphere in a glovebox. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added of 240 mL of CH_3Cl, 404 mL of n-hexane, and 0.355 mL (0.302 g, 1.58 mmol) of D*t*BP and then the mixture was cooled to -78 °C. 15 mL (10.57 g, 0.188 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring 0.6 mL (0.525 g, 3.53 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 1.5 mL (2.68 g, 0.014 mol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 28.3 mL (29.74 g, 0.353 mol) of T was added to the polymerization system; the color of the solution changed from slightly yellow to red. T was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude product was dissolved in n-hexane and the mixture was filtered in order to remove inorganic precipitates. Then, the hexanes phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was dissolved in a small amount of *n*- hexane and precipitated two or three times into acetone in order to remove excess T.

Synthesis of α,ω-Dithiophene-Ended PIB (T-PIB-T)

The polymerizations were initiated with the difunctional initiator 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*BuDiCumCl). After the completion of IB polymerization, equal volumes of the polymer solution in the reactor were delivered into culture tubes. To each culture tube additional amount of $TiCl_4$ or D*t*BP was charged to vary the ratio of [$TiCl_4$] to [*t*BuDiCumCl] or [D*t*BP] to [*t*BuDiCumCl] in the polymer solution. The functionalization of PIB was conducted by two different methods: addition of T/CH_3Cl solution into the polymer solution (T to polymer) and addition of the polymer solution into T/CH_3Cl solution (polymer to T). 200 equiv. of T was used for the functionalization of PIB. After 1 h, the reaction mixture was quenched with prechilled methanol and poured into methanol. The polymer was purified by the precipitation of the polymer solution into methanol, followed by drying in vacuum.

Synthesis of PIB-*b*-P*t*BMA

All copolymerizations were carried out in 1 L stirred glass reactor (Büchi) with a thermostated cooling jacket, steel capillary connections to introduce gases and solvents, and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampoules via spherical joint or with dry syringe. Solutions of *n*-BuLi and macroinitiator (PIB-T) were handled with syringes. In a typical procedure 5 mL (8 mmol) *n*-BuLi solution were added to 400 mL purified THF and aged at room temperature over night. On the next day macroinitiator, monomer, and *n*-BuLi were introduced and cooled to –40 °C.[18] A 1.21 g (0.355 mmol) of PIB-T ($M_n = 3.40 \times 10^3$ g/mol) were freeze-dried from benzene solution for 8 h and then vacuum-dried for more than 10 h. On a vacuum line, the dried PIB-T was dissolved in THF and then the mixture was added to the stirred glass reactor and cooled to -40 °C. 0.23 ml (0.368 mmol) *n*-BuLi solution was added with a dry syringe afterwards. The reaction was held at -40 °C for 1 h and then 5.34 g (0.037 mol) *t*BMA was added in bulk to the macroinitiator solution. After 2.5 h the polymerization was quenched with methanol. Finally, the polymer was precipitated into isopropanol and dried under vacuum at room temperature. In a second experiment a fourfold excess of *n*-BuLi was used and the unreacted BuLi was destroyed by heating to +40 °C for 1 h.

Synthesis of 2-(1,1,3,3-tetrametylbutyl)thiophene (TMP-T)

Model reactions with TMPCl were carried out under identical conditions to living cationic polymerizations of IB at -78 °C. In a 500 mL three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added 16 mL of CH_2Cl_2, 20 mL of *n*-hexane, and 0.07 mL (0.059 g, 0.312 mmol) of D*t*BP and then the mixture was cooled to -78 C. After 10 min of stirring 5.07 mL (4.43 g, 29 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 6.57 mL (11.38 g, 60 mmol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 2.6 mL (2.73 g, 32 mmol) of T in a solution of 6 mL of *n*-hexane and 4 mL of CH_2Cl_2 was added to the system. T was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 20 mL (15.7 g, 0.51 mol) of prechilled methanol. Finally, the solvent was removed on a rotary evaporator and the product (TMP-T) was dried and distilled under reduced pressure before use.

Lithiation of TMP-T and reaction with Me_3SiCl

Reaction of lithiated TMP-T with Me_3SiCl was carried out under identical conditions to living anionic polymerizations of *t*BMA. In a 1 L stirred glass reactor were added 400 mL of THF and 1.75 g (8.93 mmol) of TMP-T and then the mixture was cooled to -40 °C. After 10 min of stirring 7.25 mL (11.6 mmol) of *n*-BuLi was transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with TMP-T for 60 min to form the anion ($PIB\text{-}T^-,Li^+$). The system was warmed to +40 °C and stirred for 1 h in order to destroy the excess of *n*-BuLi, followed by addition of 1.46 mL (1.26 g, 11.6

mmol) of Me_3SiCl. Finally, the solvent was removed on a rotary evaporator and the product (TMP-T-$SiMe_3$) was dried and distilled under reduced pressure.

Synthesis of Star-Shaped PIB using $SiCl_4$

The synthesis of star-shaped PIB using $SiCl_4$ was carried out in a glass reactor. To the reactor 40 mL of THF and 0.5081 g (0.149 mmol) of PIB-T (M_n = 3.40 x 10^3 g/mol) were added and then the mixture was cooled to -40 °C. After 10 min of stirring 0.280 mL (0.448 mmol) of *n*-BuLi was transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with PIB-T for 60 min. Afterwards the system was warmed to 40 °C and stirred for 1 h in order to destroy the excess of *n*-BuLi. Then 4.34 μL (0.037 mmol) of $SiCl_4$ was added and allowed to react with the living chain ends for 2 h at 40 ºC or for 22 h at 22 °C. Finally, the reaction was quenched by adding 5 mL (3.93 g, 0.12 mol) of prechilled methanol. The product was precipitated into isopropanol and dried under vacuum at room temperature.

4. 2. 3. Characterizations

^{1}H-NMR spectroscopy was carried out on a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$ using TMS as an internal standard. *Gas Chromatography* (GC) was carried out on a Fisons GC 8000 model equipped with flame ionization detection (FID). A DB1 methylpolysiloxane column (30 m x 0.53 mm I.D.) was used with hydrogen as carrier gas. *Size Exclusion Chromatography* (SEC) was performed using THF as eluent at a flow rate of 1 mL/min equipped with four 30 cm PSS SDVgel columns (particle size 5 μm, porosity 10^2 - 10^5 Å) heated to 40 °C. Calibration was based on PIB and PtBMA standards (PSS, Mainz). Molecular weights of PIB stars were determined by universal

calibration using three 30 cm PSS SDVgel columns of 5 μm with 10^3 , 10^5 , and 10^6 Å porosity; detectors: Shodex RI-71 refractive index detector; Jasco Uvidec-100-III UV detector (λ = 254 nm); Viscotek viscosity detector H 502B. *Liquid adsorption chromatography under critical conditions* (LACCC) was conducted on a TSP HPLC system at a flow rate of 0.5 mL/min. An Evaporative Light Scattering Detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow rate of 3.5 L/min was used for mass detection. 10 μL of ca. 0.5 wt% polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two Reversed Phase columns (YMC, 250 x 4 mm) with 5 μm average particle size, 100 Å and 300 Å pore diameter were used. The critical solvent composition for PIB is THF/Methanol 80.5/19.5 (wt/wt). Premixing of the mobile phase by weight is necessary for a constant and exact composition.

4. 3. Results and Discussion

4. 3. 1. Endcapping of PIB with Thiophene

Model experiments with TMPCl

Orienting model experiments were carried out with TMPCl, which mimics the end group structure of *tert*-chloro-terminated PIB and the living chain ends upon addition of $TiCl_4$ as a Lewis acid. These reactions were carried out in order to investigate the end-capping with T. The ^{1}H NMR spectrum of 2-(1,1,3,3-tetrametylbutyl)thiophene is shown along with the assignments in Figure 4. 1. The resonances identified in the aromatic range at 6.82 (1H on Cd), 6.89 (1H on Ce), 7.10 (1H on Cf) confirmed one thiophene ring substituted by the TMP residue). In the aliphatic region the ^{1}H NMR spectral assignments are as follows: 0.81 ppm (s, 9H, CH_3), 1.44 ppm (s, 6H, CH_3), 1.73 ppm (s, 2H, CH_2), 6.82 ppm (m, 1H, thiophene CH), 6.89 ppm (m, 1H, thiophene CH), 7.10 ppm (m, 1H, thiophene CH).

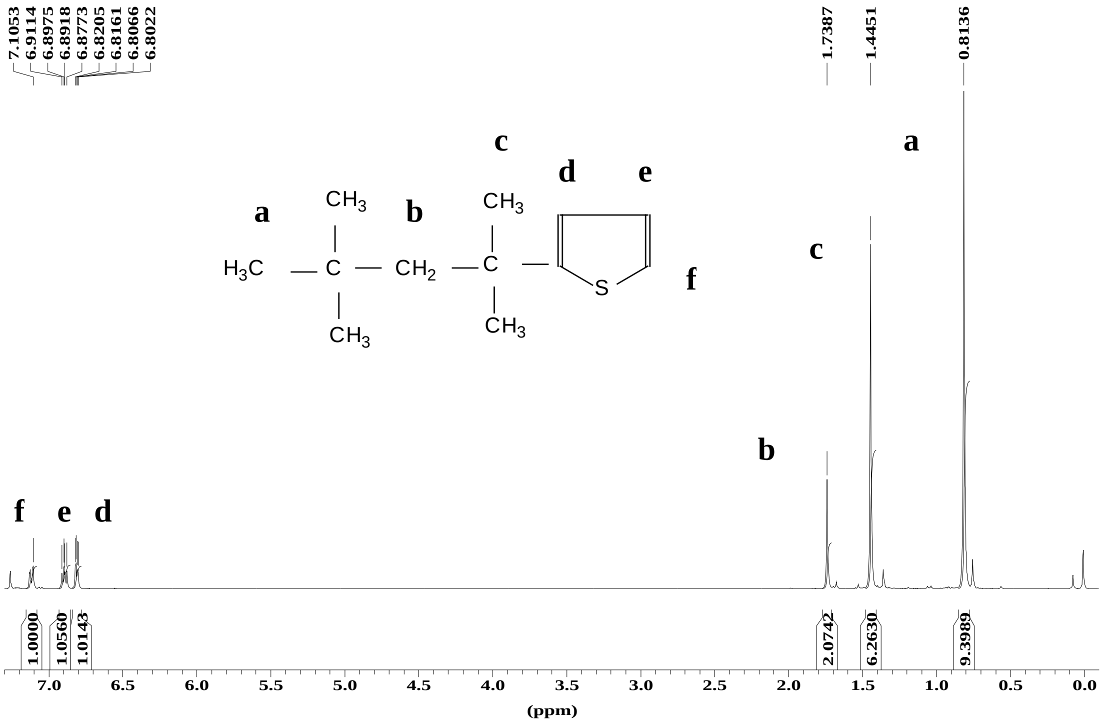


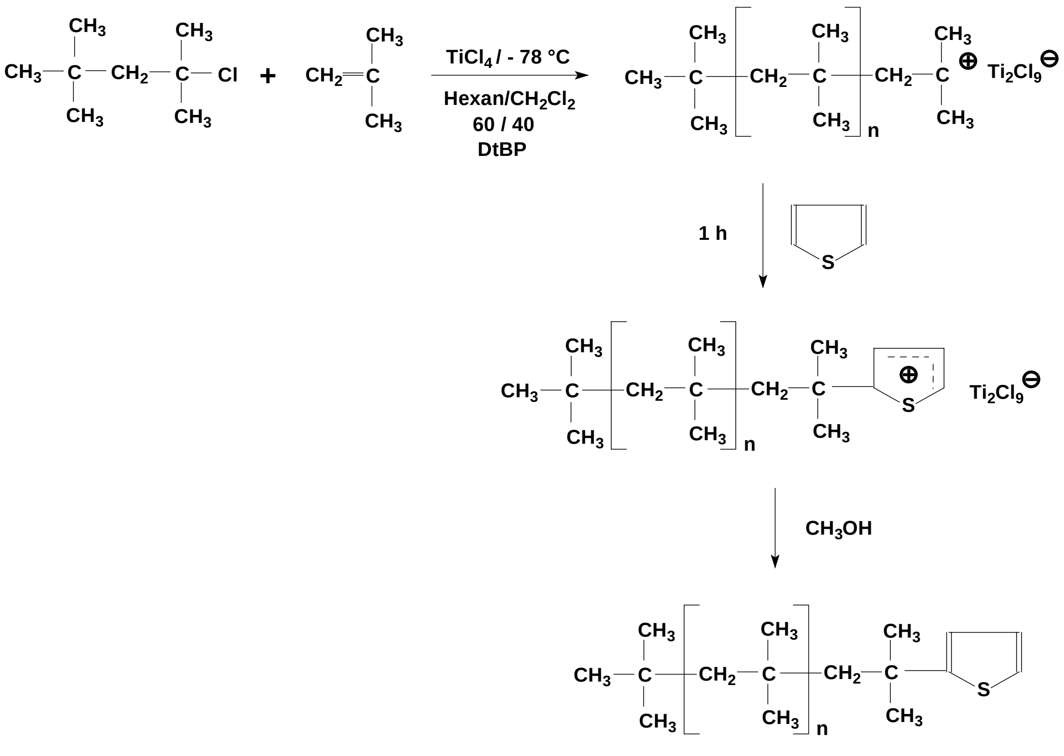
Figure 4. 1. ^{1}H NMR spectrum of 2-(1,1,3,3-tetramethylbutyl)thiophene

Synthesis of Thiophene-Ended PIB (PIB-T)

It was of interest to determine whether the end-functionalization results obtained with the model compounds could be applied to the synthesis of thiophene-ended PIB. Thiophene end-quenching of living PIB chain ends initiated by the TMPCl/$TiCl_4$ system took place at –78 °C according to Scheme 4. 1. Figure 4. 2 shows the ^{1}H NMR spectrum of the resulting polymer. This spectrum indicates quantitative end-functionalization and formation of 2-polyisobutylenyl-thiophene (PIB-T) by this process. This confirms results obtained with the corresponding model compound. Quantitative addition was indicated by the disappearance of the peaks at 1.9 ppm (PIB-**CH_2**-$C(CH_3)_2$-Cl) and 1.69 ppm (PIB-CH_2-C(**CH_3**)$_2$-Cl). A new set of peaks at 1.82, 6.80, 6.88, and 7.09 ppm appeared due to the presence of the thiophene ring at the chain end. Undesirable coupling products (double addition of PIB at thiophene[12]) or other side reactions, e.g. as determined with furan,[9,19] were not detectable under the conditions used. The details of the capping experiments are given in Table 4. 1.

Exp.No.	$[IB]_o$ M	$[TMPCl]_o$ mM	$[DtBP]_o$ mM	$[TiCl_4]_o$ mM	$[T]_o$ M	Mn x 10^{-3} g / mol	Mw / Mn
1	0.28	5.35	2.39	21	0.53	3.41	1.25
2	0.44	8.33	3.7	34	0.71	3.23	1.26
3	0.47	8.33	3.7	34	0.71	3.46	1.28

Table 4. 1. Experimental conditions and results of IB polymerization using TMPCl as initiator and thiophene endcapping



Scheme 4. 1. Capping of Living PIB with Thiophene

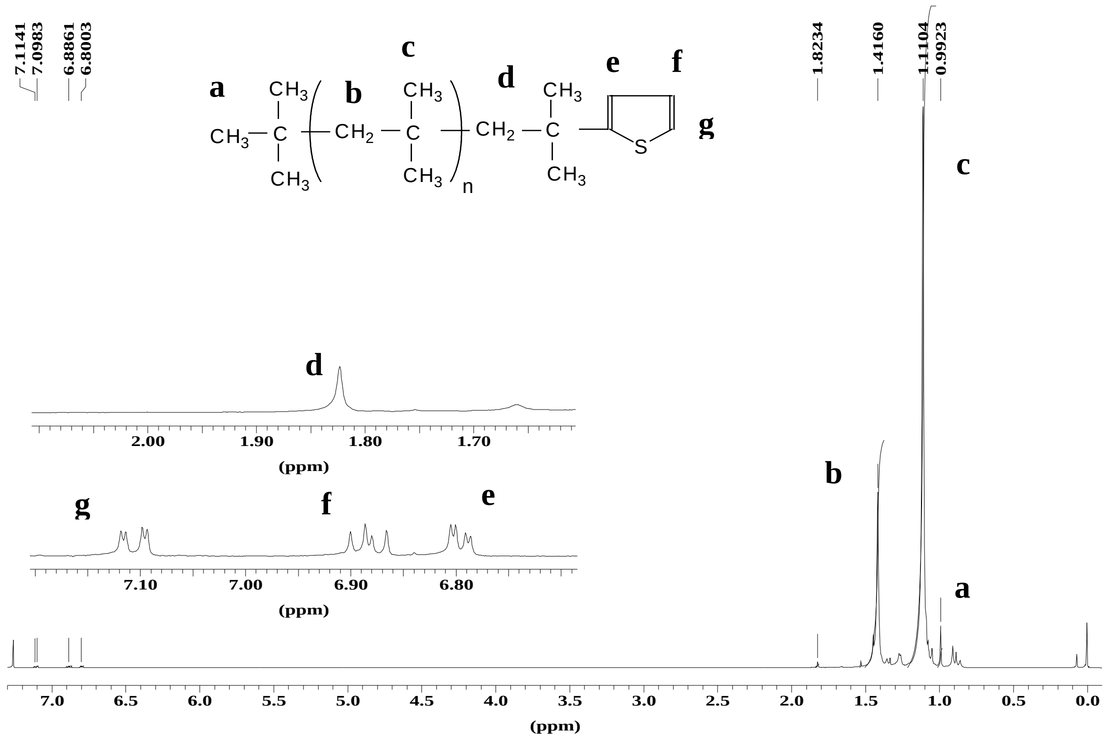


Figure 4. 2. ^{1}H NMR spectrum of thiophene-functionalized PIB

Synthesis of α,ω-Dithiophene-Ended PIB (T-PIB-T)

Living PIB was prepared by the polymerization of IB with the *t*BuDiCumCl (1.1 x 10^{-2} M)/$TiCl_4$ (1.1 x 10^{-2} M) initiator system in the presence of D*t*BP (3.0 x 10^{-3} M) as a proton trap in MeCHX/CH_3Cl at -80ºC. After polymerization of IB, the polymer solution was delivered to culture tubes to which additional amount of $TiCl_4$ were charged so that the ratios of [$TiCl_4$] to [*t*BuDiCumCl] in the polymer solution were varied from 1 to 8. T end-functionalization of PIB was conducted by using the methods as described in experimental section. Figure 4. 3. shows the ^{1}H NMR spectra of PIB and PIB-T. As the [$TiCl_4$]/[*t*BuDiCumCl] ratio increased, peaks at 2.0 ppm and 1.7 ppm assigned to methylene and methyl protons at the chain ends of PIB decreased and peak at 1.85 ppm assigned to methylene protons at the chain ends of PIB-T as well as methylene protons adjacent to initiator moiety increased. From the ^{1}H NMR spectra, the functionalities of PIBs were calculated as presented in Table 4. 2. The functionality of PIB increased with [$TiCl_4$]/[*t*BuDiCumCl] and 100% T-PIB-T could be obtained in 1h at [$TiCl_4$]/[*t*BuDiCumCl] = 8. It is noteworthy that the addition method of T did not affect the functionalization of PIB. The M_n and M_w/M_n of starting PIB and the product was independent of the ratio [$TiCl_4$]/[*t*BuDiCumCl], indicating the absence of coupling reactions.

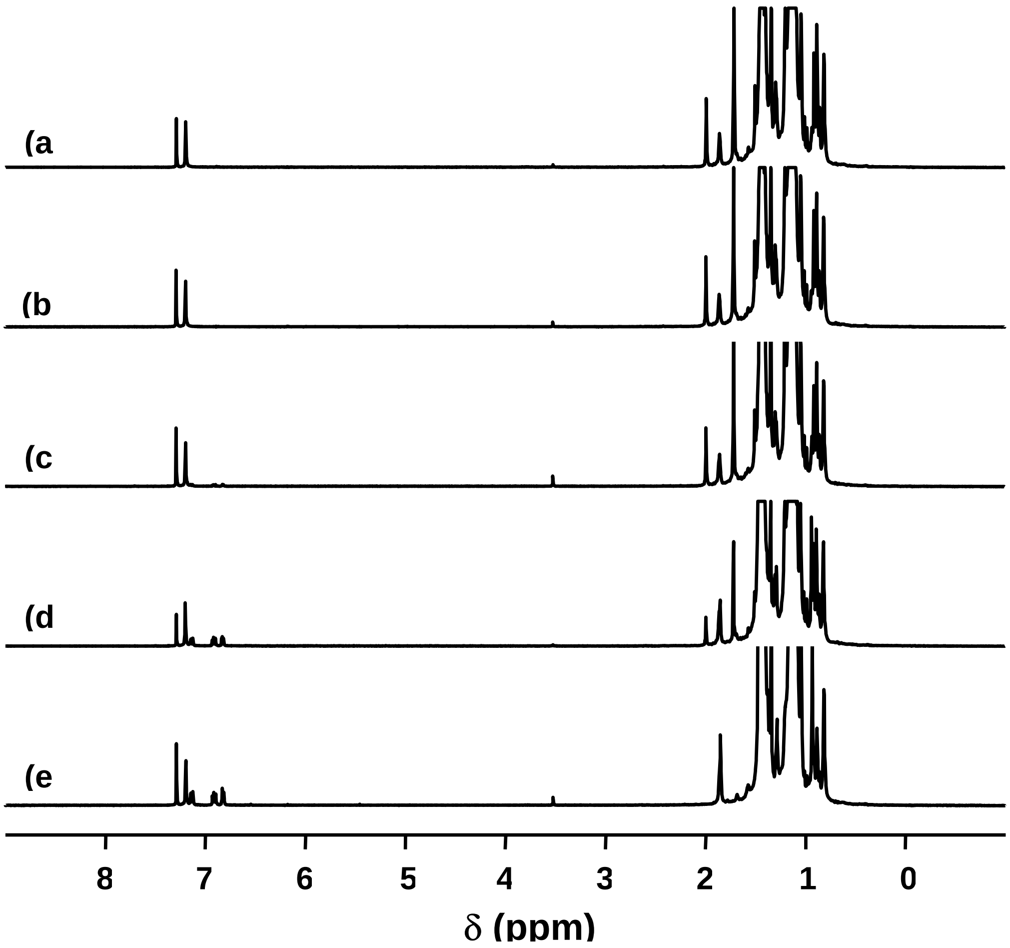


Figure 4. 3. ^{1}H NMR spectra of PIB (a) and PIB-T prepared by the addition of T to polymer at the following ratios [$TiCl_4$]/[*t*BuDiCumCl] (b) 1; (c) 2; (d) 4; (e) 8.

PIB Precursor		Capping Condition[c]	Functionality (%)
M_n (g/mol)	M_w/M_n	[$TiCl_4$]/[*t*BuDiCumCl]	
6,900[a]	1.34	1	0
		2	12
		4	50
		8	100
7,300[b]	1.11	8	36
		16	85
		24	100
		32	100

[a] polymerization condition: [*t*BuDiCumCl] = 1.1 x 10^{-2} M, [D*t*BP] = 3.0 x 10^{-3} M, [IB] = 1.1 M, [$TiCl_4$] = 1.1 x 10^{-2} M, [b] polymerization condition: [*t*BuDiCumCl] = 2.7 x 10^{-3} M, [D*t*BP] = 3.0 x 10^{-3} M, [IB] = 0.27 M, [$TiCl_4$] = 2.2 x 10^{-2} M, [c] addition method: T ([T]/[*t*BuDiCumCl] = 200/1) to polymer.

Table 4. 2. Thiophene functionalities of PIBs

While T-PIB-T of relatively low M_n could be prepared, as described above, using initiator concentrations in the range of 10^{-2} M, the preparation of high M_n T-PIB-T requires initiator concentrations in the range of 10^{-3} M. To investigate the functionalization reaction of living PIB with T under these conditions, living PIB was prepared by using the following concentrations: [*t*BuDiCumCl] = 2.7 x 10^{-3} M; [$TiCl_4$] = 2.2 x 10^{-2} M; [D*t*BP] = 3.0 x 10^{-3} M. The [$TiCl_4$]/[*t*BuDiCumCl] ratios were varied from 8 to 32. Table 4. 2. shows that when [$TiCl_4$]/[*t*BuDiCumCl] $\geq$ 24, the functionality of PIB was 100% independent of the addition method of T. While the M_n and M_w/M_n of functionalized PIB did not change with [$TiCl_4$]/[*t*BuDiCumCl], 4~5 mol% of di-substituted thiophene (PIB-T-PIB) was observed in the ^{1}H NMR spectra at [$TiCl_4$]/[*t*BuDiCumCl] ≥ 16.

Effect of D*t*BP

Since coupling involves a reaction between living PIB and PIB-T, the first step must involve proton elimination from the PIB-T cation, formed upon addition of T to living PIB. To study the role of D*t*BP, living PIB was prepared without D*t*BP with [*t*BuDiCumCl] = 1.0 x 10^{-3} M and [$TiCl_4$] = 3.6 x 10^{-2} M. The obtained PIB precursor exhibited broad molecular weight distribution (M_w/M_n = 1.67). D*t*BP was then added to the polymer solution for the functionalization to vary the [D*t*BP]/[*t*BuDiCumCl] ratios from 0 to 3. Figure 4. 4. shows the ^{1}H NMR spectra of PIB precursor and functionalized PIBs. As the [D*t*BP]/[*t*BuDiCumCl] ratio increased, the peak at 6.65 ppm assigned to protons at di-substituted T increased and peaks at 6.70~7.15 ppm assigned to protons at mono-substituted T decreased. The functionalities of all samples were calculated to be 100% irrespective of the ratio of [D*t*BP] to [*t*BuDiCumCl]. However, the mol% of di-substituted T moiety from the coupling reaction of PIB cation and T increased with [D*t*BP]/[*t*BuDiCumCl] (Table 4. 3.), resulting in the increase of M_n and M_w/M_n of functionalized PIB. From these results, it is evident that D*t*BP plays a major role in the coupling reaction.

PIB Precursor		Capping Condition[b]	Di-substituted T (mol%)
M_n (g/mol)	M_w/M_n	[D*t*BP]/[*t*BuDiCumCl]	
9,900[a]	1.67	0	2
		1	8
		2	21
		3	22

[a] polymerization condition: [*t*BuDiCumCl]= 1.0 x 10^{-3}M, [D*t*BP]=0M, [IB]=0.15 M, [$TiCl_4$]=3.6 x 10^{-2} M.

[b] addition method: T ([T]/[*t*BuDiCumCl] = 200/1) to polymer.

Table 4. 3. Fraction of di-substituted T in PIBs

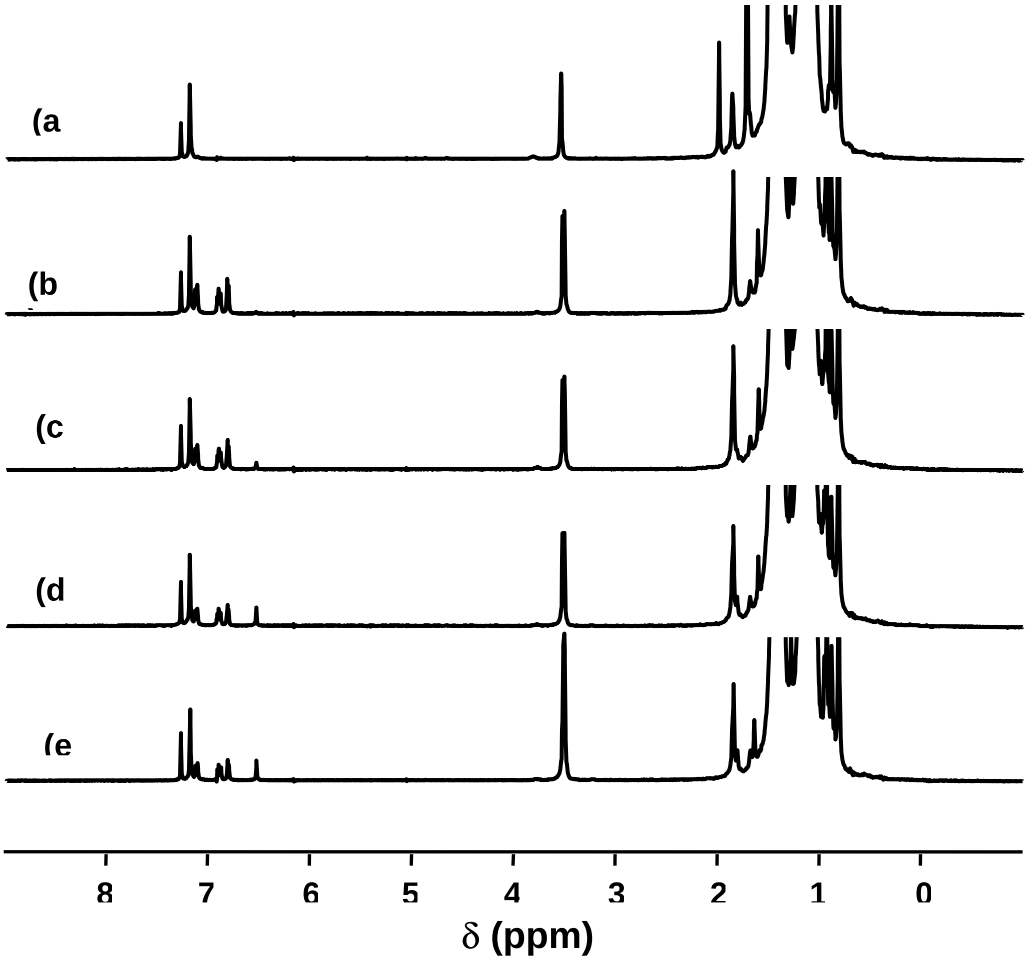
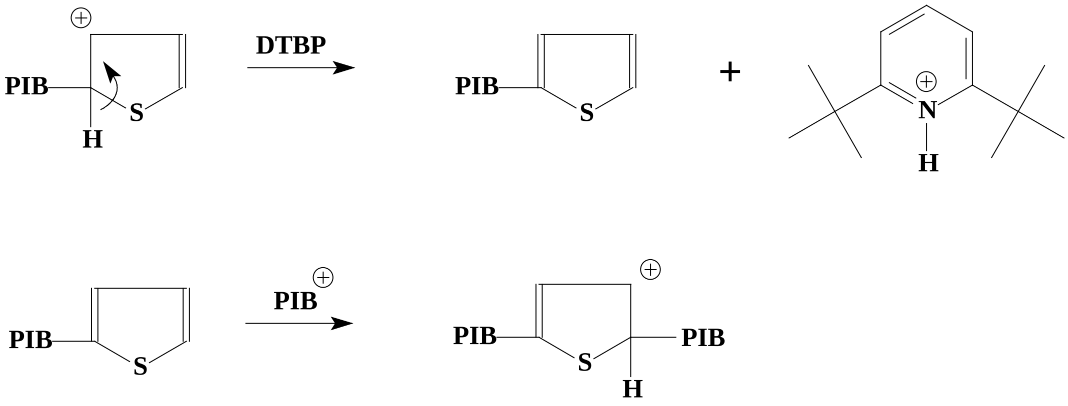


Figure 4. 4. ^{1}H NMR spectra of PIB (a) and PIB-T prepared by the addition of T to polymer at the following ratios [D*t*BP]/[*t*BuDiCumCl] (b) 0; (c) 1; (d) 2; (e) 3.

Proposed Mechanism of Coupling

The results suggest that the PIB-T cation undergoes deprotonation generating PIB-T in situ (Scheme 4. 2.). Whether proton elimination is bimolecular, induced by D*t*BP, or unimolecular and the role of D*t*BP is only to capture the eliminated proton is not known at present. It is clear, however, that successful preparation of PIB-T is not directly related to the M_n. Low M_n PIB-T could only be prepared without coupled products because high initiator concentration (~10^{-2} M) relative to that of D*t*BP (~10^{-3} M) was used.

According to this finding, D*t*BP should be used in a concentration similar to the concentration of adventitious protic impurities (~1.0×10^{-3} M) and excess of D*t*BP should be avoided especially at low initiator concentrations. Accordingly, high M_n PIB-T was prepared by following conditions: [IB] = 1.5 M, [*t*BuDiCumCl] = 1.5×10^{-3} M; [D*t*BP] = 1.0×10^{-3} M; [$TiCl_4$] = 3.6×10^{-2} M. M_n and M_w/M_n of PIB-T prepared from the reaction of living PIB with T (M_n = 52,000 g/mol) and those of PIB precursor (M_n = 50,100 g/mol) are virtually identical. ^{1}H NMR spectroscopy of the products confirmed the quantitative functionalization and di-substituted thiophene in PIB-T was undetectable.

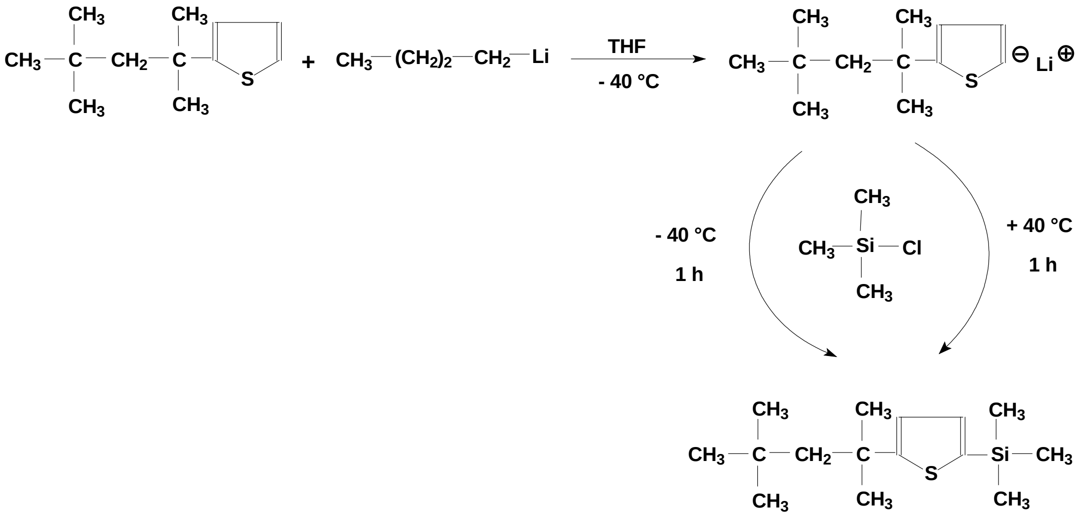


Scheme 4. 2. Mechanism for the coupling reaction of PIB cation with PIB-T

4. 3. 2. Lithiation of PIB-T

Lithiation of the Model Compound 2-(1,1,3,3-tetrametylbutyl)thiophene (TMP-T)

Orienting model experiments were carried out with TMP-T which mimics the end group structure of PIB-T. These reactions were carried out in order to optimize the lithiation of PIB-T and to test the stability of the anionic chain ends, PIB-T^-,Li^+, at elevated temperature. The major consequence of incomplete lithiation is the presence of unreacted precursor together with the desired block copolymer. Besides, unreacted *n*-BuLi can separately initiate the anionic polymerization of *t*BMA or it can attack the ester group by a nucleophilic substitution.[20] The easiest way to remove excess *n*-BuLi is to heat the THF solution, since *n*-BuLi reacts with THF at elevated temperature, forming ethylene and alkoxides.[21] Thus, an excess of *n*-BuLi can be used for the lithiation and then it can be destroyed by warming. This method can only be used if the formed anion (PIB-T^-,Li^+) is stable under these conditions. Some organolithium compounds are known to react with THF and other ethers[22] but no information exists on the thermal stability of the anion PIB-T$^-$,Li$^+$. Thus, a model reaction was carried out using TMP-T. This reaction is shown in Scheme 4. 3.



Scheme 4. 3. Lithiation of TMP-T and reaction with Me_3SiCl.

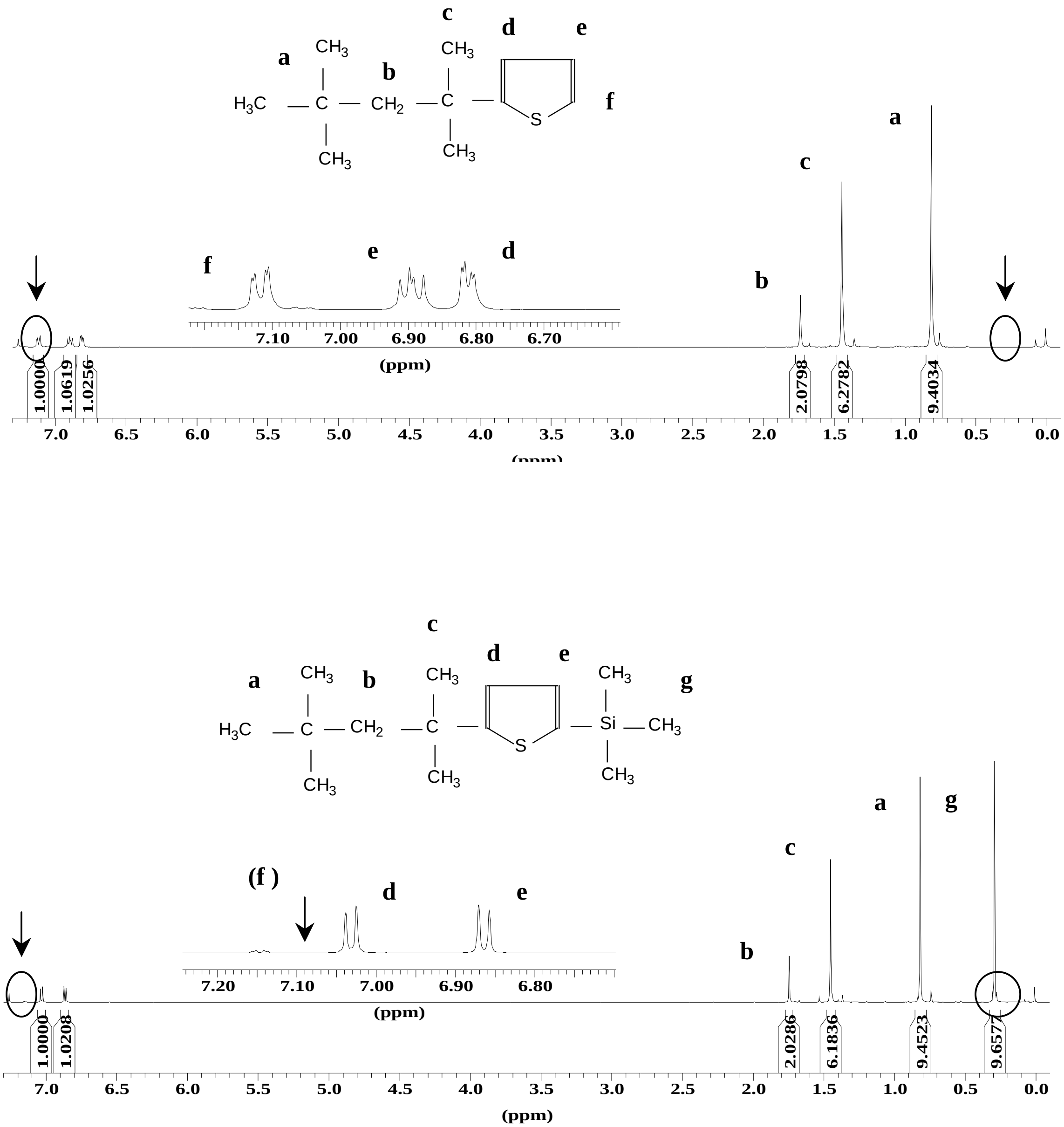


Figure 4. 5. ^{1}H NMR spectrum of TMP-T before and after quenching with Me_3SiCl at +40 °C

The lithiation of TMP-T was performed at -40 °C, using an excess of *n*-BuLi. Prior to the lithiation, a sample was taken to determine the exact concentration of TMP-T from gas chromatography (GC) and NMR spectroscopy. After 1 h of reaction Me_3SiCl was added to part of the reaction solution. Then the remaining reaction mixture was warmed to +40 °C for 1 h, in order to destroy the residual *n*-BuLi. After 1 hour at +40 °C,

Me_3SiCl was added. The reaction products were characterized by GC and NMR spectroscopy. Figure 4. 5. shows the ^1H NMR spectrum of the resulting product. This spectrum indicates quantitative formation of 2-(trimethylsilyl)-5-(1,1,3,3-tetramethylbutyl)thiophene. Quantitative addition was indicated by the disappearance of the peak at 7.10 ppm. A new peak at 0.29 ppm appeared due to the presence of the trimethylsilyl group. The conversion of this reaction was determined by GC (Figure 4. 6). The GC characterization was carried out using decane as an internal standard. Both samples taken at -40 °C and at +40 °C showed high yields (> 98.9 %) in the formation of 2-(trimethylsilyl)-5-(1,1,3,3-tetramethylbutyl)thiophene. This means that the anion formed during the lithiation ($TMP\text{-}T^-,Li^+$) is stable for an hour even after the warming of the reaction mixture to 40 °C. Thus the results of the model experiments indicated that the lithiation of the precursor (PIB-T) should be carried out using an excess of *n*-BuLi and then the excess can be destroyed by warming without affecting the stability of the formed anion ($PIB\text{-}T^-,Li^+$).

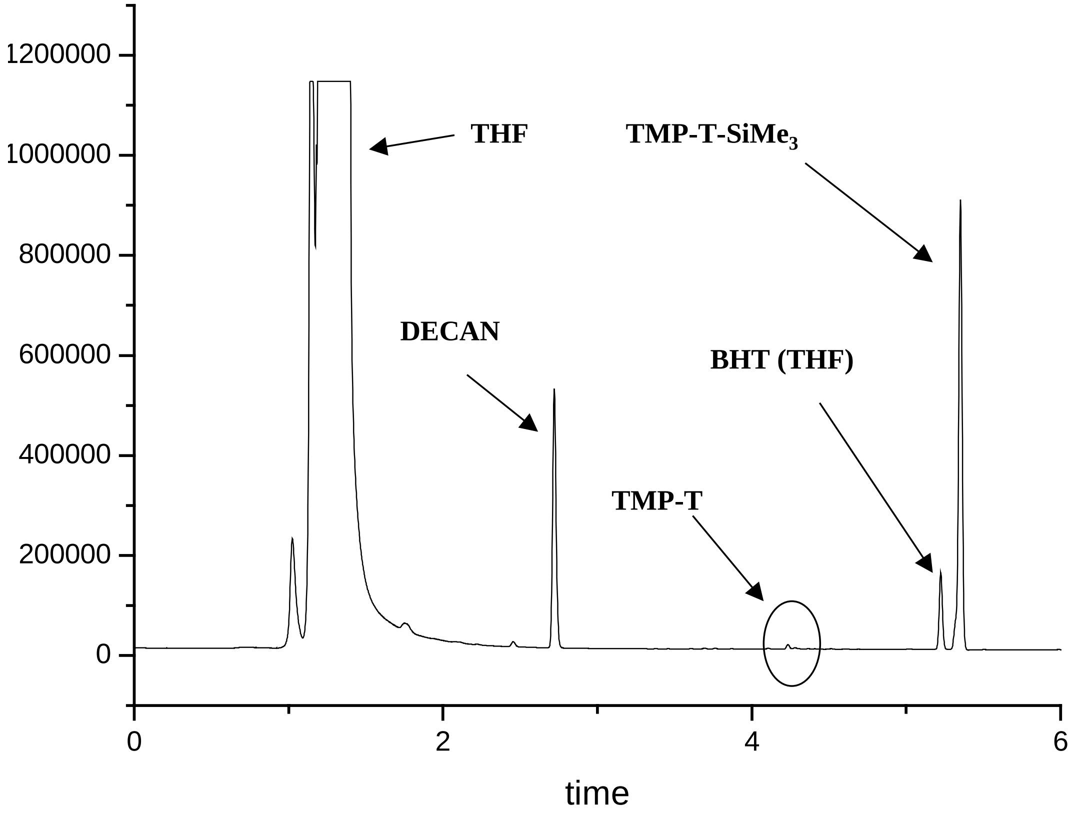
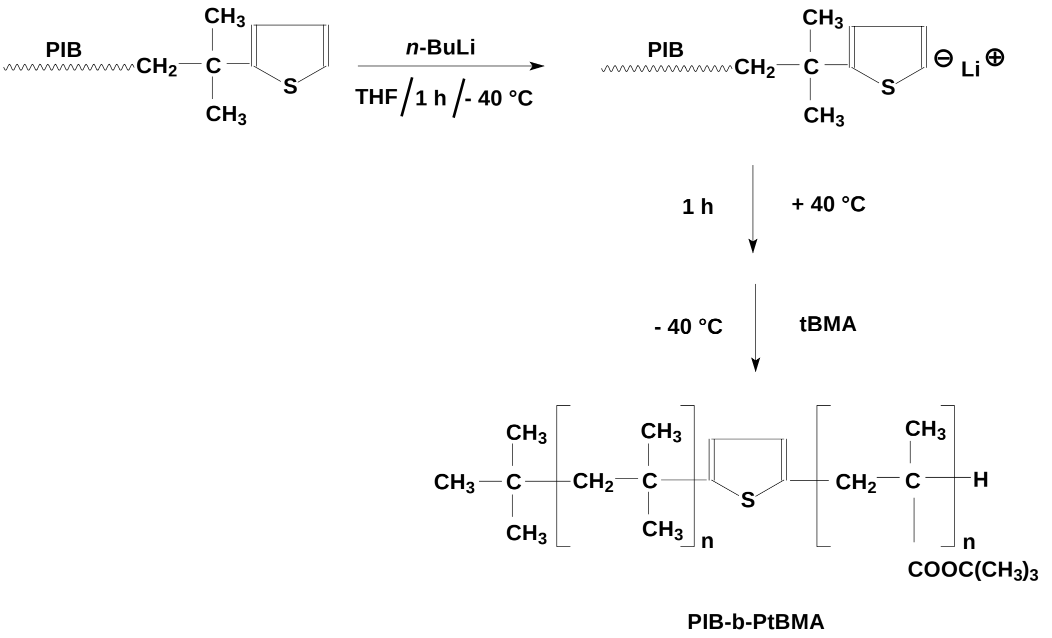


Figure 4. 6. Gas chromatography analysis of TMP-T after quenching with Me_3SiCl at +40 °C, indicating complete conversion of TMP-T to TMP-T-$SiMe_3$

4. 3. 3. Synthesis of PIB-*b*-P*t*BMA

The synthesis of PIB-*b*-P*t*BMA was accomplished by using lithiated PIB-T as an anionic macroinitiator of *t*BMA polymerization in THF (Scheme 4. 4.). In the first experiment an equimolar amount of *n*-BuLi was used for the metalation, in the second one a fourfold excess. Subsequent heating in THF to 40 °C was used to destroy the residual *n*-BuLi. The lithiated precursor PIB-T^-,Li^+ was used to initiate the polymerization of *t*BMA.



Scheme 4. 4. Synthesis of PIB-*b*-P*t*BMA block copolymer

The complete characterization of block copolymers, i.e., the measurement of molar mass distribution in combination with the chemical distribution of the components of the desired architecture (diblock, triblock, multiblock), is necessary for optimization of synthesis methods. Thus, the resulting polymers were first investigated by SEC. Figure 4. 7. shows the SEC eluograms (RI signal) for these block copolymers. The molecular weights determined by GPC using PtBMA standards are apparent values, which can be higher than the real ones. Accordingly, the blocking efficiencies given in Table 4 should be taken as apparent ones, too. In addition, the blocking efficiencies were calculated from the area of the PIB precursor in the GPC eluogram. Since only thiophene is UV-active at 254 nm, the relative area under UV signal of the PIB-T precursor is directly related to the molar fraction of unreacted precursor. It can be seen that a peak appears for the unreacted PIB in the polymer lithiated by an equimolar amount of *n*-BuLi, however, much less precursor is detected when an excess of *n*-BuLi is used.

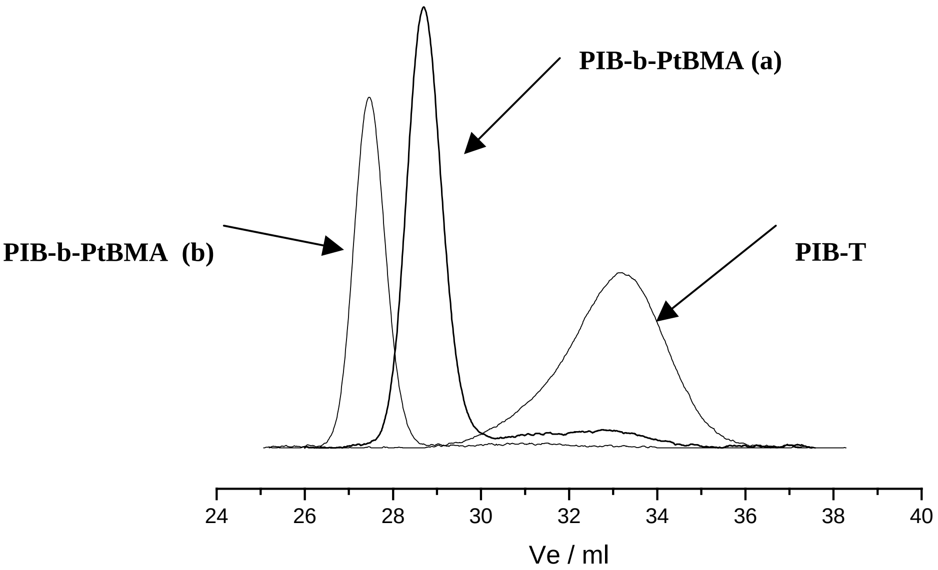


Figure 4. 7. SEC traces (RI detector) of PIB-*b*-P*t*BMA (a) [*n*-BuLi]:[PIB-T] = 1:1 (b) [*n*-BuLi]:[PIB-T] = 4:1

Exp No.	[BuLi]/ [PIB-T]	[PIB-T] mM	[tBMA] M	10^{-3} $M_{n,th}$[b]	10^{-3} $M_{n,GPC}$ (block copolymer)	M_w/M_n (block)	10^{-3} $M_{n,GPC}$ (PtBMA block)	f_{block} (GPC) (Mn^c)	f_{block} (GPC) ($area^d$)	f_{block} (LACCC) ($area^e$)
2	1	1.18	0.125	15.0	27.3	1.02	24.1	0.62	0.67	0.77
3	4	0.93	0.196	30.0	47.3	1.02	43.8	0.63	0.82	0.87

---

[a] SEC molecular weights of block copolymers were determined with P*t*BMA standards and represent apparent values only., [b] expected molecular weight of PTBMA block, [c] blocking efficiency, $f_{block} = M_{n,GPC;PTBMA}/M_{n,th}$, [d] blocking efficience determined by GPC from the area of PIB precursor (UV at 254 nm), [e] as determined by LACCC with UV detector (245 nm).

Table 4. 4. SEC and LACCC characterization of PIB-*b*-P*t*BMA[a].

Liquid chromatography at critical conditions of adsorption (LACCC) is a recent and most powerful method for the characterization of block copolymers according to the chemical heterogeneity.[23-25] Separation of polymers at critical conditions of adsorption allows for the elution of homopolymers independent of their molar mass on porous separation phases using mixed mobile phases. Under these conditions, homopolymers can be separated according to the number and nature of functional groups, e.g., end groups or comonomers. Due to a better separation LACCC is more sensitive for a quantitative determination of the precursor content than SEC. Figure 4. 8. shows the LACCC chromatograms of the two PIB-*b*-P*t*BMA's at critical conditions of PIB. In line with the results of the lithiation of TMP-T, it is verified that the excess of *n*-BuLi is deactivated and that PIB-T^-,Li^+ is stable at +40 °C and it can initiate the polymerization of *t*BMA. These results clearly show high blocking efficiency and the formation of the desired PIB-*b*-P*t*BMA block copolymer (Table 4). For the quantitative evaluation of the data the UV signal was used (similar to GPC).

In order to prove the absence of homo-poly(*tert*-butyl methacrylate), we conducted a chromatography (LACCC) measurements of PIB-*b*-P*t*BMA at critical conditions of PtBMA (THF/acetonitrile 49,5/50,5), which should confirm the absence of homopolymer. Although the block copolymer completely adsorbs to the stationary phase under these conditions, no traces of PtBMA homopolymer were found.

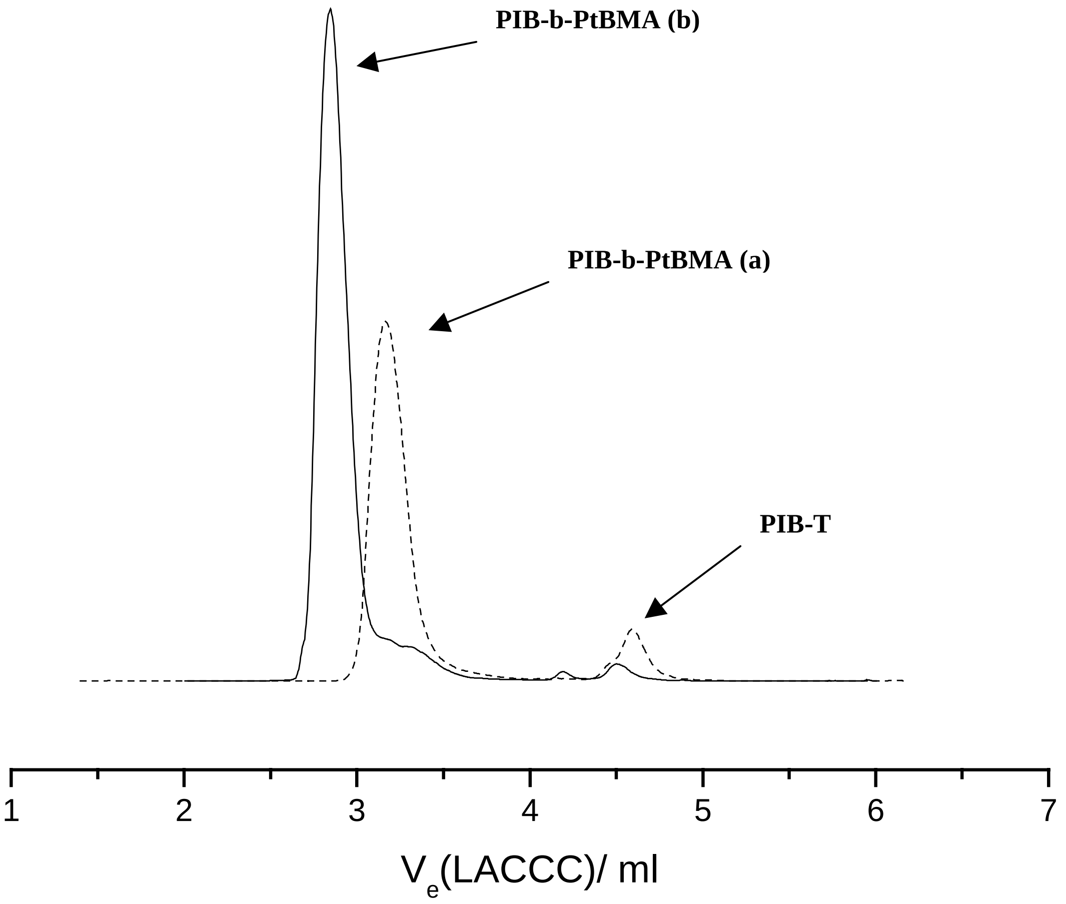


Figure 4. 8. LACCC chromatograms of PIB-*b*-P*t*BMA at critical conditions of PIB (ELSD Detector (a) [*n*-BuLi]:[PIB-T] = 1:1 . (b) [*n*-BuLi]:[PIB-T] = 4:1 .

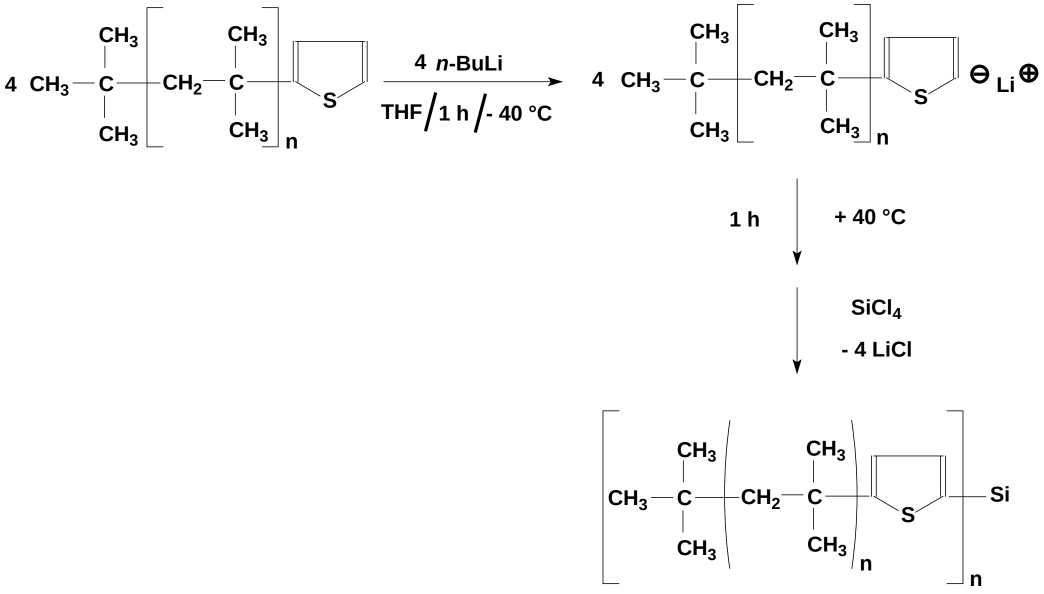
Initiation of tBMA polymerisation by thienyllithium

In order to obtain more information on the initiation process, we conducted a polymerisation of tBMA, which was initiated by the model compound thienyllithium (2-lithiothiophene) in THF at -40 °C. 30.8 mmol tBMA were added to 1.37 mmol thienyllithium. After 2 h, 96 % conversion were found by GC. ($M_{n,th}$ = 3152 g/mol). GPC resulted M_n = 4100 g/mol and M_w/M_n = 1.17, leading to an initator efficiency f = 0.77.

NMR resulted M_n = 3740 g/mol and f = 0.84. NMR also showed the expected peaks of the thiophene moiety. Details are given as Appendix information. Thus we can conclude that lithiated thiophene has a high but not quantitative initiator efficiency.

4. 3. 4. Synthesis of star-shaped PIB using $SiCl_4$.

In the synthesis of star polymers the linking reaction is usually the slowest step and star polymers made by cationic polymerization usually require cryogenic cooling.[26] Up to now, no star coupling agent is known for living carbocationic PIB chain ends. Usually, coupling is brought about by the use of bifunctional monomers, e.g. divinylbenzene,[26] yielding a mixture of star with different arm numbers. Thus, it was one of our incentives to develop a room-temperature linking method. We hypothesized that this objective may be reached by reacting lithiated PIB-T with chlorosilanes, e.g. $SiCl_4$. Chlorosilanes have been frequently used to couple anionic chain ends, e.g. living polybutadiene. Scheme 4. 5 shows the synthetic strategy for the preparation of star PIB using lithiated PIB-T and $SiCl_4$.



Scheme 4. 5. Synthesis of PIB stars

An experiment was conducted at room temperature (Mp (precursor) = 4000 g/mol). After 12 h, star formation was well under way, however, a large fraction of unreacted PIB chains remained (see Figure 4. 9.). The final star polymer was obtained after 22 h reaction time. The polymer at this stage shows the formation of a polymer with Mp = 14.600 g/mol (as determined by SEC-viscosity measurement using universal calibration), corresponding to a star with 3.7 arms on average. A certain amount of three-armed stars cannot be excluded, which may be due to insufficient reaction times or to steric hindrance caused by the thiophene ring. However, it was shown earlier that the addition of 4 molecules of thienyllithium to tetrachlorosilane or tetramethoxysilane is possible.[27,28]

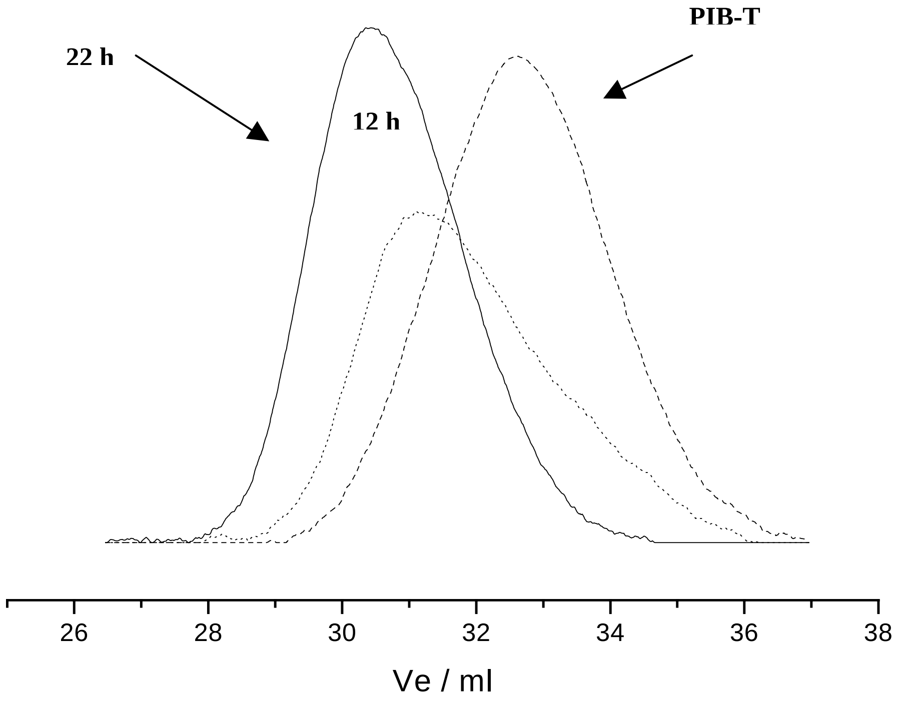


Figure 4. 9. SEC traces (RI detector) of the arm precursor and samples taken during the linking reaction of PIB-T with $SiCl_4$

4. 4. Conclusions

Quantitative functionalization of living PIB with thiophene has been achieved. The process is complicated by coupling between living PIB and PIB-T formed by in situ deprotonation, in which D*t*BP plays an important role. Deprotonation can be avoided by using D*t*BP at a lowest concentration necessary to avoid protic initiation from adventitious protic impurities. By lithiation of PIB-T a new, convenient method has been demonstrated for the synthesis of PIB-based block copolymers, involving anionic initiation of methacrylic monomers. A major improvement is that for an industrial process, lithiation by *n*-BuLi is much more convenient than metalation by Na/K alloy.

Linear block copolymers with narrow and unimodal MWD were synthesized under well-controlled conditions. The lithiated thiophene-capped PIB was used to prepare four-armed stars via chlorosilane coupling. The resulting products are potential new thermoplastic elastomers, dispersing agents, compatibilizers, emulsifiers, nonionic surfactants or biomaterials.

Summary

A new synthetic route for the synthesis of polyisobutylene (PIB) stars and PIB-poly(methacrylate) block copolymers was developed by combining living carbocationic and anionic polymerizations. Rapid and quantitative monoaddition of thiophene to living PIB chains has been observed in conjunction with $TiCl_4$ as Lewis acid in *n*-hexane/CH_2Cl_2 60/40 v/v at –78 °C leading to the formation of 2-polyisobutylenyl-thiophene (PIB-T). PIB-T was quantitatively metalated with *n*-butyllithium in THF at –40 °C. ^{1}H NMR spectroscopic and GC studies of the corresponding model compound, 2-(1,1,3,3-tetramethylbutyl)thiophene clearly verified quantitative metalation. The resulting stable macrocarbanion (PIB-T^-,Li^+) was used to initiate living anionic polymerization of *tert*-butyl methacrylate (*t*BMA) yielding PIB-*b*-P*t*BMA block copolymers with high blocking efficiency. PIB stars were prepared via the coupling reaction of the stable macrocarbanion with $SiCl_4$ as a coupling agent. Characterization of these block copolymers and PIB stars was carried out by Size Exclusion Chromatography (SEC), Liquid Adsorption Chromatography at Critical Conditions (LACCC), and NMR spectroscopy.

4. 5. References

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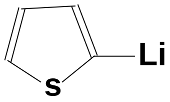
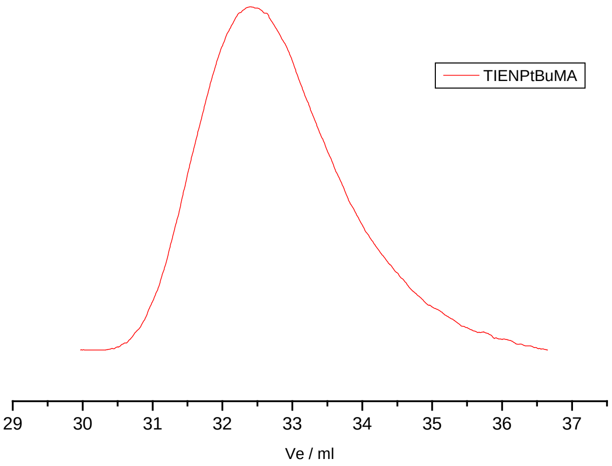
Appendix to Chapter 4 : Polymerization of tert-butyl methacrylate (tBMA) with thienyllithium



Experimental Conditions :
tBMA : 4,375 g (30.8 mmol)
THF : 200 ml
Thienyllithium : 2 ml (0,685 M molarity determined using Gilman´s method (J.Organometal. Chem. **1964**, *2*, 447-454).
T = – 40 °C
time = 2 h.
Conversion : 96 % (determined by GC)

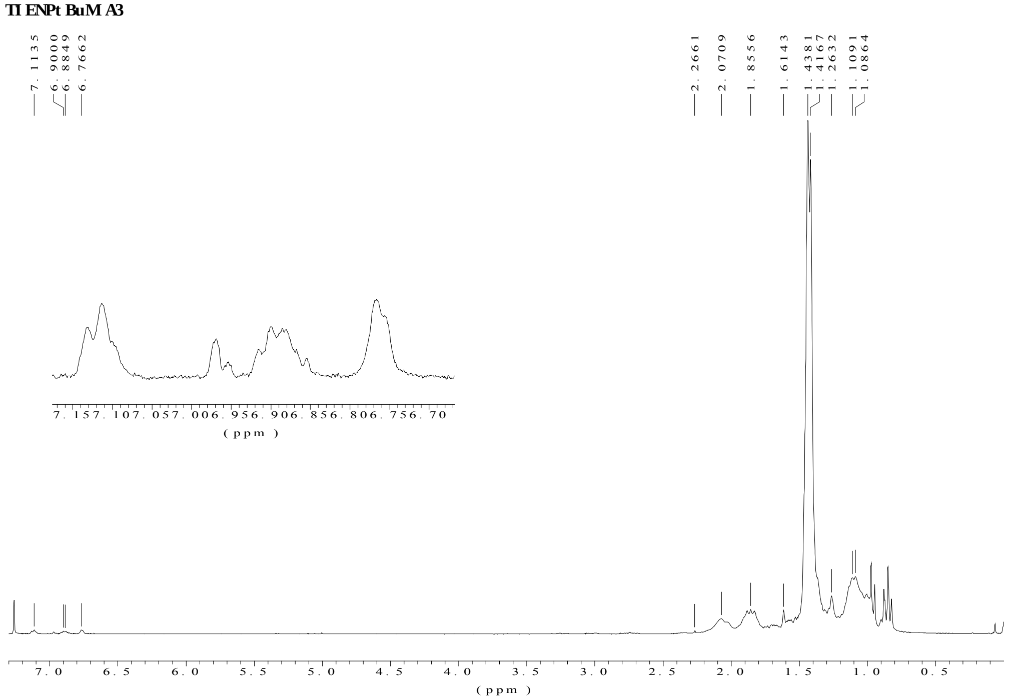


GPC eluogram of PtBuMA synthesized using thienyllithium.

GPC results:

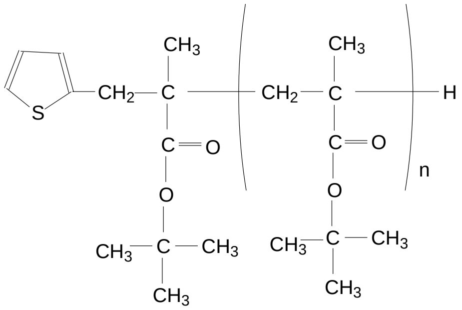
M_n = 4100 g/mol and M_w/M_n = 1.17, leading to an initator efficiency f = 0.77.

NMR resulted M_n = 3740 g/mol and f = 0.84.



^{1}H NMR spectrum of the resulting PtBuMA synthesized with thienyllithium.

The set of peaks at 7,11, 6,88 and 6,76 show the presence of thiophene (thienyllithium) in the polymer



5. Anionic Polymerization of N,N-Dimethylacrylamide with Thienyllithium and Synthesis of Block Copolymers of Isobutylene and N,N-Dimethylacrylamide by Site Transformation of Chain Ends

5. 1. Introduction

One of the major objectives of this project is to find a suitable way to combine cationic and anionic polymerizations in order to overcome the limited number of monomers which can be used in each procedure an thus, to obtain new materials. In chapter 4 the efforts reported so far in this field have been introduced.

Polyacrylamides have found numerous applications because of their biocompatibility and hydrophilic properties.[1] Practical applications include specific drug-delivery hydrogels or polymeric supports for polypeptide synthesis and catalytic reactions. Some polyacrylamides, such as poly(N,N-dimethylacrylamide), are water-soluble and others, e.g. poly(N-isopropylacrylamide) or poly(N,N-diethylacrylamide) show LCST behaviour in water close to body temperature. Recent interest in the design and synthesis of block copolymers has been focused on materials with a combination of unique compositional and architectural properties, especially when hydrophobic/hydrophilic, amorphous/crystalline, dendritic/linear, or heteroarms star blocks are combined.[2,3] The synthesis of polylacrylamides in a controlled fashion, i.e., with predetermined molecular weights and narrow molecular weight distributions, is necessary for the preparation of polymer with a controlled structure for model studies and the elucidation of structure-property relationships. Living polymerizations offer the opportunity to tailor-make model macromolecules as well as polymers of technical interest such as graft, block, star, or functional polymers. In recent years considerable efforts have been made to polymerize N,N-dialkylacrylamides by anionic polymerization. The feasibility of anionic polymerization was examined by Nakahama,[4] Hogen-Esch[5] and Arest-Yakubovich[6].

By synthesizing block copolymers using different living/controlled polymerization procedures, new materials with improved and predictable properties can be obtained. Polyisobutylene (PIB) has interesting properties: it is extremely hydrophobic, biocompatible, and it has a very low glass transition temperature (T_g = -65 °C); however PIB can be synthesized only by cationic polymerization. The site transformation technique provides a useful alternative for the synthesis of block copolymers consisting of two monomers that are polymerized only by two different mechanisms. In this method, the propagating active center is transformed to a different kind of active center, and a second monomer is subsequently polymerized by a mechanism different from the preceding one. The key process in this method is the precocious control of the chain-end functionality, to make it capable of initiating the second monomer. We have already reported that thiophene end-capped PIB can be readily prepared by the capping reaction of living PIB with thiophene (T). After lithiating the formed PIB-T, it was already used as a macroinitiator for the polymerization of *tert*-butyl methacrylate[7], and for the functionalization with ethylene oxide to form PIB-OH, which in turn was used to synthesize block copolymers of PIB with L-lactide and ε-caprolactone.[8].

Here we report the use of lithiated PIB-T as a macroinitiator for anionic poloymerization of N,N-dimethylacrylamide (DMAAm). The resulting block copolymers combine the high environmental stability of elastomeric, hydrophobic PIB with the hydrophilic properties of PDMAAm. Characterization of these block copolymers and Poly(N,N-Dimethylacrylamide) was carried out by Size Exclusion Chromatography (SEC), Liquid Adsorption Chromatography at Critical Conditions (LACCC) and , NMR spectroscopy, Dynamic Light Scattering (DLS), DSC, and AFM .

5. 2. Experimental

5. 2. 1. Materials

Thiophene-capped polyisobutylene (PIB-T) was synthesized as described previously[7]. N,N-Dimethylacrylamide (DMAAm, Aldrich) was dried over CaH_2 and stirred for 2 days, distilled under reduced pressure five times, and degassed by the freeze-thaw method. Thienyllithium (1.0 M in tetrahydrofuran) (TLi) was purchased from Aldrich and its concentration was titrated by a standard method. Triethylboron (Aldrich, 1.0 M, THF solution) was purified by distillation from CaH_2. Triethylaluminium and diethylzinc were purchased from Aldrich and used without further purification. THF (Merck p.a) was purified first by distillation under nitrogen from CaH_2 and then by refluxing over potassium. TMEDA (Merck) was dried over CaH_2 and stirred for 2 days, distilled under reduced pressure, and degassed by the freeze-thaw method. A solution of *n*-butyllithium (1.6 M in hexane) was purchased from Aldrich and its concentration was titrated by a standard method.

5. 2. 2. Synthesis

Synthesis of PDMAAm using Thienyllithium

The anionic polymerizations of DMAAm using thienyllithium in presence and absence of additives (Et_3Al, Et_2Zn or Et_3B, TMEDA) were carried out in a 1 L stirred glass reactor (Büchi) with a thermostatted cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. The monomer was introduced from a glass ampoule via a spherical joint or with a dry syringe. The solution of thienyllithium (T-Li) was handled with syringes. In a typical procedure 0.11 mL (0.11 mmol) T-Li solution and 2 molar equivalents of Et_2Zn were added to 400 mL purified THF. The reactor was cooled to –40 °C and after few minutes of stirring 9.3 ml (0.09 mol) of the purified monomer were added to the initiator/Et_3Al solution.. After completion of the reaction, it was quenched with methanol. The conversion, as estimated by gas chromatographic detection of the residual monomer in the reaction mixture, was 95 %. The reaction mixture was concentrated by rotational evaporation and poured into a large excess of hexane to precipitate the polymer. Finally, the polymer was dried under vacuum at room temperature. The ^1H NMR spectrum of the polymer is identical to the spectrum reported by Hogen-Esch et al. [9] The ^1H NMR spectrum of PDMAAm shows the absence of vinyl protons and the presence of methylene and methine protons. The $N(CH_3)_2$ group shows a resonance at 2.8-3.2 ppm, the CH proton absorbs at 2.3-2.7 ppm, and CH_2 protons absorbs at 1.2 and 1.7 ppm.

Synthesis of PDMAAm using Thienyllithium in presence of alkoxides

All polymerizations were carried out in a similar manner to that described before, however, in this case alkoxides (lithium enolate of acetaldehyde) was indirectly synthetized by the reaction of *n*-BuLi and THF. 5 mL (8 mmol) of *n*-BuLi solution in *n*-hexane was added to 400 mL of purified THF. The mixture was then allowed to stir at room temperature over night.[10] On the next day 0.06 mL (0.06 mmol) thienyllithium and 8 equivalents of Et_3Al were introduced into the reactor. After few minutes of stirring 9.3 ml (0.09 mol) of purified DMAAm were added to the initiator / Et_3Al mixture. After completion of the reaction, the reaction was terminated with methanol.

Synthesis of Polyisobutylene-*b*-Poly(N,N-Dimethylacrylamide)

All copolymerizations were carried out in 1 L stirred glass reactor (Büchi) as described above for the homopolymerization of DEAAm. Solutions of *n*-BuLi and additives were handled with syringes. A typical procedure proceeded as follows: 1.93 g (0.728 mmol) of PIB-T ($M_n = 2.66 \times 10^3$ g/mol) were freeze-dried from benzene solution for 8 h and then vacuum-dried for more than 10 h. On a vacuum line, the dried PIB-T was dissolved in THF and then the mixture was added to the stirred glass reactor and cooled to –40 °C. 0.455 mL (0.73 mmol) *n*-BuLi solution was added with a dry syringe afterwards**.** The reaction was held at -40 °C for 1 h and 8 equiv mol of Et_3Al vs initiator was introduced into the macroinitiator solution and maintained for 20 minutes at 0 °C and then 9.46 g (0.095 mol) DMAAm were added in bulk to the macroinitiator solution. The polymerization was quenched with methanol. Finally, the polymer was precipitated into hexane and dried under vacuum at room temperature.

5. 2. 3. Characterizations

^{1}H and ^{13}C NMR spectroscopies were carried out on a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$ using TMS as internal standard. *Gas Chromatography* was carried out on a Fisions GC 8000 model equipped with flame ionization detection (FID). A DB1 methylpolysiloxane column (30 m x 0.53 mm I.D.) was used with hydrogen as carrier gas. *Size Exclusion Chromatography* (SEC) was performed using THF as eluent at a flow rate of 1 mL/min equipped with a four column set of PSS SDV gel (particle size 5μm, 10^2 - 10^5 Å) heated to 40 °C. Calibration was based on PIB and PS standards (PSS, Mainz). SEC in NMP was performed using NMP + LiBr (0.05 M) as eluent at a flow rate of 1 mL/min equipped with a two column set of PSS Gram (particle size 7 μm, 10^2-10^3 Å) heated to 70 °C. Calibration was based on PS standards (PSS, Mainz).

Liquid Adsorption Chromatography under Critical Conditions (LACCC) was conducted on a TSP HPLC system at a flow rate of 0.5 L/min. An Evaporative Light Scattering Detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow of 3.5 L/min was used for mass detection. 10 μL of ca. 0.5 wt % polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two Reversed Phase columns (YMC, 250 x 4 mm) with 5 μm average particle size, 100 Å and 300 Å pore diameter were used. The critical solvent composition for PIB is THF:Methanol = 80.5:19.5. Premixing of the mobile phase by weight is necessary for a constant and exact composition.

Differential Scanning Calorimetry (DSC). For thermal analysis a Perkin-Elmer DSC 7 with a CCA 7 liquid nitrogen cooling device was used. For all measurements a two-point calibration with n-decane and indium was applied. All experiments were performed at a scanning rate of 10 K/min. The displayed heating traces correspond to the second heating run in order to exclude effects resulting from any previous thermal history of the samples.

UV-VIS spectra were recorded in a quartz cuvette (10 mm, equipped with a 9.8 mm spacer) attached to a glass reactor .

Dynamic light scattering was performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E correlator and a He–Ne laser (λ_0 = 632.8 nm). Prior to the light scattering measurements the sample solutions were filtered using Millipore Nylon filters (housing: polypropylene, membrane: poly(tetrafluoroethylene)) with a pore size of 0.2 or 0.45 μm. Both CONTIN and cumulant analysis were used for data evaluation. The polydispersity index of the micellar aggregates was estimated from the μ_2/Γ^2 ratio, in which μ_2 was determined from the cumulant analysis

$$\ln(g_1(t)) = \ln(A) - \Gamma t + \frac{\mu_2}{2}t^2 - \frac{\mu_3}{6}t^3 + \cdots$$

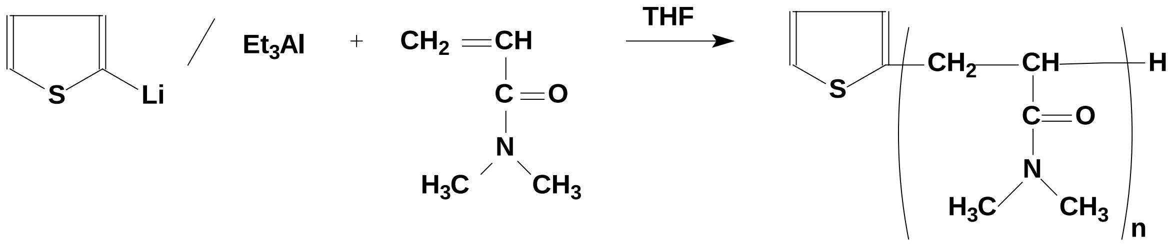
5. 3. Results and Discussion

5. 3. 1. Polymerization of N,N-Dimethylacrylamide using Thienyllithium

Anionic polymerization of DMAAm in the presence Et_3Al, Et_2Zn or Et_3B

In order to optimize the block copolymerization of PIB-T^-,Li^+ with DMAAm, orienting model experiments were carried out with thienyllithium which mimics the end group structure of PIB-T^-,Li^+. DMAAm is a very reactive monomer. It polymerizes not only with organo-metallic compounds containing the carbon-alkali metal bond, but also under the action of considerably less basic compounds with O-M and N-M bonds such as *tert*-AmOLi, *tert*-Am OK. Besides derivatives of alkali metals, various alkaline earth metal compounds including metal alkyls and bimetallic metal-aluminium complexes were also found to be reactive initiators for DMAAm polymerization. These initiators usually produce polymer quantitatively within a few minutes, if not seconds. [11]

Hogen-Esch and Nakahama[9] reported that the tacticity of poly(DMAAm) obtained in the presence of alkali metal compounds in THF strongly depends on the counterion nature. In the absence of Lewis acids, the lithium-initiated polymerization of DMAAm leads to a highly isotactic crystalline polymer which is an only partially soluble in water, in contrast to the amorphous, water-soluble free-radical polymer of syndiotactic structure. Addition of Lewis acids dramatically changes the tacticity and solubility of the polymers. This has been attributed to interactions with the active chain end, an amidoenolate, and with the carbonyl group of the monomer. Thus, we first examined the polymerization of DMAAm by using thienyllithium (T-Li) in the presence of various Lewis acid such as Et_3Al, Et_2Zn or Et_3B A series of polymerizations of DMAAm were performed according to Scheme 5. 1.



Scheme 5. 1. Synthesis of Poly (N,N-Dimethylacrylamide) using Thienyllithium as Initiator.

In this study, a series of PDMAAm were synthesized with thienyllithium in THF using different monomer/initiator/Lewis acid ratios and different temperatures. The polymerizations was initiated by adding the monomer into a THF solution of T-Li and Lewis acid. In the absence of Lewis acid, the resulting polymer was insoluble in THF, precipitating during polymerization. The conditions and results are summarized in Table 1.

run	T, °C	Lewis acid	[Lewis acid]/$[I]_0$	$[I]_0$, mmol/L	$[M]_0$, mol/L	conv., %	$M_n \times 10^{-3}$		M_w/M_n
							calcd	SEC[a]	
1	27	Et_3Al	8 /1	0.015	0.10	0.99	650	862	1.3
2	0	Et_3Al	6 / 1	0.03	0.07	0.97	220	274	1.6
3	27	Et_3Al/ TMEDA	8 / 1 / 1	0.198	0.10	1.0	500	669	1.4
4	27	Et_2Zn	8 / 1	0.022	0.08	0.98	350	452	1.2
5	-78	Et_2Zn	12 / 1	0.06	0.06	0.80	90	119	1.18
6	-40	Et_2Zn	18 / 1	0.11	0.09	0.95	76	96	2.0
7	0	Et_3B	2 / 1	0.021	0.08	1.0	370	471	1.18
8	27	Et_3Al/ ROLi	2 / 84 / 1	0.095	0.10	0.60	62.0	84.7	1.8
9	27	Et_3Al/ ROLi	8 / 137/ 1	0.058	0.09	0.80	122.0	164.2	2.2

[a] with PS standards in NMP as an eluent.

Table 5. 1. Anionic Polymerization of N,N-Dimethylacrylamide with Thienyllithium in THF.

Tacticity of PDMAAm

A series of ^{13}C NMR spectra of PDMAAm produced are shown in Figure 5.1., where the signals were assigned to mm (isotactic), mr (heterotactic) and rr (syndiotactic) triads with increasing chemical shift, according to Nakahama et al.[12]. PDMAAm produced with T-Li in the presence of Et_3B (run 7) shows sharp peaks around 174.7 ppm, attributed to syndiotactic configuration, and a small signal at 174.3 ppm, attributed to isotactic configuration. Several small peaks observed in the range from 174.4 to 174.6 ppm might be attributable to heterotactic triads, although the exact assignment is not clear yet. Thus, predominantly syndiotactic polymer was generated with T-Li / Et_3B at 0 °C, as was also produced with T-Li / Et_2Zn at 27 °C (run 4). In contrast to Et_3B, a much larger amount of Et_2Zn is required to obtain a similar degree of syndiotacticity. Low temperatures seem to increase heterotactic sequences (runs 5,6).

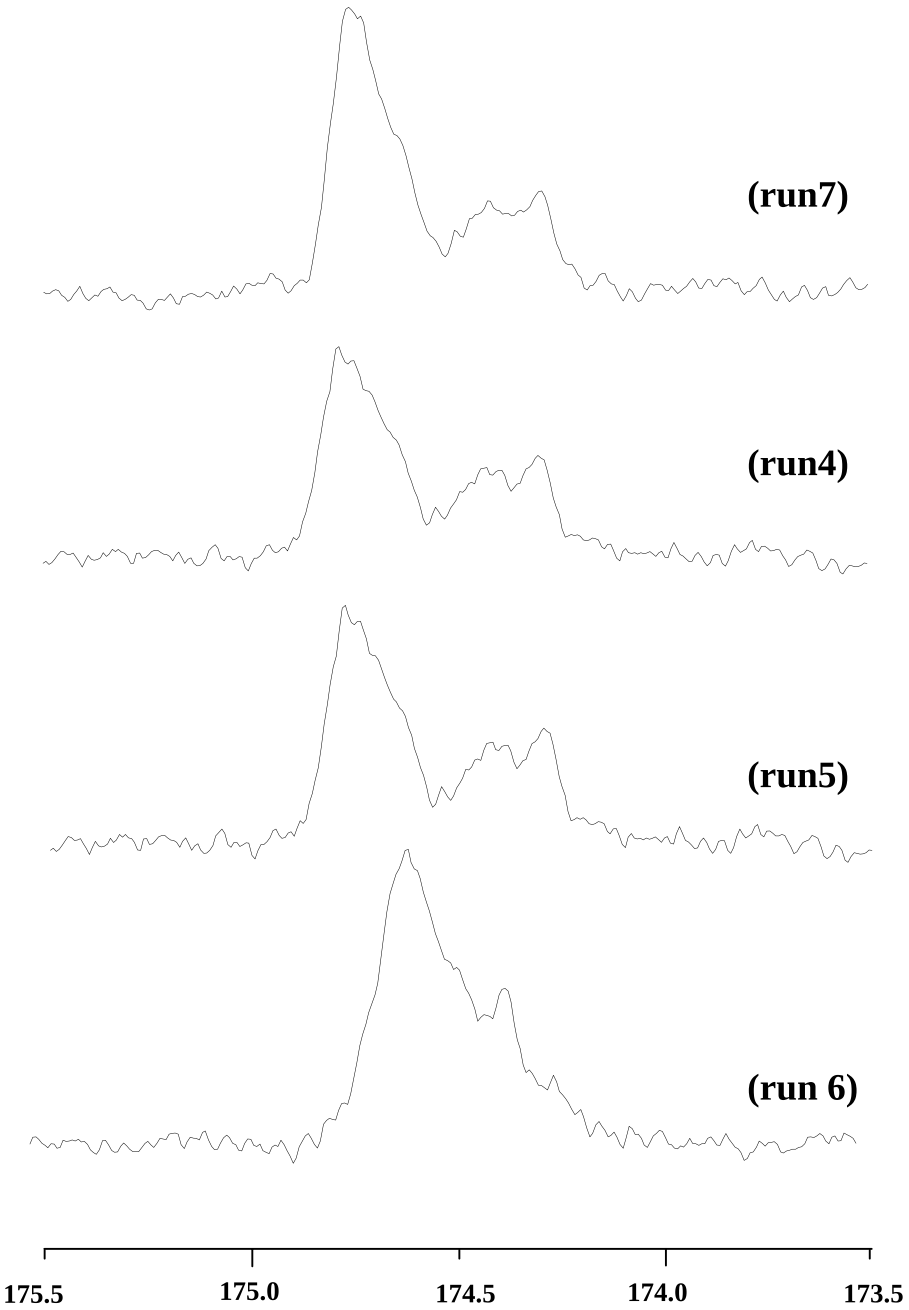


Figure 5. 1. ^{13}C NMR of PDMAAm produced by thienyllithium (T-Li) using differents T-Li / Et_3B or T-Li / Et_2Zn ratios (see Table 5. 1.)

We also examined the activity of Et_3Al in the polymerization of DMAAm (Figure 5. 2.), all the polymerizations initiated by T-Li in the presence of Et_3Al proceeded homogeneously in THF at 27 °C to give a mixture of syndiotactic and heterotactic triads (run 1). The presence of TMEDA in the system T-Li / Et_3Al does not affect the isotactic content, but changes the relative intensity of the signals at 174.7 and 174.6 (run 3). Taking into account that the polymerization of DMAAm with T-Li / Et_3Al at 27 °C was possible, we tried to see the effect of the temperature and ratio of T-Li / Et_3Al (run 2). The poly(DMAAm) generated with T-Li in the presence of Et_3Al (run 35) at 0 °C shows a highly heterotactic poly(DMAAm).

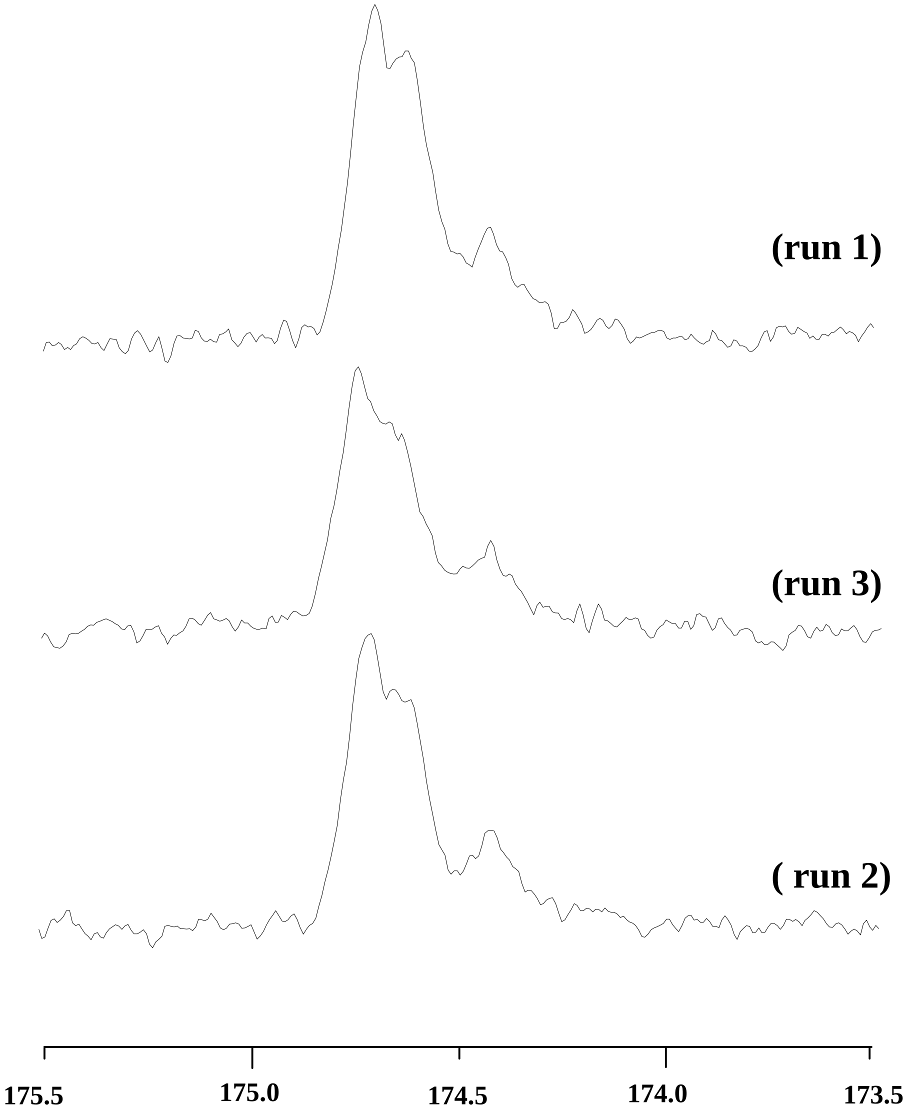


Figure 5. 2. ^{13}C NMR of PDMAAmA produced by thienyllithium (T-Li) using differents T-Li / Et_3Al ratios (Table 5.1.)

Effect of Alkoxides

It is well known that *n*-butyllithium deprotonates tetrahydrofuran at room temperature, the anion then decomposed to give butane, ethylene and the lithium enolate of acetaldehyde [13] Mixed complexes of the general formula [RLi:LiOR] have long been known and alkoxides have a large effect on the reactivity of organolithium compounds.[14] They have been reported to increase the stability of chain ends in the anionic polymerization of styrene, butadiene, methyl methacrylate and tert-butyl acrylate.[15] Thus, in the synthesis of PIB-*b*-PTBMA[7] an excess of *n*-butyllithium was used to metalate PIB-T, the excess was then deactivated by warming to 40 °C. The resulting, stable PIB-T^-, Li^+ was used to initiate the polymerization of tBMA. Taking this into consideration, we wanted to see the effect of the alkoxides in the polymerization of DMAAm before using the same method in order to synthesize PIB-*b*-PDMAAm. The results are summarized in Table 5. 1.

The polymers generated in presence of alkoxides were insoluble in THF, but soluble in N-methylpyrrolidone (NMP). Monomer conversions were lower, presumably due to the precipitation of the polymer during polymerization. GPC measurements in NMP showed that the polymers possess a much broader, even bimodal MWD than those obtained in absence of alkoxides (Figure 5. 3.).

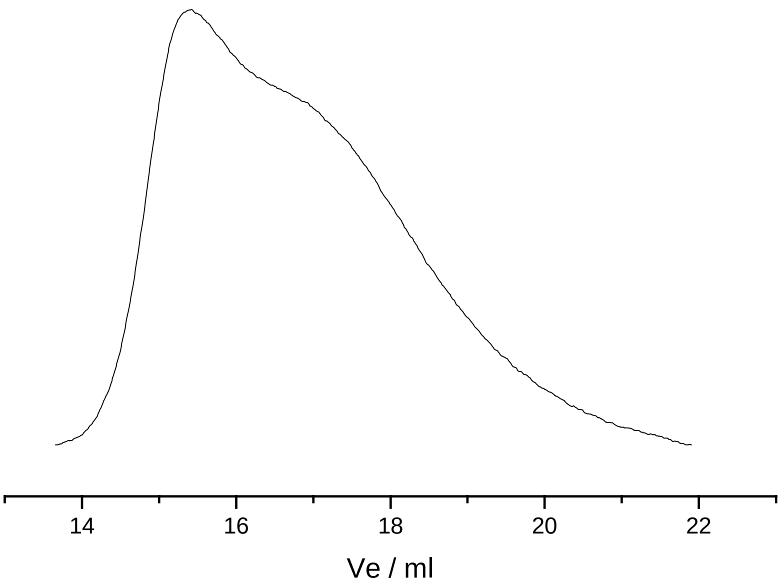


Figure 5. 3. SEC trace (RI detector) of PDMAAm (run 9) produced in presence of alkoxides.

The polymerizations of DMAAm with T-Li / Et_3Al in the presence of alkoxides give highly isotactic poly(DMAAm) at low T-Li / Et_3Al and heterotactic at higher ratio (run 8 and 9) . The results are summarized in Figure 5. 4., the addition of alkoxides did not seem to facilitate the polymerization of DMAAm even in presence of Et_3Al.

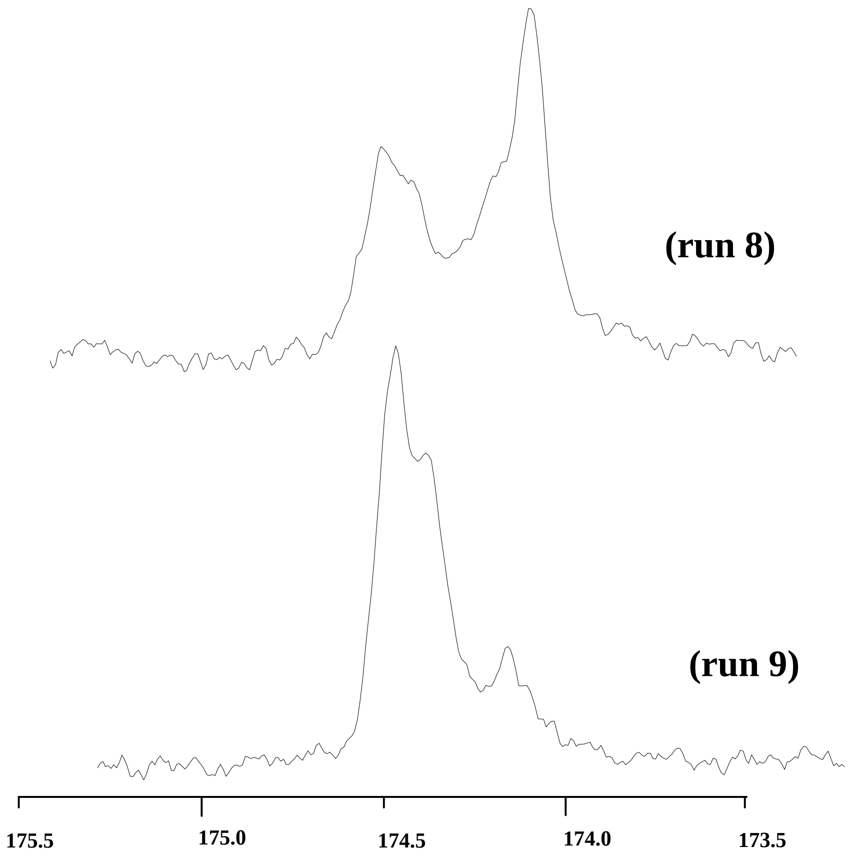


Figure 5.4. ^{13}C NMR of PDMAAmA produced by thienyllithium (T-Li) in presence of lithium alkoxide using differents T-Li / Et_3Al ratios (see Table 5. 1.).

In order to gain more insight into nature of the propagating species, the initiator was studied by UV-visible spectroscopy (Figure 5. 5.). UV-visible spectroscopy had already been used to study the influence of additives on alkyllithium by Deffieux et al.[16,17] T-Li in THF shows a maximum at 250 nm and a shoulder at ca. 310 nm. Addition of Et_3Al to T-Li in THF leads to a shift of the maximum (with decreased intensity) to ca. 300-310 nm. The same experiment was done in presence of lithium alkoxides (i.e., the decomposition products of n-BuLi in THF). Upon addition of alkoxides, the T-Li absorption is shifted to 330 nm, indicating that a new complex is formed. On further addition of Et_3Al, the T-Li / alkoxide peak decreases at the expenses of a new, less intense peak located at 340 nm.

Indeed, the comparison of the UV-visible spectra in Figure 5. 5. shows numerous spectral changes in the presence of alkoxide. This suggests that the complexation between T-Li and Et_3Al species changes in presence of alkoxide, producing new types of complex. This would explain the changes of tacticity of PDMAAm produced in presence of alkoxides.

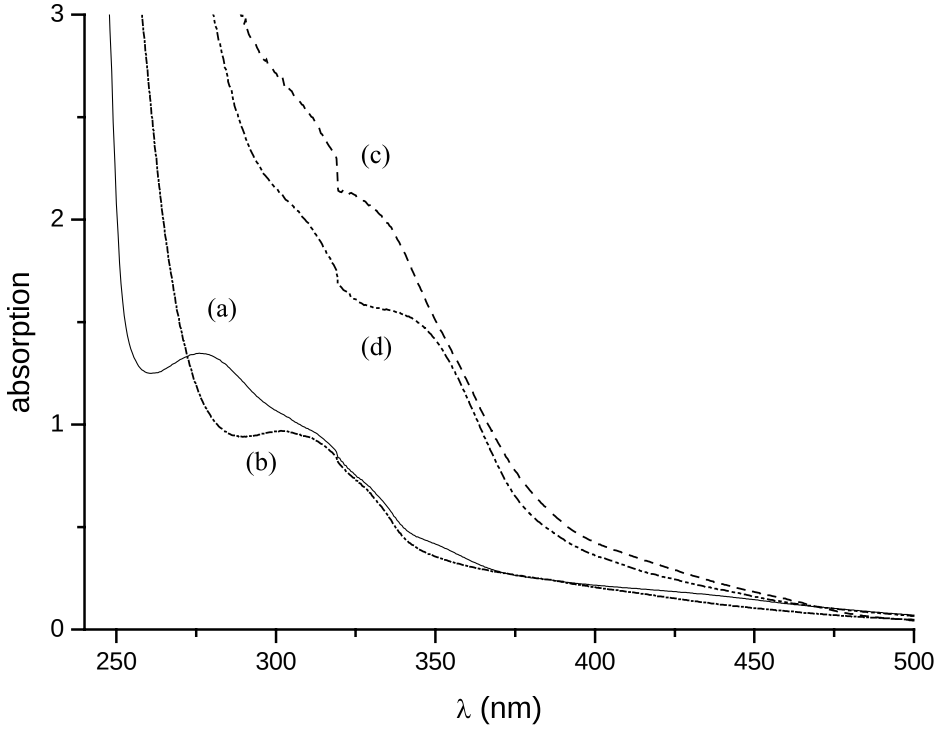
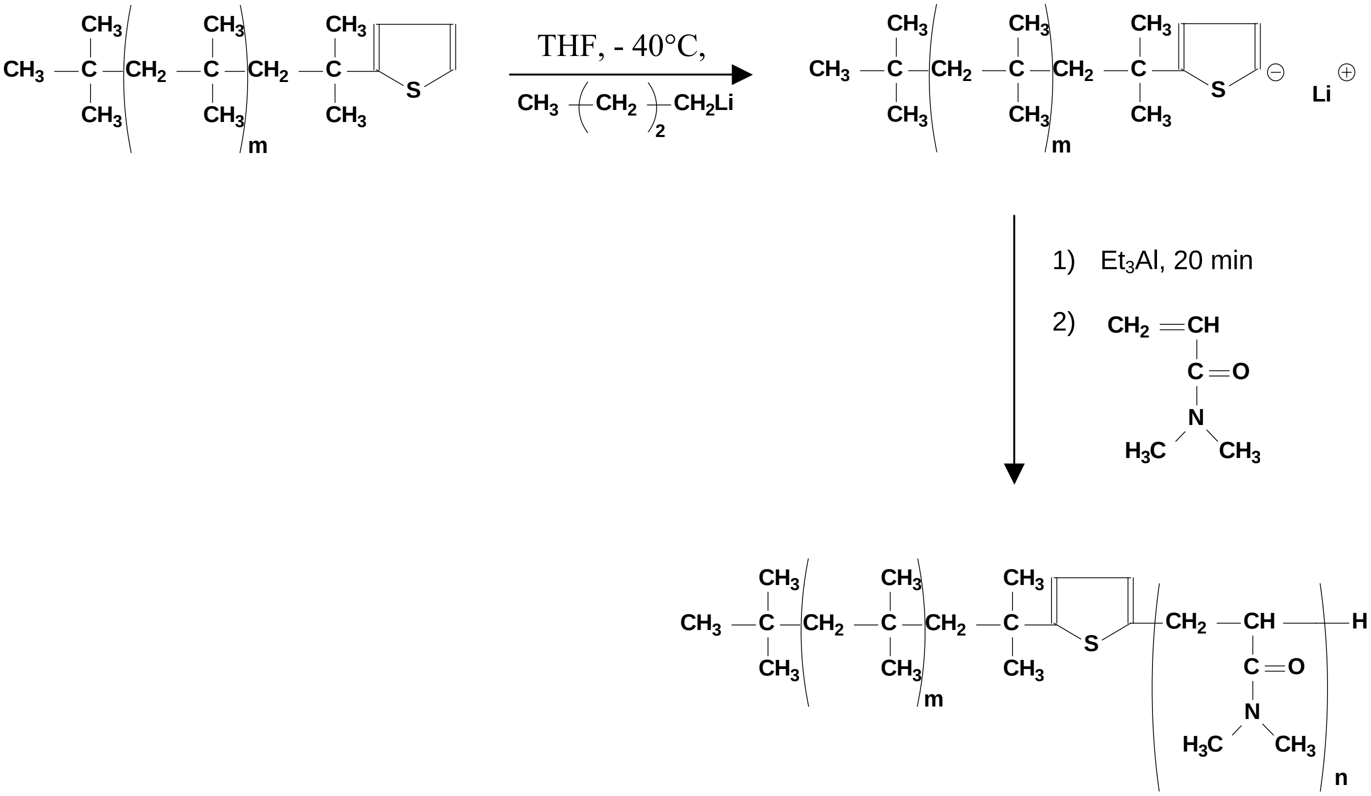


Figure 5. 5. Influence of Et_3Al and alkoxides on the UV-visible spectrum of thienyllithium in tetrahydrofuran at room temperature (c = 3.70 x 10^{-3} M). (a) T-Li; (b) T-Li:Et_3Al = 1:8; (c) T-Li:alkoxides = 1:3 ; (d) T-Li:Et_3Al:alkoxides = 1:8:3.

5. 3. 2. Synthesis of Polyisobutylene-*b*-Poly(N,N-dimethylacrylamide)

The synthesis of PIB-*b*-PDMAAm was accomplished by using lithiated PIB-T as an anionic macroinitiator of DMAAm polymerization in THF (Scheme 5. 2.). The lithiated precursor PIB-T$^-$, Li$^+$ was used to initiate the polymerization of DMAAmA.

The previous results had shown that alkoxides, do not facilitate the polymerization of DMAAm even in presence of Et_3Al. Thus, it was not possible to use an excess of *n*-butyllithium in order to quantitatively lithiated PIB-T. Thus, the presence of unreacted PIB-T precursor was to be expected.



Scheme 5. 2. Synthesis of PIB-*b*-PDMAAm

The formation of the diblock copolymer PIB-b-PDMAAm was verified by its ^{1}H NMR spectrum shown in Figure 5. 6. The block copolymer shows the corresponding signals attributed to the respective characteristic resonance peaks of PIB and PDMAAm blocks. Since the DP_n of PIB-T is known, the DP_n of PDMAAm was determined from the relative integrals of the methylene and methine protons of PDMAAm (Table 5. 2.)

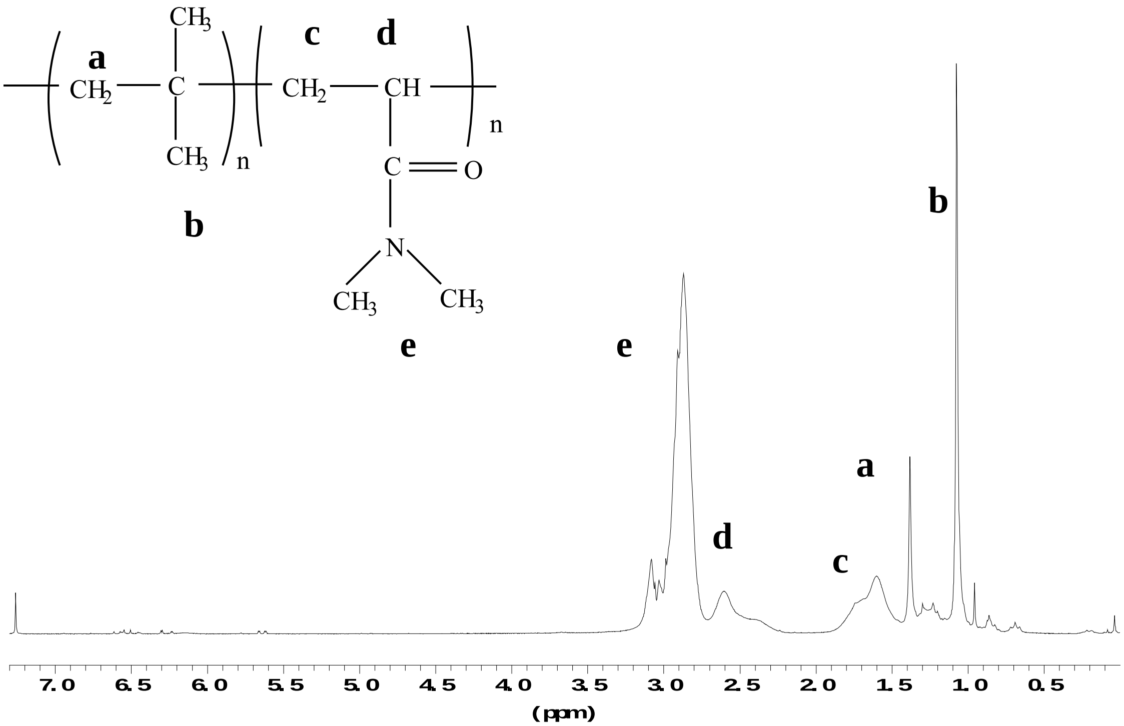


Figure 5. 6. ^{1}H NMR of PIB-b-PDMAAm (run 25).

Figure 5. 7. shows the SEC eluogram (RI signal) for one block copolymer.. The molecular weights determined by GPC using PS standards in NMP, are apparent values. Accordingly, the blocking efficiencies given in Table 2 should be taken as apparent ones, too. In addition, the blocking efficiencies were calculated from ^{1}H NMR**.** Unreacted PIB precursor cannot be detected by SEC in NMP because PIB is insoluble in that solvent.

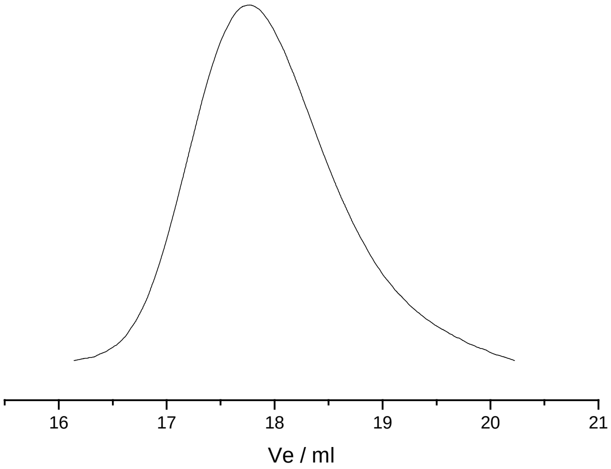


Figure 5. 7. SEC trace (RI detector) of PIB_{47}-b-$PDMAAm_{161}$ (run 25) in NMP, after precipitation in hexane.

Exp No.	10^{-3} $M_{n,SEC}$ (PIB block)[a]	[PIB-T] mM[b]	[DMAAm], M[c]	10^{-3} $M_{n,th}$[d]	10^{-3} $M_{n,SEC}$[e]	M_w/M_n	10^{-3} $M_{n,NMR}$ (PDMAAm block)	f_{block} (NMR)[f]	f_{block} (LACCC)[g]
25	2.66 m=47	0.728	0.095	13.0	91,7	1.08	16.0 n=161	0.81	0.77
36	2.25 m=40	0.267	0.199	74.0	143	1.42	93 n=940	0.79	0.75
38	4.27 m=76	0.105	0.296	280	832	1.12	359 n=3630	0.77	0.76

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[a] determined with PIB standards in THF, [b] in all cases ratio equimolar of PIB-T / *n*-BuLi was used, [c] DMAAm was polymerized until complete conversion, [d] Expected molecular weight of PDMAAm block, [e] apparent values determined with PS standards in NMP, [f] blocking efficiency, $f_{block} = M_{n,th}/ M_{n,NMR;PDMAAm}$, [g] as determined from the areas of the LACCC signal with UV detector (245 nm).

Table 5. 2. SEC and LACCC characterization of PIB_m-*b*-$PDMAAm_n$. obtained at 0 °C and a ratio Et_3Al:PIB-T = 6 : 1 in THF

For the quantitative determination of the amount of PIB homopolymer (free precursor), it must be separated from the block copolymer. Liquid Chromatography at Critical Conditions of Adsorption (LACCC) is a recent and most powerful method for the characterization of block copolymers according to the chemical heterogeneity.[18,19] Separation of polymers at critical conditions of adsorption allows for the elution of homopolymers independent of their molar mass on porous separation phases using mixed mobile phases. At the critical conditions of PIB, this part of the complex mixture behaves chromatographically invisible and separation is accomplished solely with respect to the molecular weight of the DMAAm block. Figure 5. 8. shows the LACCC chromatogram of PIB-b-P(DMAAmA) at critical conditions of PIB, before and after purification. It is seen that the block copolymers contain precursor, whereas precursor was not visible in GPC, due to the insolubility of PIB in NMP. Since there is UV-absorbing thiophene unit per macromolecule, the (molar) blocking efficiency can be elegantly calculated from ratio of the area of the block copolymer to the total area. The data are given in Table 5. 2. and they coincide well with those from NMR. The non-quantitative block formation is due to the non-quantitative metalation, since no excess of n-BuLi could be used here.

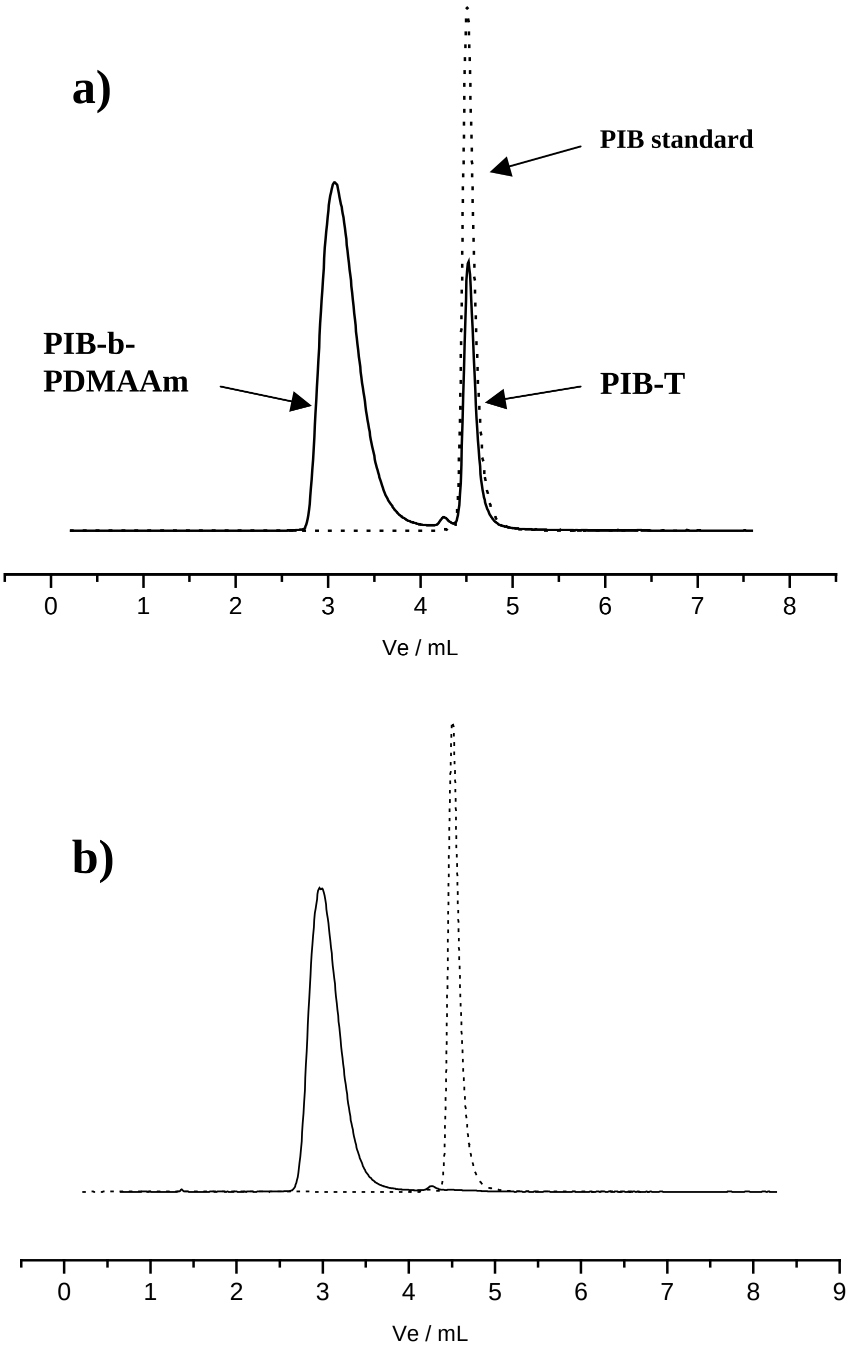

Figure 5. 8. Characterization of PIB_{47}-b-$PDMAAm_{161}$ (run 25) by LACCC a) before and b) after precipitation in hexane

The ^{13}C NMR of the PDMAAm block produced with PIBT-Li in the presence of Et_3Al shows a sharp peak around at 174.6 ppm attributed to a heterotactic configuration (Figure 5. 9.)

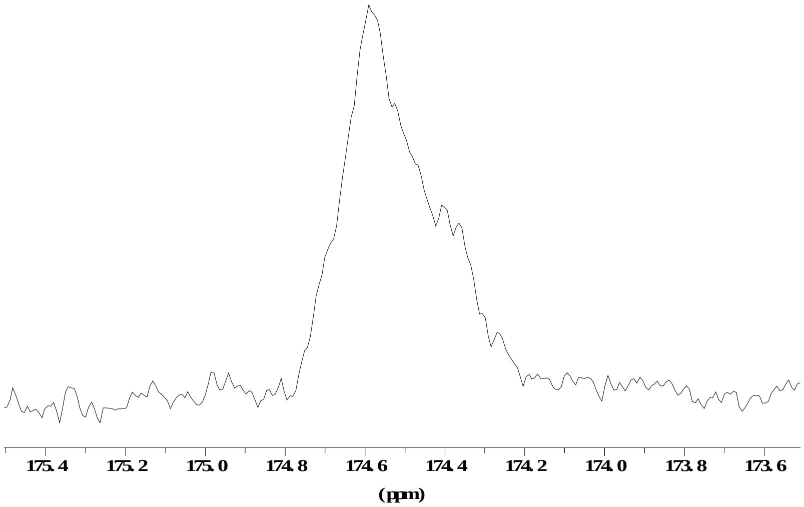

Figure 5. 9. ^{13}C NMR of PIB_{47}-b-$PDMAAm_{161}$ (run 25)

5. 3. 3. Thermal Properties

Differential scanning calorimetry was used to analyze the glass transition temperature of the PIB-b-PDMAAmA diblock copolymer. Thermograms of the PIB prepolymer used for the synthesis and a representative PDMAAm homopolymer are given in Figure 5. 10. The DSC heating traces for the PIB and PDMAAm show a clear glass transition at – 68 and 125 °C, respectively. The DSC scan for the representative PIB-b-PDMAAm diblock copolymer has one glass transition temperatures that close to the value of PDMAAm homopolymer; the second transition cannot be observed, since the fraction of PIB (2 wt-%) is too low.

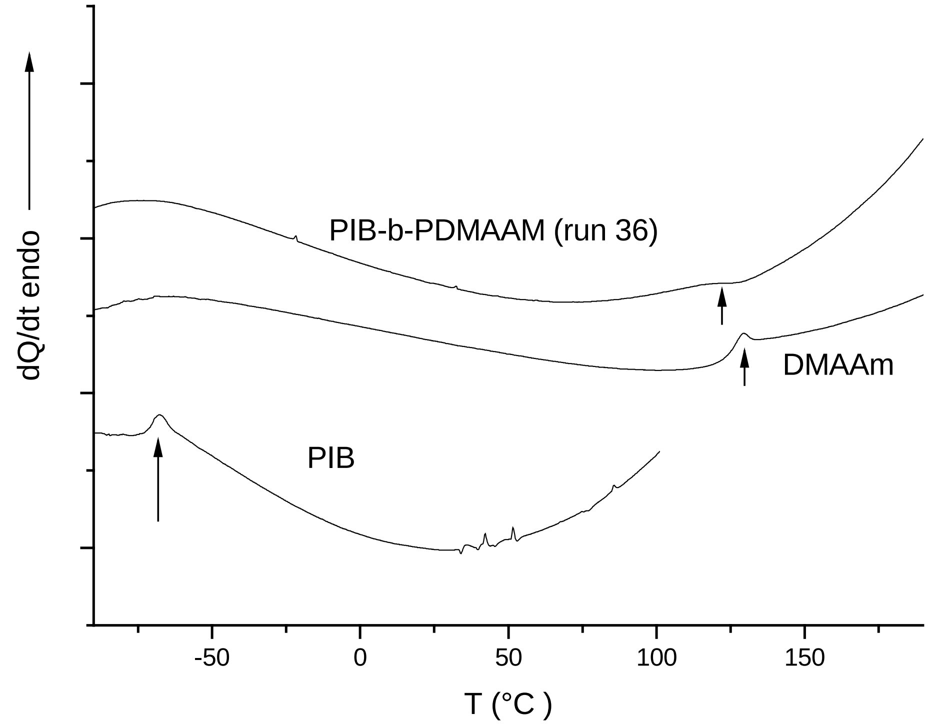

Figure 5. 11. DSC heating traces homo- and copolymers

5. 3. 4. Micelle Characterization by Dynamic Light Scattering (DLS)

The size distribution of the micellar aggregates formed by PIB-b-PDMAAm diblock copolymers in water was investigated by DLS in an attempt to approach the structure of the micelles formed by the diblock copolymers with various compositions. The DLS studies clearly indicated the formation of micelles in water when the concentration of PIB-b-PDMAAm diblock copolymer was higher than cmc. Since the hydrophobic PIB blocks are very short compared to the PDMAAm blocks, the formation opf star-shape micelles was expected. Moreover, PIB has a low glass transition temperature, thus one should expect the formation of dynamic micelles.

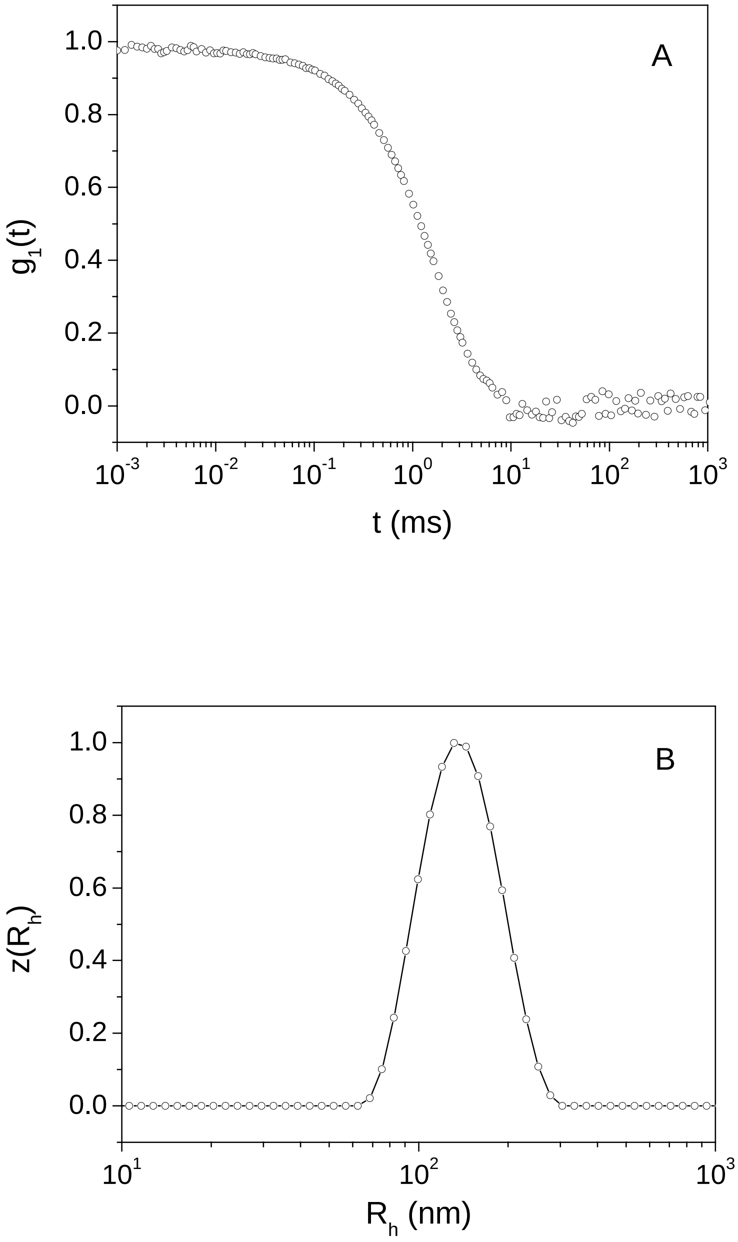

Figure 5. 12. (A) Field autocorrelation function and (B) the corresponding intensity-weighted hydrodynamic radius distribution (obtained from CONTIN analysis) of micelles of PIB_{47}-b-$PDMAAm_{161}$ (run 25) in water at the scattering angle of 90°; C = 0.08 g/L.

Figure 5. 12. shows a typical field autocorrelation function of PIB_{47}-b-$PDMAAm_{161}$ in water at the scattering angle of 90º. The relatively high scattering intensity and the resulted hydrodynamic radius from CONTIN analysis indicated the existence of micellar aggregates. The size distribution of the micelles is relatively narrow, as shown in Figure 5. 12B. Measurements performed at various scattering angles (from 30º to 150º) showed nearly no angular dependence of the hydrodynamic radius.

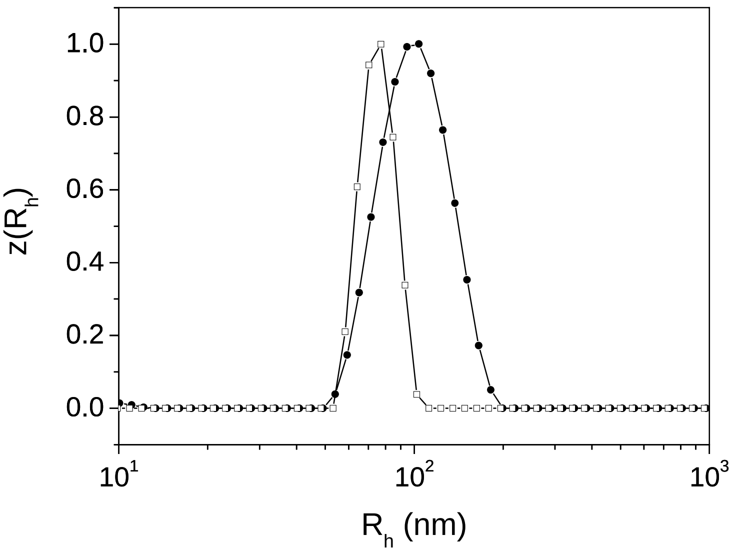

Figure 5. 13. Intensity distribution of hydrodynamic radii of micelles of PIB_{40}-b-$PDMAAm_{940}$ (run 36) in water with various concentrations at the scattering angle of 90°; (open square) C = 0.08 g/L , (solid circle) C = 0.93 g/L.

The copolymer concentration has an dramatic effect on the size of the aggregates. As shown in Figure 5. 13., the hydrodynamic radius increases with increasing polymer concentration, along with a broadening of the size distribution. This is due to either the increase of the micellar size or the formation of new larger aggregates.

The aggregates size decreases with decreasing the PIB composition in the block copolymer, as shown in Table 5. 3.

PIB_m-b-$PDMAAm_n$ *m/n*	$<R_h>_z$ (nm) CONTIN	$<R_h>$ (nm) first cumulant	$<R_h>$ (nm) second cumulant	PDI second cumulant
47/161 (run 25)	137.2	133.8	127.6	0.131
40/940 (run 36)	74.9	77.4	75.8	0.062
76/3630 (run 38)	65.5	63.0	50.6	0.416

Table 5. 3. Hydrodynamic radii of PIB-b-PDMAAm micelles in aqueous solution with the polymer concentration of 0.08 g/L at the scattering angle of 90º

5. 4. Conclusions

A method for the synthesis of PIB-b-PDMAAmA, involving living carbocationic polymerization of isobutylene and subsequent living anionic polymerization, has been demonstrated, this study clearly showed the influence of alkoxides in the polymerization of DMAAmA and his effect in the configuration of the polymer resulting. Polymeric micelles composed of PIB as hydrophobic core and PDMAAmA as hydrophilic shell were prepared from aqueous solution.

This amphiphilic block copolymers have numerous promising potential applications, e.g. as reagents for removal of non-polar pollutants from water, dispersing agents, etc.

Summary

The anionic polymerization of N,N-dimethylacrylamide (DMAAm) was carried out with a binary initiator system prepared from Thienyllithium and the Lewis acids triethylaluminium (Et_3Al), diethylzinc (Et_2Zn) or triethylborane (Et_3B) in THF. Polymerizations proceeded in a homogeneous manner and gave polymers having controlled molecular weights. However, in presence of alkoxides the polymerization results in polymers insoluble in THF even using Et_3Al. A synthetic route for the synthesis of polyisobutylene-*b*-PDMAAm was developed by combining living carbocationic and anionic polymerizations. Thiophene end-capped polyisobutylene (PIB-T), prepared by cationic polymerization, was quantitatively metalated with *n*-butyllithium in THF at –40 °C. The resulting stable macrocarbanion ($PIB\text{-}T^-,Li^+$), in conjunction with Lewis acids, was used to initiate the living anionic polymerization of DMAAm, resulting in the new amphiphilic block copolymer PIB-b-PDMAAm.

5. 5. References

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6. Synthesis of Block Copolymers of Isobutylene with Ethylene Oxide by Site Transformation of Chain Ends and their Micellization in Aqueous Solution

6. 1. Introduction

Amphiphilic block copolymers are used for a broad variety of applications, e.g., as reactors for nanoparticles, as thickening agents in paints, in cosmetics, for enhanced oil recovery etc.[1,2] Hydrophobically modified water-soluble polymers (HMWSP) are gaining importance due to their unique rheological and structural properties.[3] There are several possible ways to combine hydrophobic and hydrophilic block: by living polymerization technique.[4-6] The water-soluble block can be ionic or non-ionic e.g., ethylene oxide. There is a large variety of hydrophobic blocks ranging, e.g., from polystyrene to poly(methacrylates) with long alkyl side chains.

Oxiranes, such as ethylene oxide or propylene oxide, are basic building blocks for the technologically important polyglycols.[7] The anionic polymerization initiated by alkaline-, alkaline earth- or ammonium-alkoxides allows the synthesis of polymers with high molecular weights. Multistep dissociation equilibrium and ion pair association leads in the case of metal alkoxides to complex kinetics of the initiation and propagation reactions.[8-10] Because of insufficient solubility, the control of the molecular weight distribution and the synthesis of well-defined blocks is not generally possible when polyalkoxides are used as multifunctional starting agents. The use of softer, non-metal cations, like Bu_4N^+, is limited because of their lack of thermal stability.[11] As a new alternative, the extremely strong, non-metallic polyiminophosphazene bases, like t-Bu-P_4 offer the possibility to generate a very soft counterion. The rather thermostable protonated polyiminophosphazene show an exceptional low tendency for ion pair association and should consequently be highly efficient for the initiation of oxirane polymerization.[12,13]

The shape of the micelles depends on the block lengths and the temperature. Spherical, oblate, and rodlike structures can be observed. Generally, the hydrophobic (A) blocks build a core covered by a shell of the hydrophilic (B) parts in water.[14] For ABA triblock copolymers, single chains may form loops (both ends belongs to the same micelle) or bridges (two micelles are connected). Block copolymers have a long history as industrial surfactants. [15] The major types of block copolymers, such as those made from ethylene oxide (EO) and propylene oxide (PO) (Pluronics) or EO and styrene, are cheap and easy to tailor-make for specific applications. The water-soluble EO-PO block copolymers are stable over a wide pH range and compatible with all other types of surfactants. In addition, they are mild to the skin and hair, a property related to their high molecular weight. Sometimes it is advantageous to use a more hydrophobic segment than poly(propylene) in the block copolymer. Well-known examples of block copolymers with an extremely hydrophobic segment are the silicone-EO-PO polymers used to stabilize non-aqueous foams.[15]

In this work combination of cationic and anionic polymerization is employed for the preparation of amphiphilic block copolymers. The hydophobicity is introduced by polyisobutylene and the hydrophilic block is the poly(ethylene oxide). The solutions of the amphiphilic block copolymers in water are characterized by fluorescence spectroscopy, TEM and dynamic light scattering.

6. 2. Experimental

6. 2. 1. Materials

2,6-Di-*tert*-butylpyridine (D*t*BP, Aldrich, 97%) was purified by distillation from CaH_2. Isobutylene (BASF) was passed through in-line gas purifier columns packed with $CaSO_4$ and no. 13 molecular sieves and condensed at -15 °C prior to polymerization. CH_2Cl_2 was purified by washing it with 10% aqueous NaOH and then with distilled water until neutral and dried over anhydrous $MgSO_4$ overnight. It was refluxed for 24 h and distilled from CaH_2, just before use. *n*-hexane was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with 10% NaOH aqueous solution and then with deionized water until neutral and stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled. Titanium (IV) chloride ($TiCl_4$, 99.9%, Aldrich) was used as received. Thiophene (99%, Aldrich) was distilled the day before use and stored at 4 °C. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by hydrochlorination of 2,4,4-trimethyl-1-pentene (Fluka, 98 %, used as received) with hydrogen chloride gas in dry dichloromethane at 0 °C.[16] The product was dried over $CaCl_2$ and distilled under reduced pressure before use. Ethylene oxide (EO, Linde) was condensed onto CaH_2 and stirred at 0 °C for 3 h before being transferred into glass ampules and before use it was purified with *n*-butyllithium. Thienyllithium (1.0 M in tetrahydrofuran) (TLi) was purchased from Aldrich and its concentration was titrated by a standard method. 2-(2-Thienyl)-ethanol (Aldrich 98%) was distilled from CaH_2 the day before use and stored at 4 °C. Polyiminophosphazene base t-Bu-P_4 was purchased from

Fluka as 1.0 M solution and used without further purification. THF (Merck p.a) was purified first by distillation under nitrogen from CaH_2 and then by refluxing over potassium. A solution of *n*-butyllithium (1.6 M in hexane) (*n*-BuLi) was purchased from Aldrich and its concentration was titrated by a standard method.

Synthesis of Thiophene-Ended PIB (PIB-T)

The synthesis of PIB-T was carried out under a dry nitrogen atmosphere. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask (reactor) equipped with a septum, an magnetic stirring and a nitrogen inlet were added of 120 mL CH_2Cl_2, 202 mL of *n*-hexane (olefin-free) and 0.177 mL (0.15 g, 0.788 mmol) of 2,6-di-*tert*-butylpyridine (D*t*BP) and then the mixture was cooled to -78 °C. 10.5 mL (6.66 g, 0.119 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring 0.3 mL (0.30 g, 2.02 mmol) of TMPCl were transferred to the reactor by a transfer needle. After 5 min of stirring, 0.78 mL (1.34 g, 7.11mmol) of $TiCl_4$ were transferred to the reactor by a transfer needle. One hour later 34.6 mL (36.31 g, 0.431 mol) of thiophene were added to the polymerization system; the color of the solution changed from slightly yellow to red. Thiophene was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude mixture was filtered in order to remove the titanium complexes. During filtration, additional *n*-hexane was added. Then, the *n*-hexane phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was redissolved in a small amount of *n*-hexane and precipitated two or three times into acetone in order to remove excess thiophene.

Synthesis of α-hydroxy-functionalized PIB (PIBT-OH)

The reaction of lithiated PIB-T with ethylene oxide was carried out in a 250 mL stirred glass reactor. 200 mL of THF were added and 3.50 g (1.08 mmol) of PIB-T and then the mixture was cooled to -40 °C. After 10 min of stirring 0.93 ml (1.5 mmol) of *n*-BuLi were transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with PIB-T for 60 min to form the anion ($\text{PIB-T}^{-},\text{Li}^{+}$). Chain end hydroxylation was affected by reacting the resulting $\text{PIB-T}^{-},\text{Li}^{+}$ with 2.5 g (56.75 mmol) of ethylene oxide. After 24 h of the reaction, the reaction was terminated with mixture of methanol / acetic acid (1/5: v/v). Finally, the crude polymer was isolated in quantitative yield by precipitating the product into excess methanol and drying under vacuum at room temperature. The pure hydroxylated polymer was isolated by column chromatography of the crude polymer, isolating the corresponding fraction, precipitating the product into excess methanol, and drying under vacuum at room temperature.

The nonfunctionalized polymer was separated by column chromatography technique. For example 3 g of polymer was chromatographed on column of activated silica gel. *n*-Hexane and Toluene were used as the eluents. The column was prepared in *n*-hexane. Once the front running polyisobutylene eluted out of the column the eluent was gradually changed to pure Toluene to elute the remaining functional polymer. Quantitation of functional and nonfunctional polymer was achieved by LACCC measurements.[17]

Synthesis of Poly(ethylene oxide) using Thienyllithium

Anionic polymerizations of ethylene oxide using thienyllithium in presence of t-Bu-P_4 were carried out in 1 L stirred glass reactor (Büchi) with a thermostatted cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampoules via spherical joint or with dry syringe. Solution of thienyllithium (T-Li) was handled with syringes. In a typical procedure 0.49 mL (0.49 mmol) T-Li solution was added to 200 mL purified THF. The reactor was cooled to –40 °C and after few minutes of stirring the purified monomer 4.62 g (0.105 mol) was added to the initiator. To this solution 0.58 mL (0.58 mmol) of t-Bu-P_4 was added, and the mixture was stirred for 48 h at 40 °C. After completion of the reaction, the reaction was terminated with methanol/acetic acid. The reaction mixture was concentrated by evaporation and poured into a large excess amount of hexane to precipitate the polymer. Finally, the polymer was dried under vacuum at room temperature as a white powder.

Synthesis of Poly(ethylene oxide) using 2-(2-Thienyl)-ethanol T-OH

Anionic polymerizations of ethylene oxide using 2-(2-Thienyl)-ethanol in presence of Ph4 were carried out in 250 mL stirred glass reactor (Büchi) with a thermostatted cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampoules via spherical joint or with dry syringe. Solution of 2-(2-Thienyl)-ethanol (T-OH) was handled with syringes. In a typical procedure 0.29 mL (0.344 g, 2.69 mmol) T-OH solution was added to 200 mL purified THF. The reactor was cooled to –40 °C and after few minutes of stirring the purified monomer 6.43 gr (0.146 mol) was added to the initiator. To this solution 0.32 mL (0.32 mmol) of t-Bu-P_4 was added, and the mixture was stirred for 48 h at 40 °C. After completion of the reaction, the reaction was terminated with methanol/acetic acid. The reaction mixture was concentrated by evaporation and poured into a large excess amount of hexane to precipitate the polymer. Finally, the polymer was dried under vacuum at room temperature as a white powder.

Synthesis of Polyisobutylene-*b*-Poly(ethylene oxide) using PIB-T as macroinitiator

All copolymerizations were carried out in 250 mL stirred glass reactor (Büchi) with a thermostatted cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampoules via spherical joint or with dry syringe. Solutions of *n*-BuLi and additives were handled with syringes. In a typical procedure macroinitiator, monomer, and n-BuLi were introduced and cooled to –40 °C. 0.813 g (0.252 mmol) of PIB-T ($M_n = 3.23 \times 10^3$) were freeze-dried from benzene solution for 8 h and then vacuum-dried for more than 10 h. On a vacuum line, the dried PIB-T was dissolved in 10 mL of THF and then the mixture was added to the stirred glass reactor and cooled to –40 °C. 0.16 mL (0.252 mmol) *n*-BuLi solution were added with a dry syringe afterwards. The reaction was held at -40 °C for 1 h and 6.29 gr (0.143 mol) of ethylene oxide was introduced into the macroinitiator solution and maintained for 20 minutes at 0 °C and then 0.27 ml (0.27

mmol) t-Bu-P_4 were added, and the mixture was stirred for 48 h at 40 °C. The polymerization was quenched with methanol/acetic acid. Finally, the polymer was precipitated into hexane and dried under vacuum at room temperature.

Synthesis of Polyisobutylene-*b*-Poly(ethylene oxide) using PIB-TOH as macroinitiator

All copolymerizations were carried out in 250 mL stirred glass reactor (Büchi) with a thermostatted cooling jacket, steel capillary connections to introduce gases and solvents and devices to measure temperature and pressure. Solvents were directly introduced from the distillation apparatus into the reactor. Monomer was introduced from glass ampoules via spherical joint or with dry syringe. In a typical procedure macroinitiator and monomer were introduced and cooled to –40 °C. 0.50 g (0.157 mmol) of PIB-TOH ($M_n = 3.23 \times 10^3$) were freeze-dried from benzene solution for 8 h and then vacuum-dried for more than 10 h. On a vacuum line, the dried PIB-T was dissolved in 10 mL of THF and then the mixture was added to the stirred glass reactor and cooled to –40 °C. 0.172 mL (0.172 mmol) t-Bu-P_4 solution were added with a dry syringe afterwards. The reaction was held at -40 °C for 1 h and 6.29 gr (0.143 mol) of ethylene oxide was introduced into the macroinitiator solution and maintained for 20 minutes at 0 °C and then the mixture was stirred for 48 h at 40 °C. The polymerization was quenched with methanol/acetic acid. Finally, the polymer was precipitated into hexane and dried under vacuum at room temperature.

6. 2. 3. Characterizations

^{1}H-NMR spectroscopy was carried out on a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$ using TMS as internal standard. SEC was performed using THF as eluent at a flow rate of 1 mL/min equipped with a four column set of PSS SDV gel (particle size 5µm, 10^2 - 10^5 Å) heated to 40 °C. Calibration was based on PIB and PS standards (PSS, Mainz). SEC in water was measured using a flow rate of 1 mL/min containing 0.1 M NaN_3 and 0.01 M NaH_2PO_4, equipped with a two column set of PL Aquagel-OH (particle size 8µm, 10^2 - 10^5 Å) heated to 35 °C. Calibration was based on PEO standards (PSS, Mainz).

Liquid adsorption chromatography under critical conditions (LACCC) measurements were conducted on a TSP HPLC system at a flow rate of 0.5 L/min. An Evaporative Light Scattering Detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow of 3.5 L/min was used for mass detection. 10 µL of ca. 0.5 wt % polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two Reversed Phase columns (YMC, 250 x 4 mm) with 5 µm average particle size, 100 Å and 300 Å pore diameter were used. The critical solvent composition for PIB is THF:methanol = 80.5:19.5. Premixing of the mobile phase by weight is necessary for a constant and exact composition.

Dynamic light scattering (DLS) was performed on an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E correlator and a He–Ne laser (λ_0 = 632.8 nm). Prior to the light scattering measurements the sample solutions were filtered using Millipore filters (housing: polypropylene, membrane: poly(tetrafluoroethylene)) with a pore size of 3 µm (filters with smaller pore sizes were rapidly clogged).

Differential Scanning Calorimetry (DSC). For thermal analysis a Perkin-Elmer DSC 7 with a CCA 7 liquid nitrogen cooling device was used. For all measurements a two-point calibration with n-decane and indium was applied. All experiments were performed at a scanning rate of 10 °K/min. The displayed heating traces correspond to the second heating run in order to exclude effects resulting from any previous thermal history of the samples. Fluorescence spectroscopy, the samples for fluorescence measurements were prepared according to a procedure described elsewhere.[18-20] Aliquots of 60µl of 2.5×10^{-5} M solution of pyrene in acetone were carefully dropped into empty dark vials by a 100 µl Hamilton microsyringe, acetone was afterwards evaporated by gentle heating. Then the sample solutions (3 ml) prepared by an appropriate dilution of the stock solutions of PIB-b-PEO were added. To equilibrate pyrene, the prepared samples were kept at 40-50°C for ca. 2 days under intensive stirring. The final concentration of the fluorescent probe in the prepared samples was kept constant at 5×10^{-7} M, that is, only slightly below the saturation concentration of pyrene in water at 22°C. Steady-state fluorescence spectra of the air-equilibrated samples were recorded with a Hitachi F-4000 fluorescence spectrophotometer (right angle geometry, 1 cm × 1 cm quartz cell). The widths of slits were chosen to be 3 and 1.5 nm for excitation and emission, respectively.

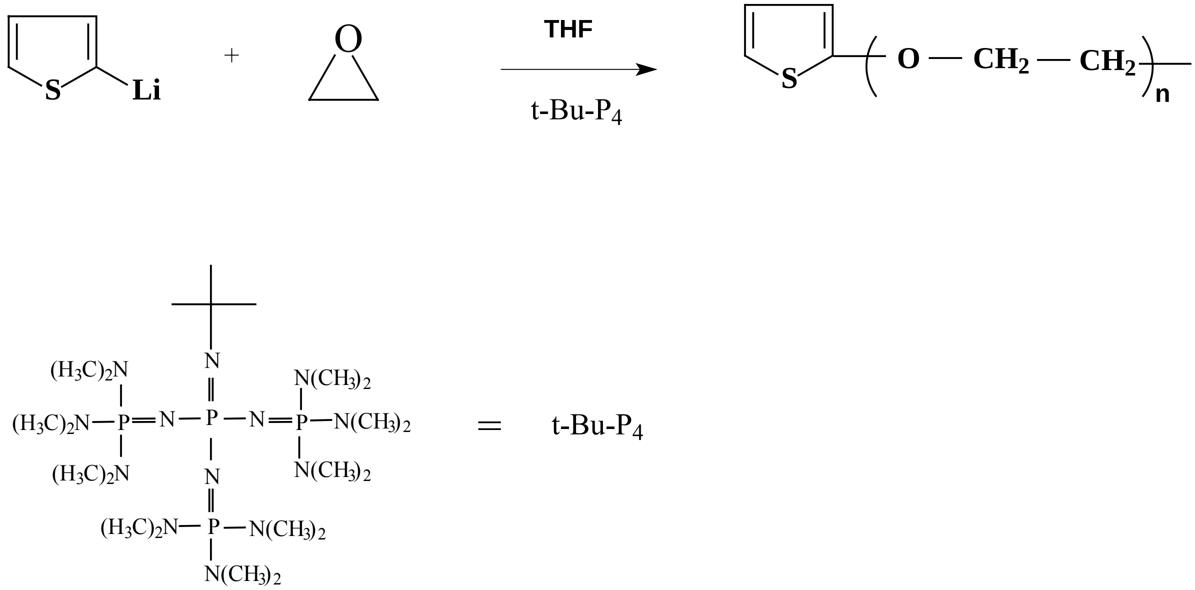
6. 3. Results and Discussion

6. 3. 1. Synthesis of Poly(ethylene oxide) using Thienyllithium

Anionic polymerization of Ethylene Oxide using Thienyllithium and 2-(2-Thienyl)-ethanol

Before using the PIB-T or PIB-OH macro-initiator for ethylene oxide polymerization, orienting model experiments were carried out with thienyllithium and 2-(2-Thienyl)-ethanol which mimic the end group structure of PIB-T$^-$,Li$^+$ and PIB-TO$^-$, [t-Bu-P$_4$,H]$^+$ respectively.

A series of polymerizations of EO were performed according to Scheme 6. 1.



Scheme 6. 1.Synthesis of Poly (ethylene oxide) using Thienyllithium as initiator

The polymerization was initiated by adding the monomer into a THF solution of T-Li or T-OH and tBuP$_4$. The conditions are summarized in Table 6. 1.

run	Initiator	[t-Bu-P_4]/$[I]_0$	$[I]_0$, mmol	$[M]_0$, mol	t, h	$M_n \times 10^{-3}$		M_w/M_n
						calcd	SEC[a]	
PEO1	T-Li	1.2	0.488	0.105	48	9.45	9.67	1.01
PEO2	T-OH	1.2	2.69	0.146	48	2.39	2.35	1.03

[a] determined with PEO standards

Table 6. 1: Anionic Polymerization of EO with Thienyllithium and 2-(2-Thienyl)-ethanol in THF at 40 °C.

The molecular weights determined by GPC using PEO standards in THF, indicate that the efficiency of T-Li and T-OH is high and leads to narrow molecular weight distributions.

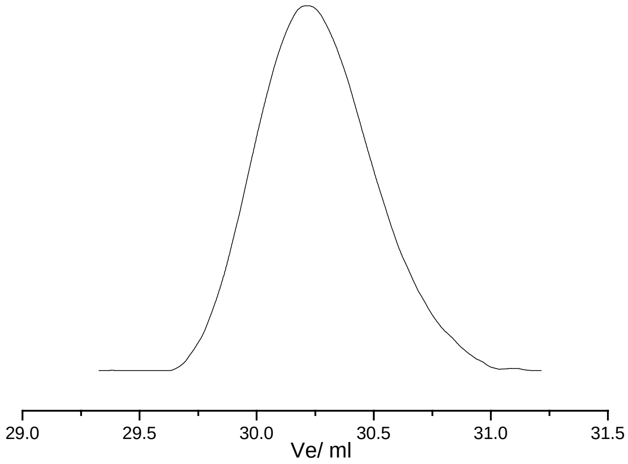
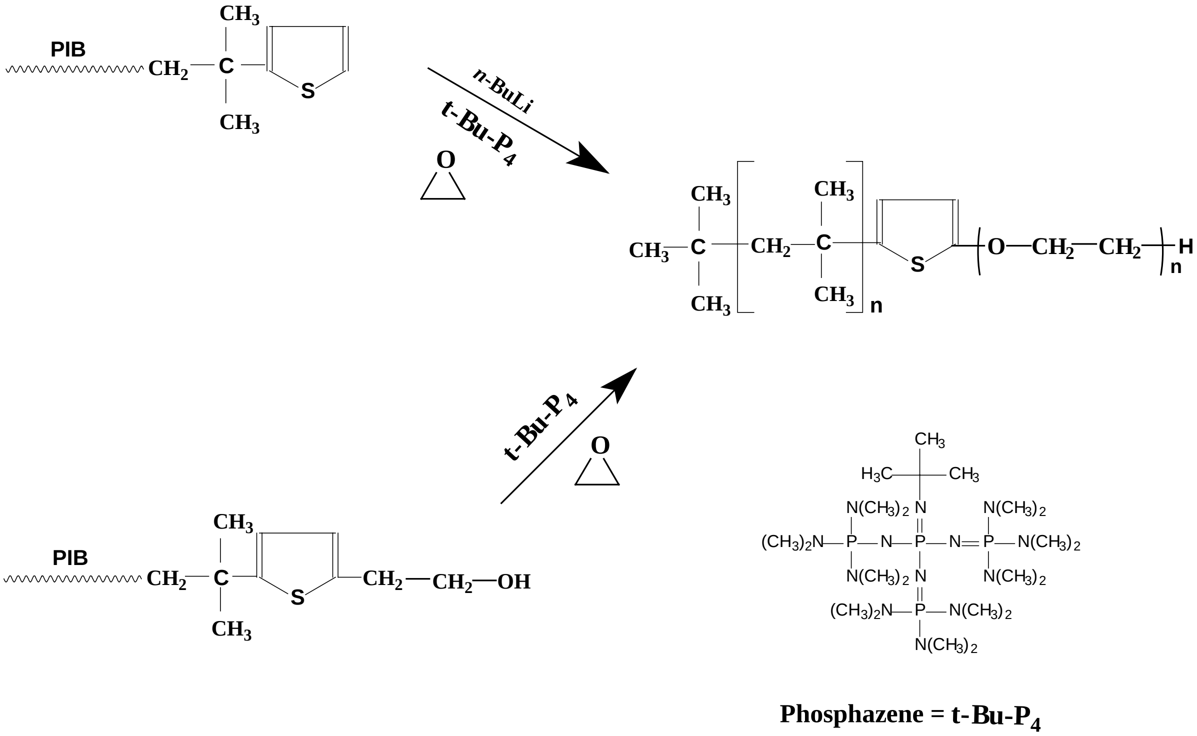


Figure 6. 1. SEC traces (RI detector) of PEO1 produced with thienyllithium.

Synthesis of PIB-b-PEO

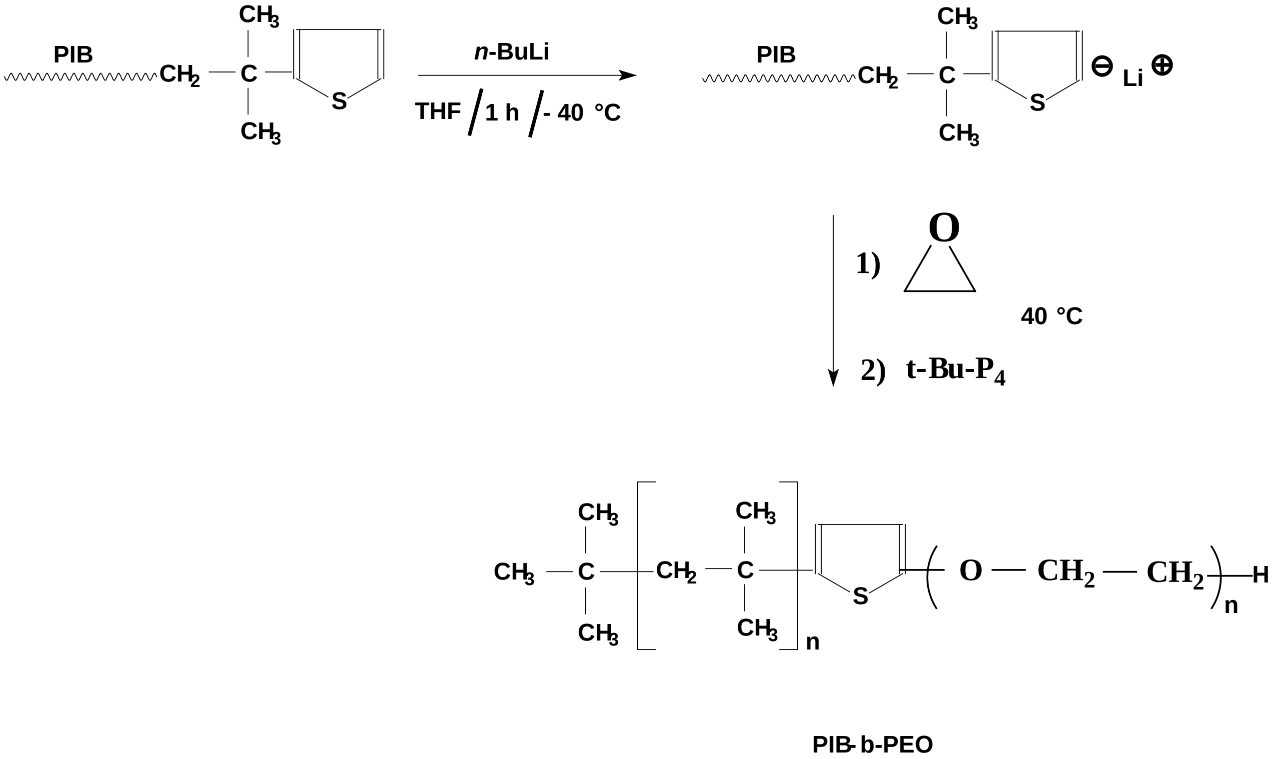
In order to obtain the desired PIB macroinitiator, two possibilities have to be taken into account, either the use of a thiophene end-capped polyisobutylene or a hydroxy end-capped polyisobutylene. First thiophene end-capped polyisobutylene (PIB-T) was prepared by cationic polymerization. PIB-T was quantitatively metalated with *n*-butyllithium in THF at –40 °C. The resulting stable macrocarbanion (PIB-T$^-$,Li$^+$) in conjunction with tBu-P$_4$ was used to initiate the living anionic polymerization of ethylene oxide yielding polyisobutylene-*b*-poly(ethylene oxide) (PIB-b-PEO). In the second method PIB-b-PEO was synthesized using a hydroxyl end-capped polyisobutylene as macroinitiator in conjunction with t-Bu-P$_4$. . Scheme 6. 2 describes the synthetic steps involved in the preparation of PIB-b-PEO.



Scheme 6. 2. Synthetic approaches for the Polyisobutylene-b-Poly(ethylenoxide) synthesis

Synthesis of PIB-*b*-PEO using PIB-T as macroinitiator

The synthesis of PIB-*b*-PEO was accomplished by using lithiated PIB-T as an anionic macroinitiator of EO polymerization in THF (Scheme 6. 3.). It is important to use a equimolar amount of *n*-BuLi since excess of *n*-BuLi could initiate the homopolymerization of EO. The lithiated precursor PIB-T$^-$,Li$^+$ was used to initiate the polymerization of EO.



Scheme 6. 3. Synthesis of Polyisobutylene-b-Poly(ethylenoxide) using PIB-T as macroinitiator.

Thus, the resulting polymers were first investigated by SEC. Figure 6. 2. shows the SEC eluograms (RI signal) for these block copolymer. The molecular weights determined by GPC using PEO standards are apparent values, which can be different than the real ones. Accordingly, the blocking efficiencies given in Table 6. 2. should be taken as apparent ones, too. In addition, the blocking efficiencies were calculated from the area of the PIB precursor in the GPC eluogram. Since only thiophene is UV-active at 254 nm, the relative area under UV signal of the PIB-T precursor is directly related to the molar fraction of unreacted precursor. It can be seen that a small peak appears for the unreacted PIB in the polymer lithiated by an equimolar amount of *n*-BuLi.

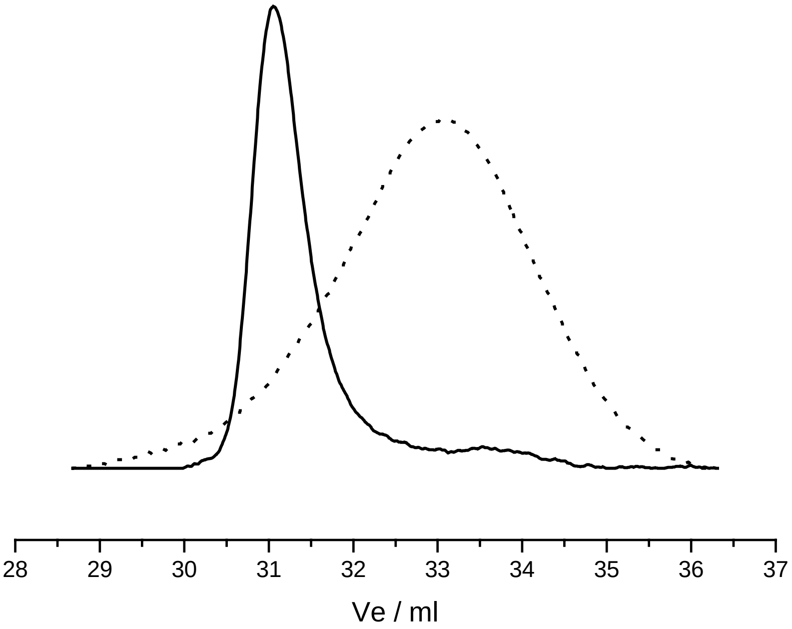


Figure 6. 2. SEC eluograms (RI signal) of the PIB-*b*-PEO1 (—) and PIB-T (----)

ExpNo.	[BuLi]/ [PIB-T]	[PIB-T] mM	[EO] M	$10^{-3}M_{n,GPC}$ (PIB block[a])	$10^{-3}M_{n,th}$[b] (PEO)	$10^{-3}M_{n,GPC}$ (block copolymer[c])	M_w/M_n (block)	f_{block} (GPC) (area[d])
PIBPEO1	1	0.252	0.143	3.23	25.0	9.57	1.10	0.84

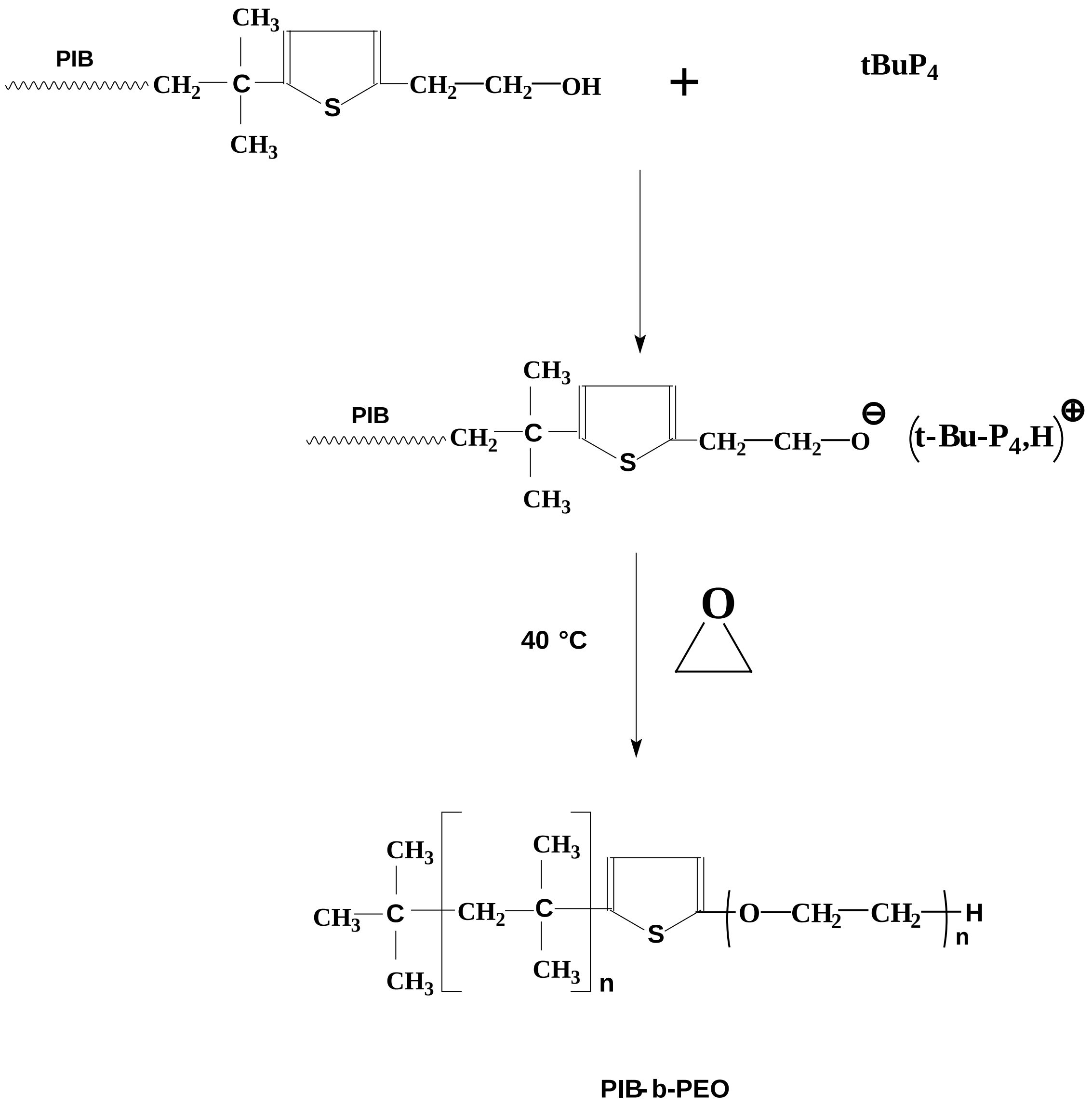
[a] determined with PIB standards, [b] Expected molecular weight of PEO block, [c] determined in THF with PEO standards and represent apparent values only, [d] blocking efficiency determined by GPC from the area of PIB precursor (UV at 254 nm).

Table 6. 2. SEC characterization of PIB-*b*-PEO[a].

Synthesis of PIB-*b*-PEO using PIB-TOH as macroinitiator

In the second method PIB-b-PEO was synthesized using a hydroxyl end-capped polyisobutylene as macroinitiator in conjunction with tBu-P_4 in THF using a similar procedure to that described for the synthesis of PIB-*b*-PEO using PIB-T as macroinitiator. Scheme 4 shows the synthetic strategy for the preparation of PIB-b-PEO using hydroxyl end-capped polyisobutylene as macroinitiator.

In this polymerization, the PIB-*b*-PEO copolymer product was virtually free of unreacted PIB-OH. The SEC traces shown in figure 6. 3. of the resulting diblock copolymer exhibited a monomodal distribution shifted to a lower elution volume compared to that of the PIB-OH precursor. The molecular weights determined by GPC of the block copolymer using PEO standards are apparent values. The results are collected in Table 6. 3.



Scheme 6. 4. Synthesis of Polyisobutylene-b-Poly(ethylenoxide) using PIB-T as macroinitiator.

It can be seen that in the first method, a peak appears for the unreacted PIB in the polymer lithiated by an equimolar amount of *n*-BuLi, however, virtually free of unreacted PIB-OH precursor is detected when a second method is used.

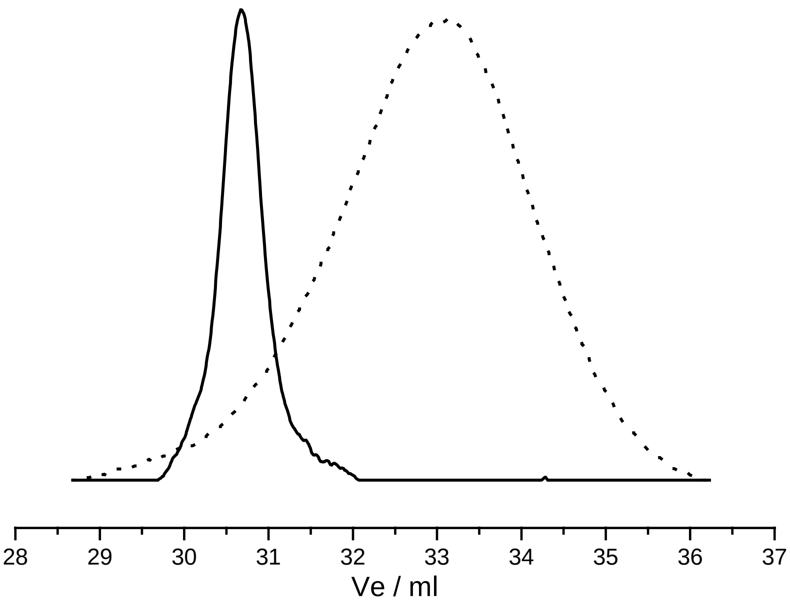


Figure 6. 3. SEC eluograms (RI signal) of the PIB-*b*-PEO2 (—) and PIBT-OH (----)

ExpNo.	$[t\text{-Bu-}P_4]$/ [PIB-TOH]	[PIB-T] mM	[EO] M	10^{-3} $M_{n,GPC}$ (PIB block[a])	10^{-3} $M_{n,th}$[b] (PEO)	10^{-3} $M_{n,GPC}$ (block copolymer[c])	M_w/M_n (block)	f_{block} (GPC) (area[d])
PIBPEO2	1.1	0.157	0.143	3.23	40.0	11.70	1.10	1.0

[a] determined with PIB standards, [b] Expected molecular weight of PEO block, [c] determined in THF with PEO standards and represent apparent values only, [d] blocking efficiency determined by GPC from the area of PIB precursor (UV at 254 nm).

Table 6. 3. SEC characterization of PIB-*b*-PEO[a].

6. 3. 2. Thermal Properties

Differential scanning calorimetry was used to analyze the glass transition temperature of the PIB-b-PEO diblock copolymer. Thermograms of the PIB-b- PEO copolymers are given in Figure 6. 4. The DSC scan for the representative PIB-b-PEO diblock copolymers have one glass transition temperatures that close to the value of PEO homopolymer; the second transition cannot be observed, since the fraction of PIB is too low. The PEO blocks display a melting endotherm at approximately 60-64 °C (Figure 6. 5.). The crystallization of PEO occurs in all diblock copolymers at about 35-39 C (Figure 6. 4.).

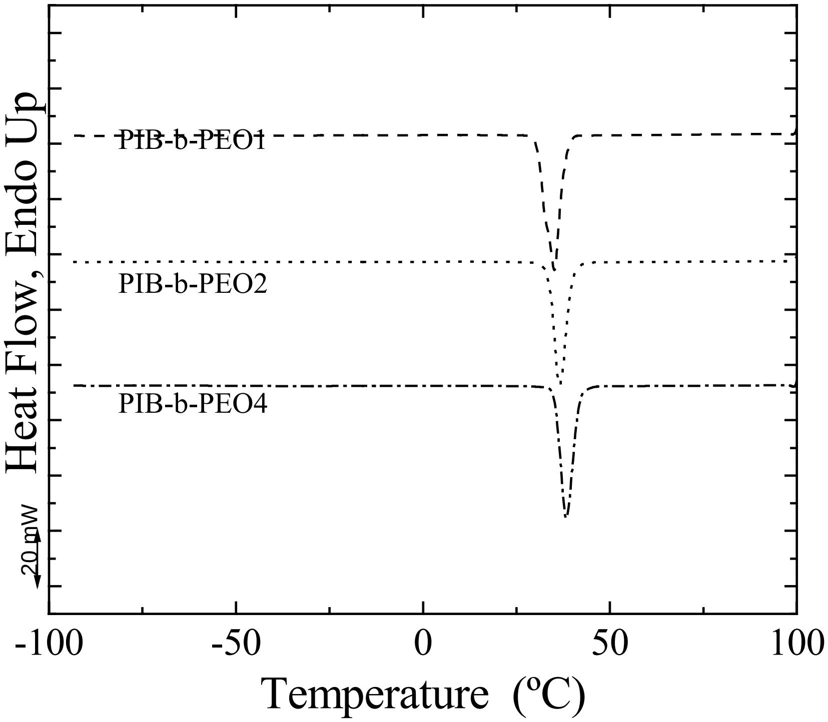


Figure 6. 4. DSC cooling traces for several PIB-b-PEO copolymers.

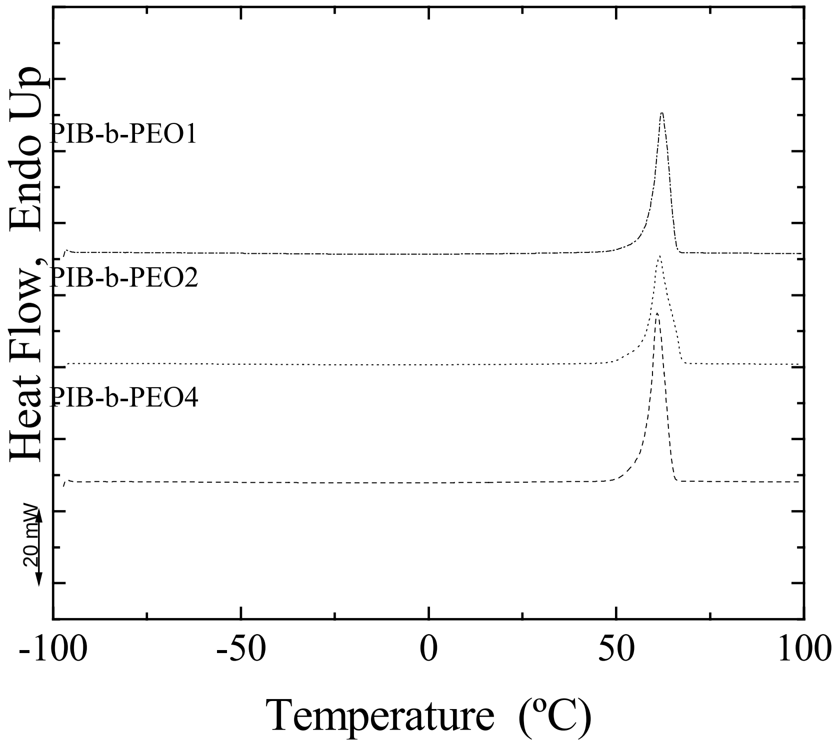


Figure 6. 5. DSC heating traces for several PIB-b-PEO copolymers.

6. 3. 3. Micelle Characterization by Dynamic Light Scattering (DLS)

The size distribution of the micellar aggregates formed by PIB-b-PEO diblock copolymers in water was investigated by DLS in an attempt to approach the size of the micelles formed by the diblock copolymers with various compositions. The DLS studies indicate the formation of micelles. Figures 6. 6. shows the hydrodynamic radius distribution functions (CONTIN plots) of block copolymer micelles in aqueous solutions at different concentrations. Since the hydrophobic PIB blocks are very short compared to the PEO blocks, the formation of star micelles was expected. Moreover, PIB has a low glass transition temperature, thus one should expect the formation of dynamic micelles.

SAMPLE	SEC PIB[b]		SEC PIB-b-PEO[c]		DLS C = 2 x 10^{-5} M (0.23 g/L)		DLS C = 1 x 10^{-4} M (1.16 g/L)	
	Mn x 10^{-3} g / mol	Mw/Mn	Mn x 10^{-3} g / mol	Mw/Mn	$\langle R_h \rangle_z$ (nm)	PD	$\langle R_h \rangle_z$ (nm)	PD
PIB-b-PEO4[a]	1.34	1.15	11.50	1.23	34.5	1.33	41.0	1.40

[a] synthesized using PIB-TOH as macroinitiator, [b] determined with PIB standards, [c] determined with PEO standards in water and represent apparent values only.

Table 6. 4. Hydrodynamic radii of PIB-b-PEO micelles in aqueous solution

The dynamic light scattering results indicate that the micelles formed by PIB-b-PEO4 have a somewhat wide distribution of radii. The ratio μ_2 / Γ^2, taken as measure of the polydispersity in size, is more than 0.30. Contin analysis shows only one distribution peak, moreover an increase in the concentration of the PIB-b-PEO4, leads to a shift increase in the hydrodynamic radius and polydispersity (Table 6. 4.).

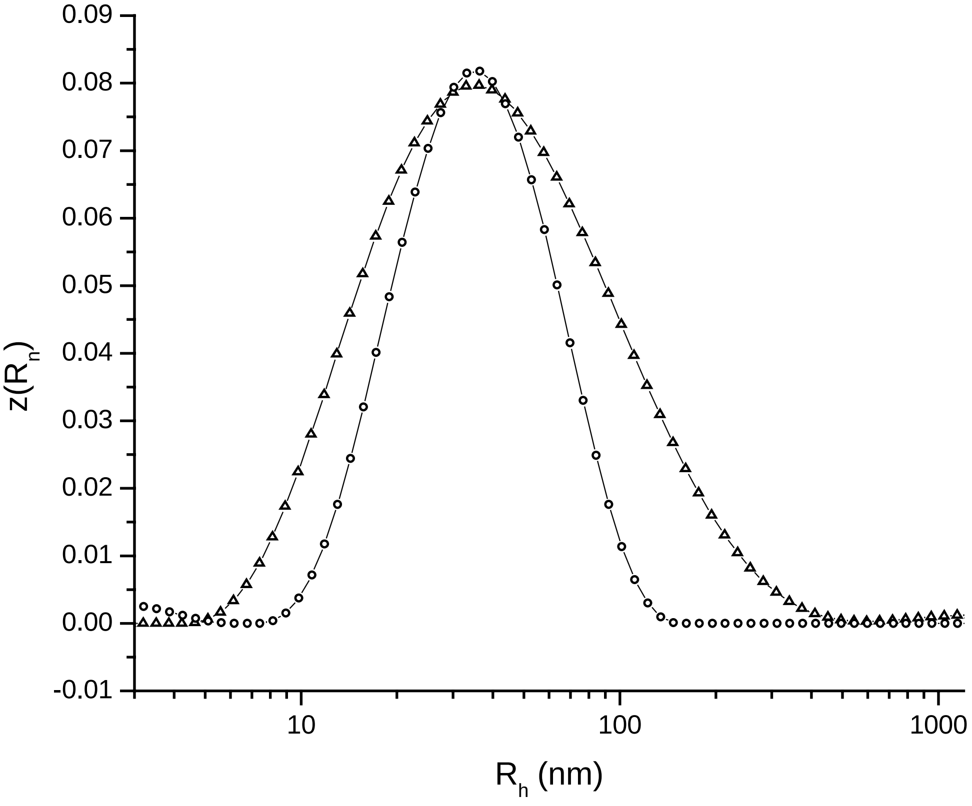


Figure 6. 6. Intensity distribution of hydrodynamic radii of micelles of PIB-b-PEO4 in water at scattering angle of 90°; (-O-) C= 0.23 g/l , (-△-) C= 1.16 g/l.

6. 3. 4. Micelle Characterization by Fluorescence Spectroscopy

The photophysical properties of pyrene are known to be strongly dependent on the polarity of its environment.[21] This feature has allowed using this fluorophore as a probe to determine critical micellization concentrations (cmc) for some nonionic and ionic amphiphilic block copolymers in aqueous solutions.[18-20] In particular, the fine structure of the emission spectrum of pyrene, especially the ratio between the intensities of first and third vibrational bands, I_1/I_3, is rather sensitive to the polarity of its surrounding medium : this ratio was demonstrated to decrease if the environment of the fluorescent probe becomes less polar. The complete dependence of I_1/I_3 on the concentration of PIB-b-PEO4 is presented in Figure 6. 7. The values of , I_1/I_3 remain fairly constant at low concentrations of the copolymer. Above a certain concentration of the PIB-b-PEO4, the values of I_1/I_3 demonstrate a pronounced fall upon the rising concentration of the copolymer. The concentration determined as the intersection of the tangent to the dependence curve of I_1/I_3 on PIB-b-PEO4 concentration at its inflection with horizontal tangent through points corresponding to low concentrations of PIB-b-PEO4 can be considered as cmc. As is seen, the molar value of cmc is around 9.0 x 10^{-6} M.

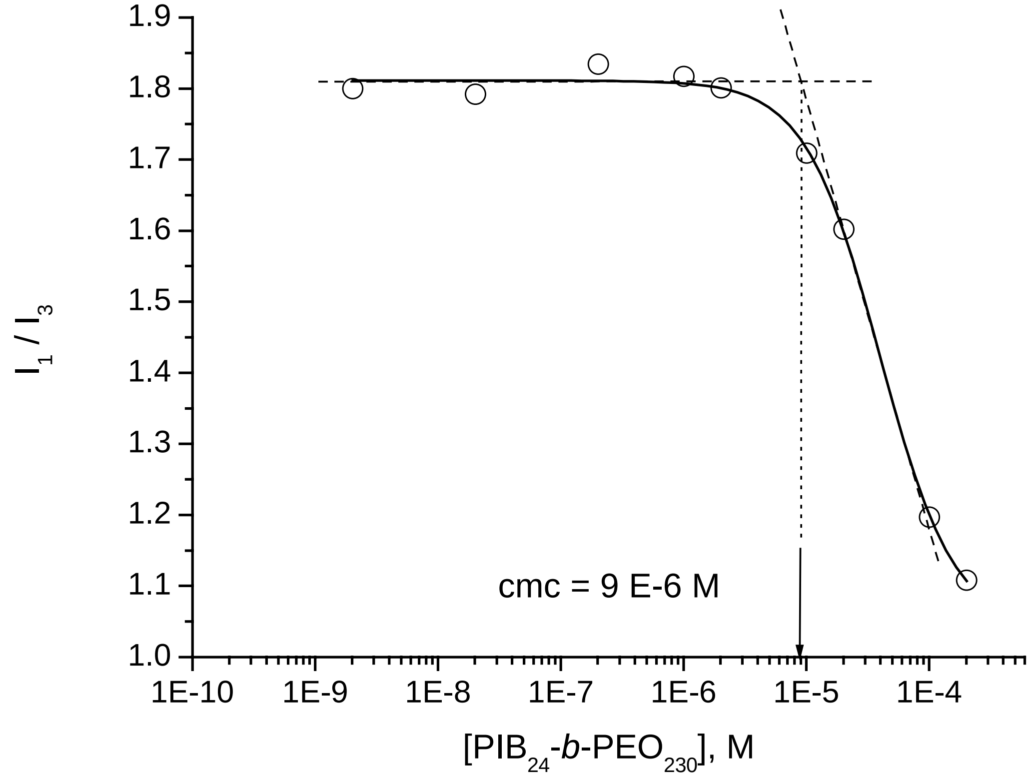


Figure 7. Dependence of the intensity ratio I_1/I_3 on the molar concentration of PIB-b-PEO4; the excitation wavelength is 333 nm.

6. 4. Conclusions

A method for the synthesis of PIB-b-PEO, involving living carbocationic polymerization of isobutylene and subsequent living anionic polymerization, has been demonstrated. Polymeric micelles composed of PIB as hydrophobic core and PEO as hydrophilic shell were prepared from aqueous solution.

This amphiphilic block copolymers have numerous promising potential applications, e.g. as reagents for removal of non-polar pollutants from water, dispersing agents, etc.

Summary

The anionic polymerization of ethylene oxide (EO) was carried out with a binary initiator system prepared from thienyllithium and the polyiminophosphazene base tBu-P_4 in THF. A synthetic route for the synthesis of polyisobutylene-*b*-poly(ethylene oxide) (PIB-b-PEO) was developed by combining living carbocationic and anionic polymerizations using two methods. First thiophene end-capped polyisobutylene (PIB-T) was prepared by cationic polymerization. PIB-T was quantitatively metalated with *n*-butyllithium in THF at – 40 °C. The resulting stable macrocarbanion (PIB-T^-, Li^+) in conjunction with tBu-P_4 was used to initiate the living anionic polymerization of ethylene oxide. In the second method PIB-b-PEO was synthesized using a hydroxyl end-capped polyisobutylene as macroinitiator in conjunction with tBu-P_4. The aggregation behavior in dilute aqueous solutions of a PIB-*b*-PEO copolymer, produced from the combination of cationic and anionic polymerizations, was investigated by dynamic light scattering. Micellar characteristics, including aggregation number, size, and polydispersity depend on the molecular weight and the composition of the copolymers.

6. 5 .References

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7. Synthesis and Characterization of Hydroxy-Thiophene End-Capped Polyisobutylene and Block Copolymers of Isobutylene with L-Lactide and ε-Caprolactone by Site Transformation of Chain Ends

7. 1. Introduction

Recent interest in the design and synthesis of block copolymers has been focused on materials with a combination of unique compositional and architectural properties, especially when hydrophobic/hydrophilic, amorphous/crystalline, or branched/linear, blocks are combined. This is due to recent advances in living polymerization techniques, which allow the precise control of the architecture, molecular weight, and molecular weight distribution of each block segment. Therefore, block copolymer synthesis has utilized living polymerization systems including, e.g., anionic, cationic, radical, or group transfer polymerization.

Controlled ring-opening polymerizations of cyclic esters, such as lactide, glycolide, cyclic carbonates, and ε-caprolactone, have been attracting much attention with respect to their applications as biodegradable, nontoxic scaffolds for regeneration of organs, matrices for drug delivery systems, and alternatives for commercial polymers such as polyethylene, polypropylene, and polystyrene.[1,2] Both polylactide and poly(ε-caprolactone) have been extensively studied for their potential uses in the biomedical field and have also been investigated as potential engineering materials.[3,4]

Block copolymers of isobutylene (IB) and biodegradable monomers, such as L-lactide (LA) or ε-caprolactone (εCL) combine the high environmental stability of the elastomeric, non-polar polyisobutylene with the biodegradability and properties of aliphatic polyesters. Since PIB can only be obtained by carbocationic polymerization, however, many attempts have been undertaken to transform living cationic PIB chain ends to radical or anionic ones,[5-7] as well as to end-functionalize them with OH groups.

The site transformation technique provides a useful alternative for the synthesis of block copolymers consisting of two monomers that can be polymerized only by two different mechanisms. In this method, the propagating active center is transformed to a different kind of active center, and a second monomer is subsequently polymerized by a mechanism different from the preceding one. The key process in this method is the precious control of α- or ω–end functionality, capable of initiating the second monomer. Thiophene end-capped PIBs can be readily prepared by the intermediate capping reaction of living PIB with thiophene, followed by the addition of suitable nucleophiles.[8] Thiophene end-capped PIB (PIB-T) can be lithiated with *n*-butyllithium and produced an anionic macroinitiator. We recently reported the use of these macroinitiator for the synthesis of PIB-b-P*t*BMA.

Mononfunctional and telechelic hydroxy-functionalized polyisobutylenes (PIB-OH and HO-PIB-OH) are valuable starting materials for a large family of new products.[9] Comercially available hydroxy-telechelic liquids (e. g., polytetrahydrofurans, polybutadienes, and polysiloxanes) are important precursors for polyurethanes and polyesters, since they yield rubbery end-products upon end-linking or extension. A desirable characteristic of these extension or cross-linking reactions, particularly for molding applications, is that they proceed with little or negligible shrinkage. Scientifically, telechelics are important as prepolymers for the synthesis of model networks, i.e., networks in which the molecular weights of network elements between crosslinks are equal and that do not contain dangling chain ends. They are also important as macroinitiators to initiate the ring-opening polymerization of several monomers, such as LA, εCL, or ethylene oxide.

Since the discovery of the inifer technique and the living polymerization of isobutylene by Kennedy et al.,[10] the synthesis of well-defined telechelic PIBs capped with various useful functional groups has been a major objective of various research groups. Kennedy et al. attempted the synthesis of hydoxy end-capped polyisobutylene by dehydrochlrination, followed by hydroboration of the terminal double bonds with 9-borabicyclo(3,3,1)nonane, and oxidation with hydrogen peroxide/NaOH.[11] However, this proved to be a very tedious procedure, not readily applicape for PIB of high molecular weight. Recently Faust et al., reported the synthesis of hydroxy end-capped polyisobutylene by end-capping with 1,1-diphenylethylene followed by quenching with 1-methoxy-1-trimethylsiloxy-2-methyl-propene (MTS) and reduction of carboxyl end-functional PIB with $LiAlH_2$.[12]

We reported in chapter 4 the quantitative fuctionalization of living PIB with thiophene (T) and the subsequent lithiation of the obtained PIB-T. This carbanionic chain end is able to initiate the anionic polymerization of acrylic monomers like tert-butyl methacrylate or N,N-dimethylacrylamide . This chapter reports the synthesis of monofunctional and telechelic hydroxyl-functionalized polyisobutylenes via monoaddition of ethylene oxide to the lithiated mono- and difunctional $PIB\text{-}T^-$, Li^+. The resulting PiBOH and HO-PIB-OH are used as macroinitiators for a nearly quantitative ring-opening polymerization of LA and εCL in the presence of stannous octoate. This resulted in AB- and ABA-type block copolymers consisting of an amorphous, rubbery PIB segment and one or two segments of biodegradable, crystalline PLA or PεCL

7. 2. Experimental

7. 2. 1. Materials

2,6-Di-*tert*-butylpyridine (D*t*BP, Aldrich, 97%) was purified by distillation from CaH_2. Isobutylene (BASF) was passed through in-line gas purifier columns packed with $CaSO_4$ and no. 13 molecular sieves and condensed at -15 °C prior to polymerization. CH_2Cl_2 was purified by washing it with 10% aqueous NaOH and then with distilled water until neutral and dried over anhydrous $MgSO_4$ overnight. It was refluxed for 24 h and distilled from CaH_2, just before use. *n*-Hexane was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with 10% NaOH aqueous solution and then with deionized water until neutral and stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled. Titanium (IV) chloride ($TiCl_4$, 99.9%, Aldrich) was used as received. Thiophene (99%, Aldrich) was distilled the day before use and stored at 4 °C. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by hydrochlorination of 2,4,4-trimethyl-1-pentene (Fluka, 98 %, used as received) with hydrogen chloride gas in dry dichloromethane at 0 °C.[13] The product was dried over $CaCl_2$ and distilled under reduced pressure before use. 5-*tert*-Butyl-1,3-bis(1-chloro-1-methylethyl)benzene (Di-CumCl) was synthesized following the procedure reported elsewhere.[14] Ethylene oxide (EO, Linde) was condensed onto CaH_2 and stirred at 0 °C for 3 h before being transferred into glass ampules and before use it was purified with *n*-butyllithium using similar method to that described for the purification with CaH_2. *L*-

Lactide (Aldrich, 98.5 %) was purified by recrystallization from dried ethyl acetate in a dry nitrogen atmosphere and thoroughly dried for 24 h in a vacuum before use. Tin (II) 2-ethylhexanoate (Stannous octoate, $SnOct_2$, Aldrich) was used as received. ε-Caprolactone (Fluka 99 %) was dried over CaH_2 for 2 days, distilled under reduced pressure, and degassed by freeze-thaw cycles. 2-(2-Thienyl)-ethanol (Aldrich 98%) was distilled the day before use and stored at 4 °C. Silicagel 60 (Merck, 230-400 mesh) was used for column chromatography after activation by heating at 150 °C under vacuum for 2 h. THF (Merck p.a) was purified first by distillation under nitrogen from CaH_2 and then by refluxing over potassium. A solution of *n*-butyllithium (1.6 M in hexane) (*n*-BuLi) was purchased from Aldrich and its concentration was titrated by a standard method.[15] 2-methylthiophene was purchased from Aldrich and was dried over CaH_2 for 2 days, distilled under reduced pressure, and degassed by freeze-thaw cycles.

7. 2. 2. Synthesis

Synthesis of Thiophene-Ended PIB (PIB-T)

The synthesis of PIB-T was carried out under a dry nitrogen atmosphere. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask (reactor) equipped with a septum, an magnetic stirring and a nitrogen inlet were added of 240 mL CH_3Cl, 404 mL of *n*-hexane (olefin-free) and 0.355 mL (0.302 g, 1.58 mmol) of 2,6-di-*tert*-butylpyridine (D*t*BP) and then the mixture was cooled to -78 °C. 15.60 mL (11.0 g, 0.188 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring 0.6 mL (0.525 g, 3.53 mmol) of TMPCl were transferred to the reactor by a transfer needle. After 5 min of stirring, 1.5 mL (2.68 g, 0.014 mol) of $TiCl_4$ were transferred to the reactor by a transfer needle. One hour later 28.3 mL (29.74 g, 0.353 mol) of thiophene were added to the polymerization system; the color of the solution changed from slightly yellow to red. Thiophene was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude mixture was filtered in order to remove the titanium complexes. During filtration, additional *n*-hexane was added. Then, the *n*-hexane phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was redissolved in a small amount of *n*-hexane and precipitated two or three times into acetone in order to remove excess thiophene.

Synthesis of α,ω-Dithiophene-Ended PIB (T-PIB-T)

The synthesis of T-PIB-T was carried out under a dry nitrogen atmosphere in a similar manner to that described for the synthesis of PIB-T. The polymerizations were initiated with the difunctional initiator 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene (*t*BuDiCumCl) (1.28 mmol). After the polymerization of IB (5 g, 0.089 mol), the functionalization of PIB was conducted by addition of a T solution into the polymer solution. 200 equiv. of T was used for the functionalization of PIB. After 1 h, the reaction mixture was quenched with prechilled methanol and poured into methanol. The polymer was purified by the precipitation of the polymer solution into methanol, followed by drying in vacuum.

Lithiation of 2-methylthiophene (MT) and reaction with ethylene oxide (MT-OH)

Reaction of lithiated MT with ethylene oxide was carried out in a 250 mL stirred glass reactor. 200 mL of THF and 2.028 g (20.6 mmol) of MT were added and then the solution was cooled to -40 °C. After 10 min of stirring 10.71 ml (26.78 mmol) of *n*-BuLi solution were transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with MT for 120 min to form the anion (MT^-,Li^+). Chain end hydroxylation was affected by reacting the resulting MT^-, Li^+ with 5.5 g (124.8 mmol) of ethylene oxide. After 180 min of the reaction, the reaction was terminated with a mixture of methanol / acetic acid (1/5: v/v). Finally, the solvent was removed on a rotary evaporator and the product (MT-OH) was dried and purified.

Synthesis of α hydroxy-functionalized PIB (PIB-OH)

Reaction of lithiated PIB-T with ethylene oxide was carried out in a 250 mL stirred glass reactor. 200 mL of THF were added and 3.61 g (0.754 mmol) of PIB-T and then the mixture was cooled to -40 °C. After 10 min of stirring 0.6 ml (1.5 mmol) of *n*-BuLi were transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with PIB-T for 60 min to form the anion (PIB-T^-,Li^+). Chain end hydroxylation was affected by reacting the resulting PIB-T^-, Li^+ with 3.0 g (68.10 mmol) of ethylene oxide. After 24 h of the reaction, the reaction was terminated with mixture of methanol / acetic acid (1/5: v/v). Finally, the crude polymer was isolated in quantitative yield by precipitating the product into excess methanol and drying under vacuum at room temperature. The pure hydroxylated polymer was isolated by column chromatography of the crude polymer, isolating the corresponding fraction, precipitating the product into excess methanol, and drying under vacuum at room temperature.

The nonfunctionalized polymer was separated by column chromatography. For example, 3 g of polymer was chromatographed on a column of activated silicagel. *n*-Hexane and toluene were used as the eluents. The column was prepared in *n*-hexane. Once the front running polyisobutylene eluted from the column, the eluent was gradually changed to pure toluene to elute the remaining functional polymer. Quantitation of functional and nonfunctional polymer was achieved by LACCC measurements.

Synthesis of α,ω-dihydroxy-functionalized PIB (HO-PIB-OH)

The synthesis was carried out using a similar manner to that described for the synthesis of PIB-OH and the nonfunctionalized polymer was separated from PIB-T by column chromatography.

Synthesis of PLA and PεCL using 2-(2-thienyl)-ethanol

All operations except the polymerization were carried out in a glove box under nitrogen atmosphere. A representative polymerization procedure was as follows: L-Lactide (1.75 g, 12.15 mmol) and 2-(2-thienyl)ethanol (0.138 g , 1.08 mmol) were weighed into a round-bottom flask. Lactide and 2-(2-thienyl)ethanol were dissolved in THF and after few minutes of stirring, dry $SnOct_2$ (0.43 g , 1.08 mmol) was added. The mixture was stirred until initiator, monomer and catalyst were dissolved completely.

After few minutes of stirring the flask was sealed and the polymerization was started by immersing the flask in an oil bath at 120 °C for a certain time. The polymerization was stopped by cooling to room temperature and after removing the solvent, the monomer conversion was determined by ^{1}H NMR from monomer and polymer signals. Finally, the polymer was dissolved again and was precipitated into hexane and dried under vacuum at room temperature.

Synthesis of PIB-*b*-PLA and PIB-*b*-PεCL

All operations except the polymerization were carried out in glove box under nitrogen atmosphere. All copolymerizations were carried out in a similar manner to that described for the model reactions using 2-(2-thienyl)-ethanol. A representative polymerization procedure was as follows: Lactide (LA) (0.35 g, 2.60 mmol) and PIB-OH (0.2 g, 0.06 mmol) were weighed into a round-bottom flask and then were dissolved in THF. The mixture was stirred until all the macroinitiator and monomer were dissolved completely and finally dry $SnOct_2$ (0.025 g , 0.06 mmol) was added. After few minutes of stirring the flask was sealed and the polymerization was started by immersing the flask in an oil bath at 120 °C for a certain time. The polymerization was stopped by cooling to room temperature and after removing the solvent, the monomer conversion was determined by ^{1}H NMR from monomer and polymer signals. Finally, the polymer was dissolved again and was precipitated into cold methanol and dried under vacuum at room temperature.

7. 2. 3. Characterization

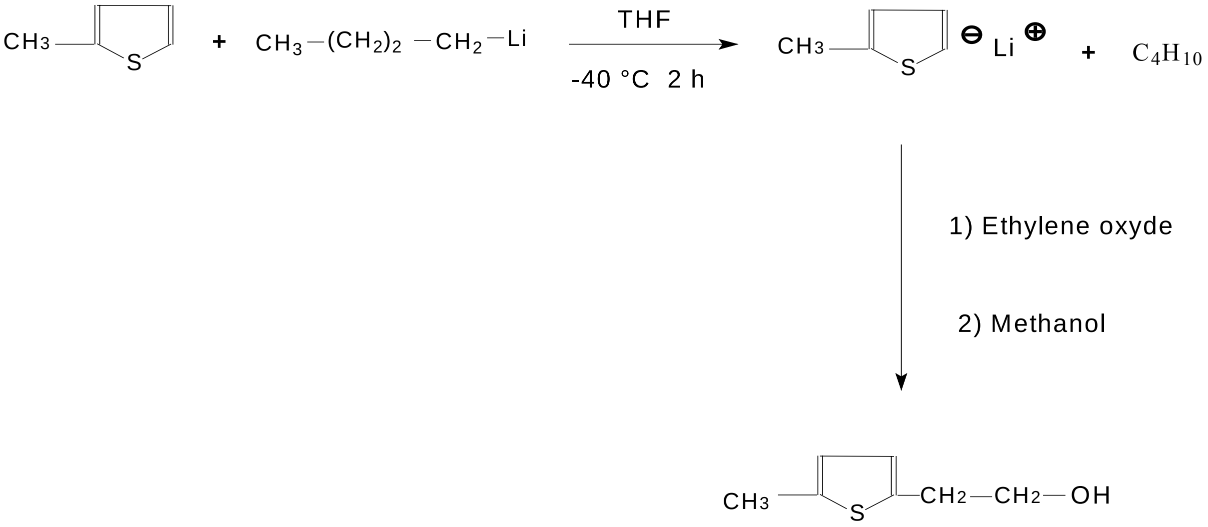
^{1}*H-NMR* spectroscopy was carried out on a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$ using TMS as internal standard. *Gas Chromatography* was carried out on a Fisions GC 8000 model equipped with flame ionization detection (FID). A DB1 methylpolysiloxane column (30 m x 0.53 mm I.D.) was used with hydrogen as carrier gas. *Size Exclusion Chromatography* (SEC, SEC) was performed using THF as eluent at a flow rate of 1 mL/min equipped with a four column set of PSS SDV gel (particle size 5µm, 10^2 - 10^5 Å) heated to 40 °C. Calibration was based on PIB and PS standards (PSS, Mainz). *Liquid Adsorption Chromatography at Critical Conditions* (LACCC) measurements were conducted on a TSP HPLC system at a flow rate of 0.5 L/min. An Evaporative Light Scattering Detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow of 3.5 L/min was used for mass detection. 10 µL of ca. 0.5 wt % polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two Reversed Phase columns (YMC, 250 x 4 mm) with 5 µm average particle size, 100 Å and 300 Å pore diameter were used. The critical solvent composition for PIB is THF:methanol = 80.5:19.5. Premixing of the mobile phase by weight is necessary for a constant and exact composition. *MALDI-TOF Mass Spectroscopy* (MALDI-TOf MS) was performed on a Bruker Reflex III with a UV laser operating at 337 nm and an accelerating voltage of 23 kV. Dithranol was used as matrix and silver triflate as cationizing agent.

7. 3. Results and Discussion

7. 3. 1. Hydroxy-functionalized PIB (PIB-OH)

Model experiments with MT

Orienting model experiments were carried out with MT which mimics the end group structure of PIB-T. These reactions were carried out in order to optimize the reaction of end-capping of PIB-T$^-$, Li$^+$ with ethylene oxide. The lithiation of MT was performed at -40 °C, using an excess of *n*-BuLi (Scheme 7. 1.). Prior to the lithiation, a sample was taken to determine the exact concentration of MT from gas chromatography (GC) and NMR spectroscopy. After 120 minutes of reaction ethylene oxide was added to part of the reaction solution. After 180 min of the reaction at room temperature, the remaining reaction mixture was quenched.



Scheme 7. 1. Synthesis of 2-(ethanol)-5-methylthiophene.

The reaction products were characterized by GC and NMR spectroscopy. Figure 7. 1. shows the ^{1}H NMR spectrum of the resulting product. This spectrum indicates formation of 2-(ethanol)-5-methylthiophene (MT-OH). Quantitative addition was indicated by the disappearance of the peaks at 7.10, 6.90 and 6.80 ppm. A new set of peaks at 6.65, 6.59, 3.80 and 2.99 ppm appeared due to the presence of the terminal hydroxyethyl group (-CH_2CH_2OH).

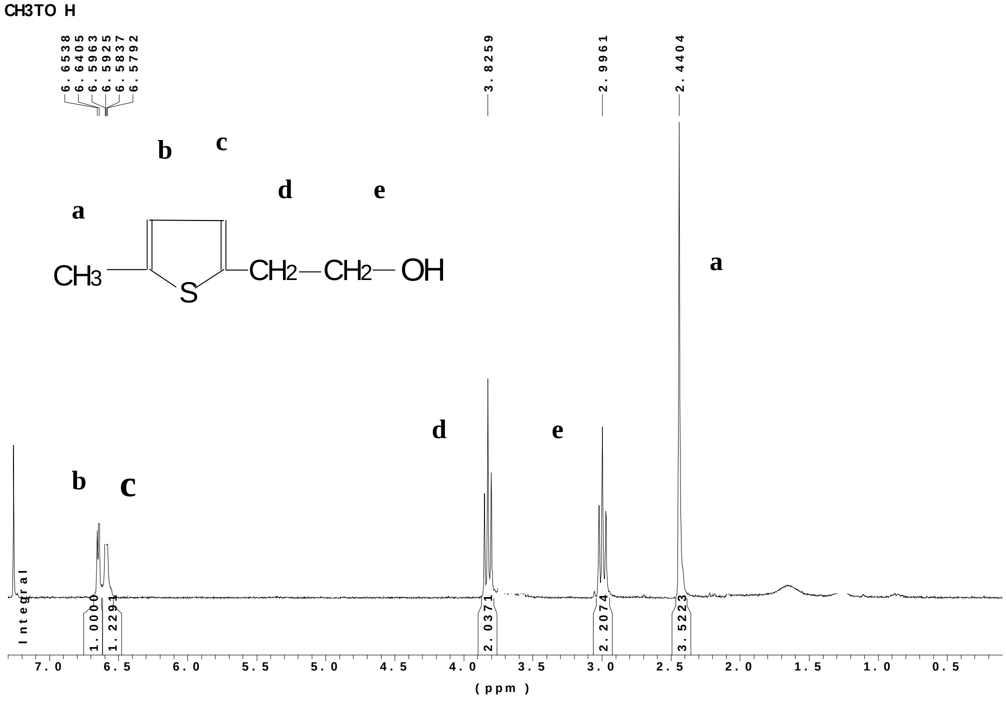
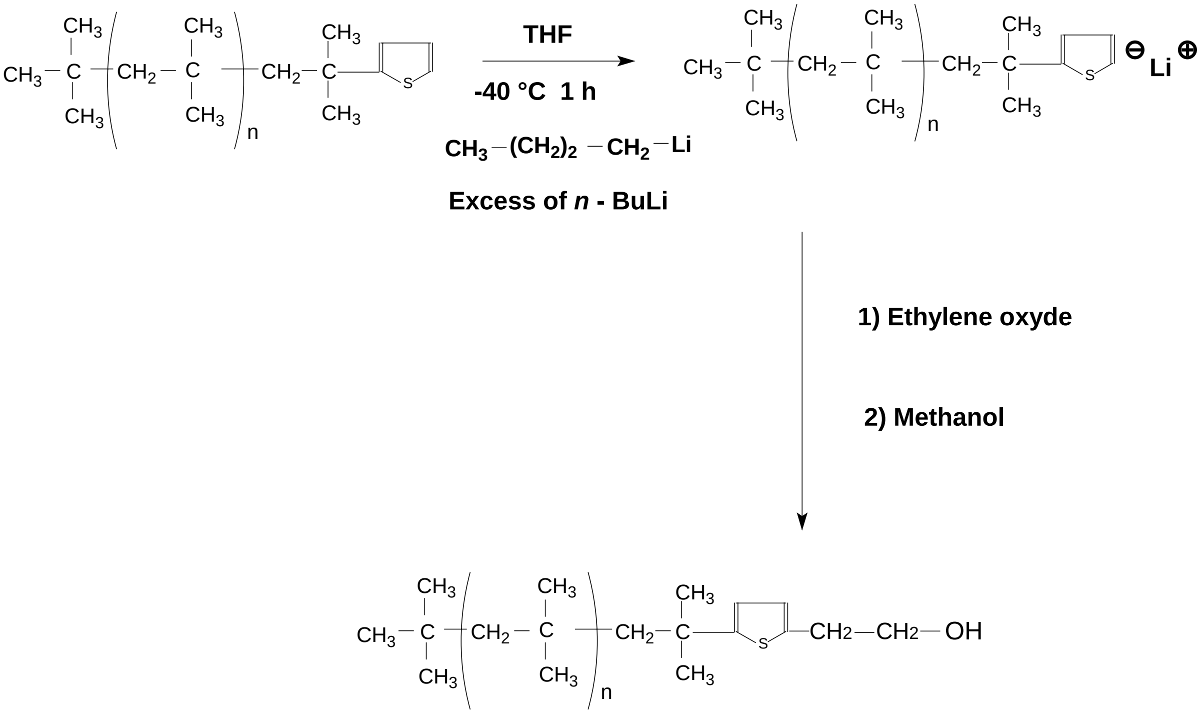


Figure 7. 1. ^{1}H NMR spectrum of 2-(ethanol)-5-methylthiophene

The conversion of this reaction was determined by GC using decane as an internal standard. During the progress of the reaction several samples were taken. Thus the results of the model experiments indicated that the end capping with ethylene oxide of the precursor (PIB-T) should be carried out and showed high yields (97.5 %) in the formation of 2-(ethanol)-5-methylthiophene. Thus the results of the model experiments indicated that the functionalization of the precursor (PIB-T) should be carried out using *n*-BuLi and then ethylene oxide.

Synthesis of ω-hydroxy-PIB (PIB-OH)

It was of interest to determine whether the end-functionalization results obtained with the model compounds could be applied to the synthesis of hydroxy-thiophene ended PIB. The synthesis was carried out in an analogous way to the synthesis of MT-OH. Ethylene oxide end-quenching of living PIB-T$^-$, Li$^+$ chain ends took place according to scheme 7. 2.



Scheme7. 2. Synthesis of hydroxy-thiophene ended PIB.

An efficient approach to determine the OH-functionality of the product is chromatographic separation using Liquid Chromatography at Critical Conditions (LACCC). LACCC has been successfully used for the separation with respect to functional groups, since it is only sensitive to end groups or comonomers of different polarity, but not to the molecular weight of the polymer under consideration.[16-18] Figures 7. 2. and 7. 3. shows the LACCC chromatograms of the PIB-OH at critical conditions of PIB before purification by column chromatography. In line with the results of the model experiments with TMP-T carried out, it is veried that the hydroxyl end-functionalization of PIB is possible.

Although, the results of the model experiments showed high conversion in the formation of 2-(2-ethanol)-5-methylthiophene, it was not the same case in the functionalization of polyisobutylene under the same conditions. It is obvious from the LACCC analyses that significant amounts of unfunctionalized PIB were obtained even at low molecular weight, the highest functionality obtained was 63 % (Table 7. 1.). Complex reaction pathways are occurring during the functionalization of PIB-T with ethylene oxide and more analysis is necessary in order to understand very well the functionalization.

PIB-T		$[PIBT]_o$	$[n\text{-BuLi}]_o$	$[EO]_o$	Temp.	Time	
Sample	Mn x 10^{-3}	mmol	mmol	mmol	C	h	f [a]
PIBTOH5	3.23	0.642	3.84	30	0	12	0.37
PIBTOH6	4.27	0.320	0.82	10	15	12	0.52
PIBTOH7	4.78	0.235	0.470	10	30	12	0.63
PIBTOH8	4.78	0.189	0.567	10	45	12	0.63

[a] OH functionality, determined by LACCC

Table 7. 1. Ethylene oxide quenching of living PIB-T^-, Li^+ chain ends

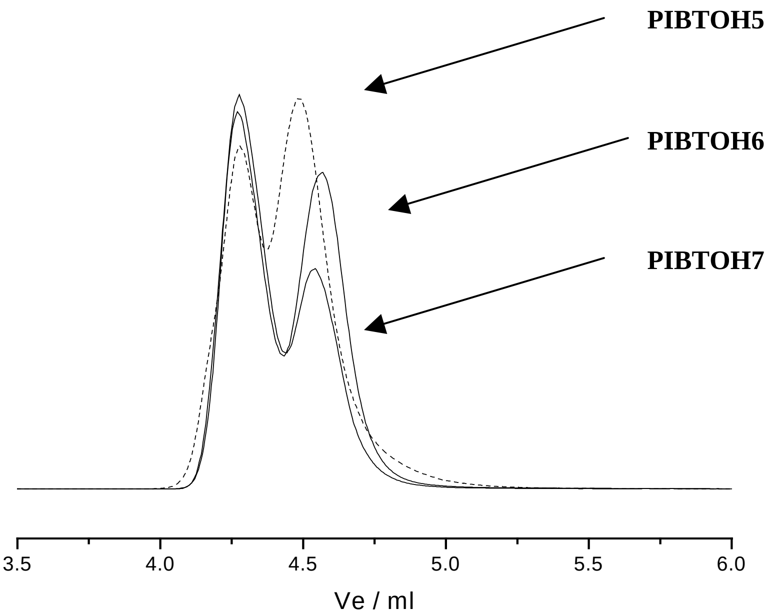


Figure 7. 2. LACCC chromatograms of PIB-T-OH at critical conditions of PIB (ELSD signal)

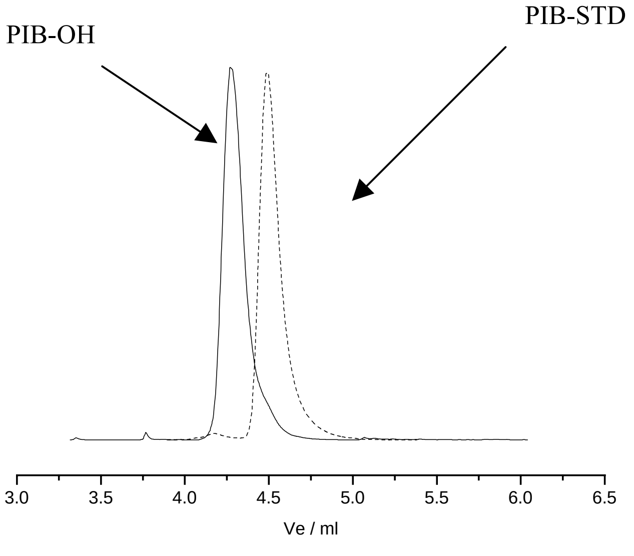


Figure 7. 3. LACCC chromatograms of PIB-T-OH after purification at critical conditions of PIB (ELSD signal)

Using the same experimental conditions, telechelic HO-PIB-OH was analyzed, see Figure 7. 4. The sample consists of predominantly α, ω-di-hydroxy-PIB, but a shoulder of the monofunctional PIB-OH is observed.

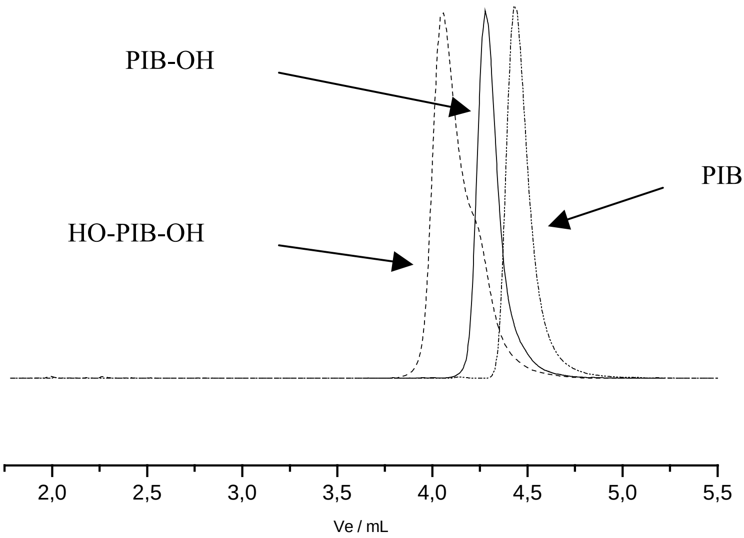


Figure 7. 4. LACCC chromatograms of HO-PIB-OH at critical conditions of PIB (ELSD signal) after purification.

Figure 7. 5. shows the ^{1}H NMR spectrum of PIB-OH after purification. This spectrum indicates end-functionalization and formation of hydroxy-functionalized PIB by this process. This confirms results obtained with the corresponding model compound, although the functionalization was not quantitative. The end-functionalization of PIB is indicated by the disappearance of the peaks at 7.09, 6.88 and 6.80 ppm. A new set of peaks at 6.64, 6.62, 3.75 and 2.94 ppm appeared due to the presence of the hydroxyethyl group ($-CH_2CH_2OH$) at the chain end. The degree of OH functionalization is of course crucial to the interpretation of the structure-property relationship of the polymer formed.

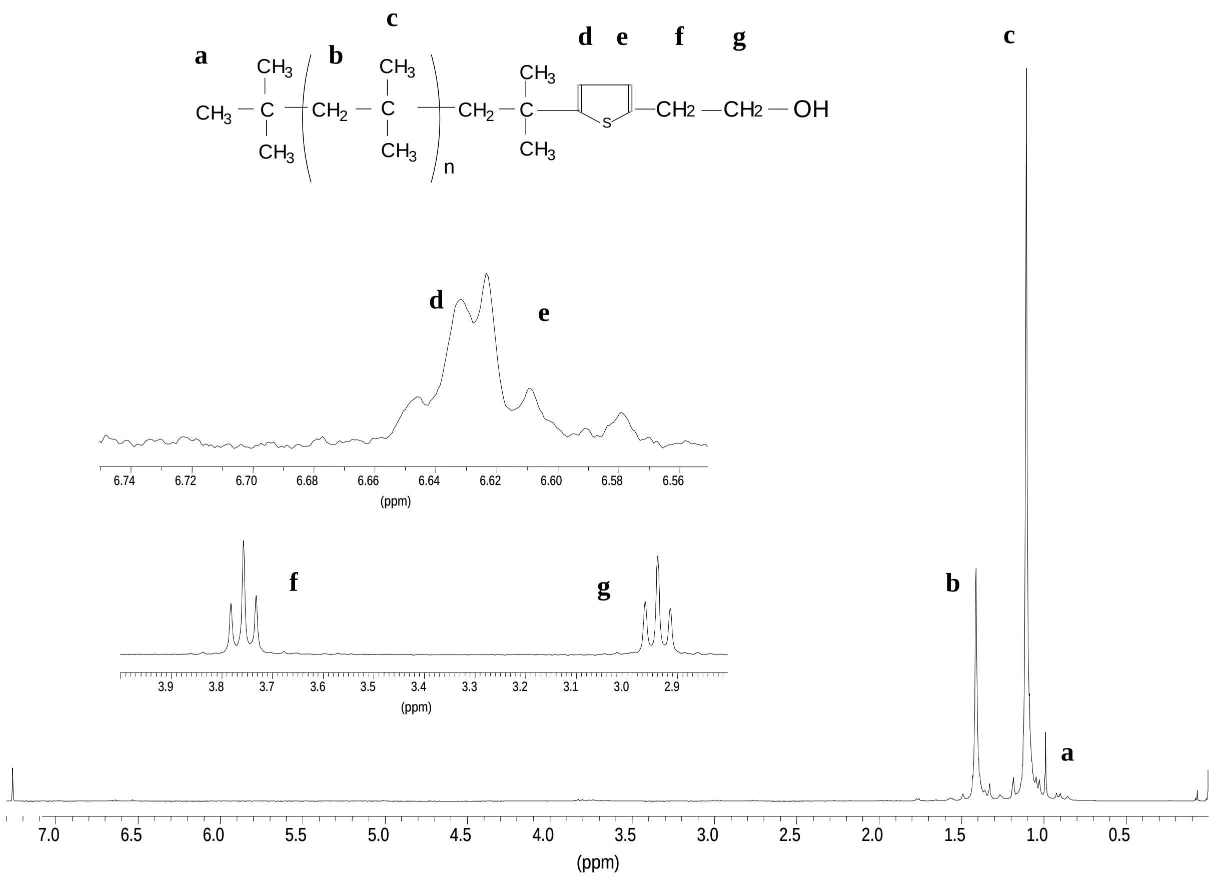
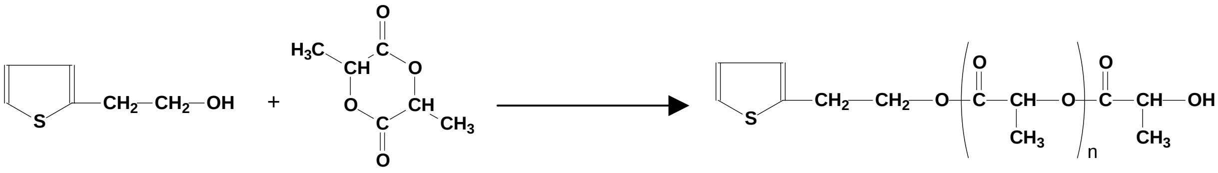


Figure 7. 5. ^{1}H NMR spectrum of hydroxy-thiophene ended PIB.

7. 3. 2. Synthesis of PIB-*b*-PLA and PIB-*b*-PεCL

Model polymerizations with 2-(2-thienyl)-ethanol (T-OH)

Before using the PIB-OH macroinitiator for L-lactide (LA) and ε-aprolactone (εCL) polymerization, orienting model experiments were carried out with anhydrous 2-(2-thienyl)-ethanol (T-OH) to provide homo-PLA and homo-PεCL. Significant control in the synthesis of PLA and PεCL has been demonstrated using aluminium and lanthanide based initiators,[19] most ROPs of lactides and εCL are carried out in the presence of tin compounds, in particular stannous octoate ($SnOct_2$).[1] $SnOct_2$ is commercially available, easy to handle and shows minimal complexation in solution. It acts as a catalyst and must be combined with alcohols to form stannous alcoholates, the actual species initiating polymerization. The synthetic route for the preparation of PLA and PεCL using T-OH and $SnOct_2$ is outlined in Scheme 7. 3. Since the initiator efficiency has been shown to be limited in the bulk polymerization of lactones and lactides,[20] the polymerization of LA and ε-CLCL were carried out using THF as solvent.



Scheme 7. 3. Synthetic route for the preparation of PLA

To determine whether T-OH had been incorporated in the polymers, the crude polymers were characterized by ^1H NMR. Figure 6 shows the ^1H NMR of the PLA obtained using T-OH as initiator. The ratio of the signals of the terminal methylene protons (a, 4.35 ppm) and the protons of the thiophene end-group (h, 7.17, g, 6.93, and f, 6.85 ppm) is 1:3. This shows that the ring opening polymerization is initiated by T-OH. Also the methyl and methylene proton signals of T-OH at 1.20 and 3.60 ppm respectively, were absent. This demonstrates that the T-OH present in the reaction mixture had quantitatively reacted with LA.

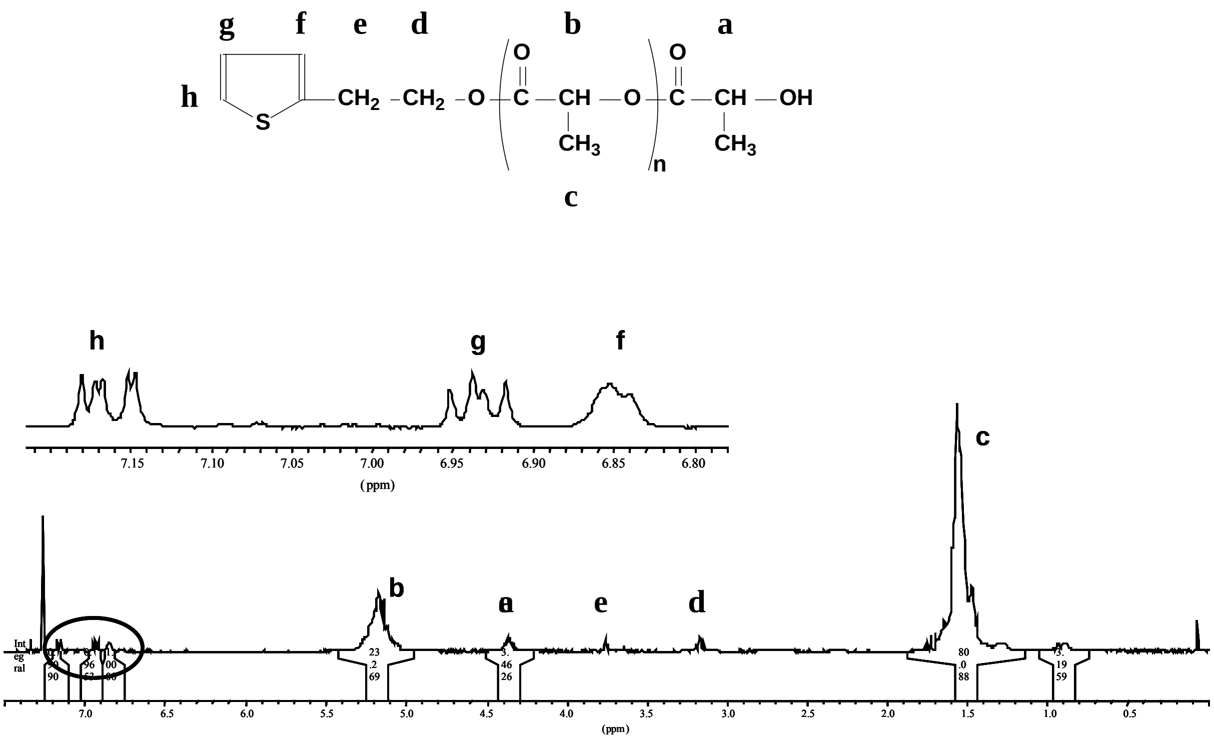


Figure 7. 6. ^{1}H NMR spectrum of PLA obtained using T-OH as initiator.

The results of the homopolymerizations of LA and εCL are compiled in the Table 7. 2. It it seen that the efficiency of T-OH is high and leads to acceptable molecular weight distributions. The M_n obtained from NMR is consistent with the theoretical value. Figure 7. 7. shows the ^{1}H NMR spectra of the PεCL obtained using T-OH as initiator. Also the methyl and methylene proton signals of T-OH at 1.20 and 3.60 ppm respectively, are absent. This demonstrates that the T-OH present in the reaction mixture had quantitatively initiated εCL.

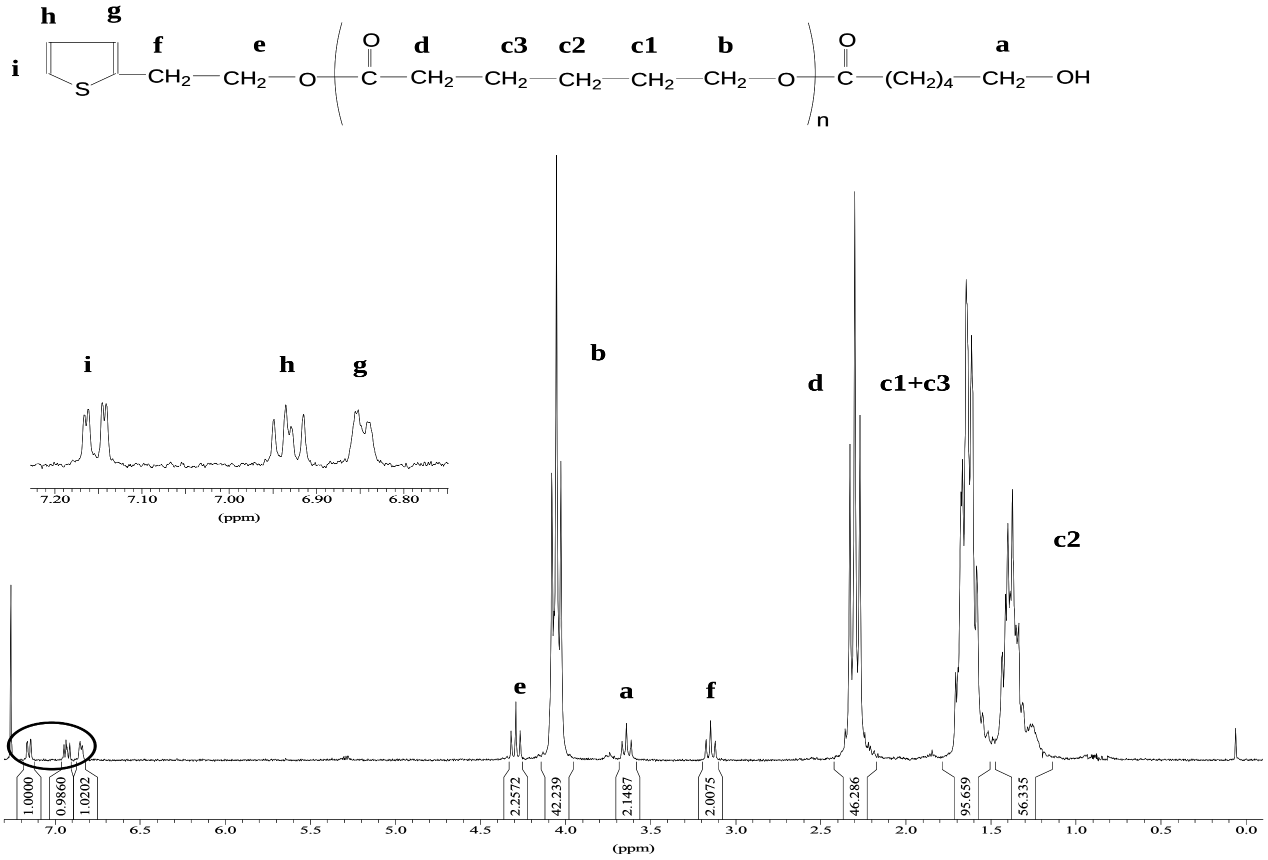


Figure7. 7. ^{1}H NMR spectrum of P εCL obtained using T-OH as initiator

Polymer	$[M]_0$ mmol	$[I]_0$ mmol	10^{-3} $M_{n,theo}$ [a] (g/mol)	10^{-3} $M_{n,SEC}$ [b] (g/mol)	10^{-3} $M_{n,NMR}$ (g/mol)	M_w/M_n	Conversion[c] (%)	f [d]
PLA	12.15	1.07	1.54	1.30	1.67	1.4	0.94	0.92
PεCL	14.27	1.17	1.28	1.89	1.32	1.3	0.92	0.96

9

[a] $[M]_0 \times M_{LA} \times \text{conversion}/[I]_0$

[b] determined with linear PS standards

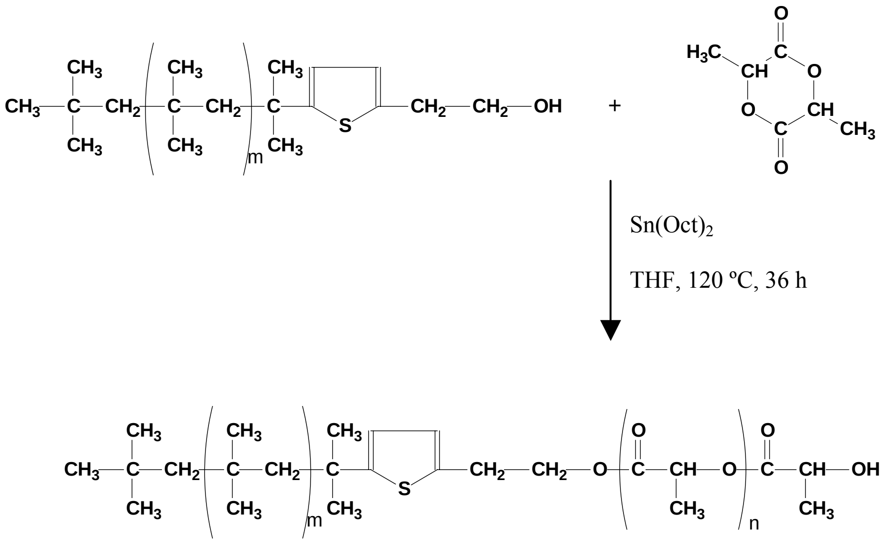
[c] determined by ^{1}H NMR from monomer and polymer signals

[d] initiator efficiency, $f = M_{n,theo}/M_{n,NMR}$

Table 7. 2. Results of LA and εCL polymerizations using T-OH as the initiator

Synthesis of PIB-*b*-PLA

The synthesis of PIB-*b*-PLA was accomplished by using hydroxy end-capped PIB as an macroinitiator of LA polymerization in THF in the presence of $SnOct_2$ (Scheme 7. 4.). In the first experiment a PIB-OH was used for the polymerization of L-LA, in the second one a telechelic HO-PIB-OH was used.



Scheme 7. 4. Synthesis of PIB-*b*-PLA

The complete characterization of block copolymers, i.e., the measurement of molar mass distribution in combination with the chemical distribution of the components of the desired architecture (diblock, triblock, multiblock), is necessary for optimization of synthesis methods. Thus, the resulting polymers were first investigated by SEC. Figure 7. 8. shows the SEC eluograms (RI signal) for this diblock copolymer. The results are collected in Table 7. 3. Due to the rather broad peak of the copolymer, SEC does not allow to determine the presence or absence of unreacted precursor.

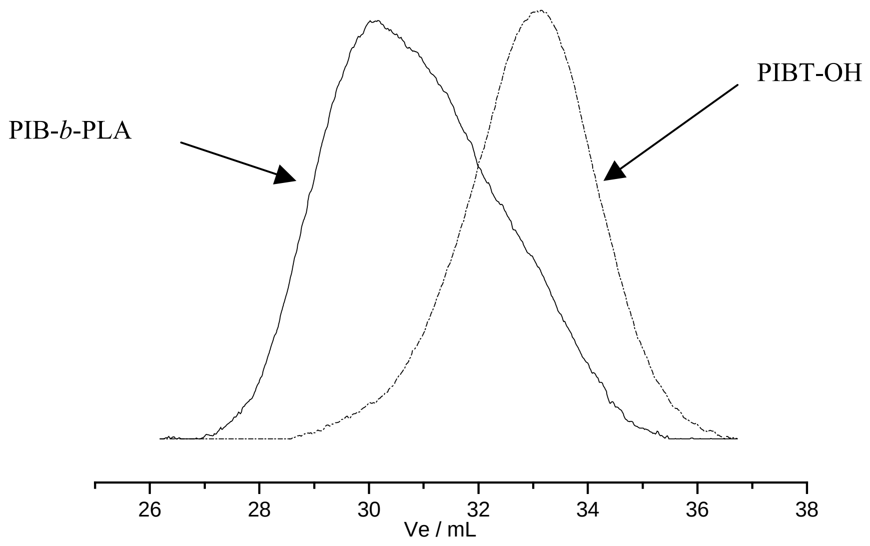


Figure 7. 8. SEC eluograms (RI signal) of the PIB-*b*-PL-LA.

Polymer	10^{-3} $M_{n,SEC}$ (PIB)	10^{-3} $M_{n,th}$[a]	conv (%)	10^{-3} $M_{n,SEC}$[b] (block)	M_w/M_n (block)	10^{-3} $M_{n,NMR}$ (block)	f_{block} (NMR) (Mn[c])	f_{block} (LACCC) (area[d])
PIB-PLA	3.36	5.54	0.95	9.45	1.3	9.51	0.90	0.96
PLA-PIB-PLA	4.73	5.2	0.96	10.6	1.3	12.1	0.93	0.90
PIB-PεCL	3.19	13.2	0.80	17.8	1.3	19.5	0.98	1.0

[a] expected molecular weight of PLA block, [b] SEC molecular weights of block copolymers were determined with PIB standards and represent apparent values only., [c] blocking efficiency, $f_{block} = M_{n,NMR;PLA}/M_{n,th}$, [d] as determined by LACCC with UV detector (245 nm).

Table 7. 3. Characterization of blockpolymers of PIB with PLA and PεCL

LACCC at critical conditions of PIB allows a separation according to the number and nature of functional groups, in this case comonomers.[21] Thus, LACCC is more sensitive for a quantitative determination of the precursor content than SEC. Figure 7. 9. shows the LACCC chromatograms of PIB-*b*-PLA at critical conditions of PIB. These results clearly show blocking efficiency and the formation of the desired PIB-*b*-PLA block copolymer. However, the analysis of LACCC reveals the presence a small fraction, which eluates at retention times between 3.5 and 4 minutes. For more detailed insight about the nature of this fraction, the sample was fractionated by SEC and each fraction analyzed by MALDI-TOF mass spectrometry. The results are shown in Figure 7. 10.

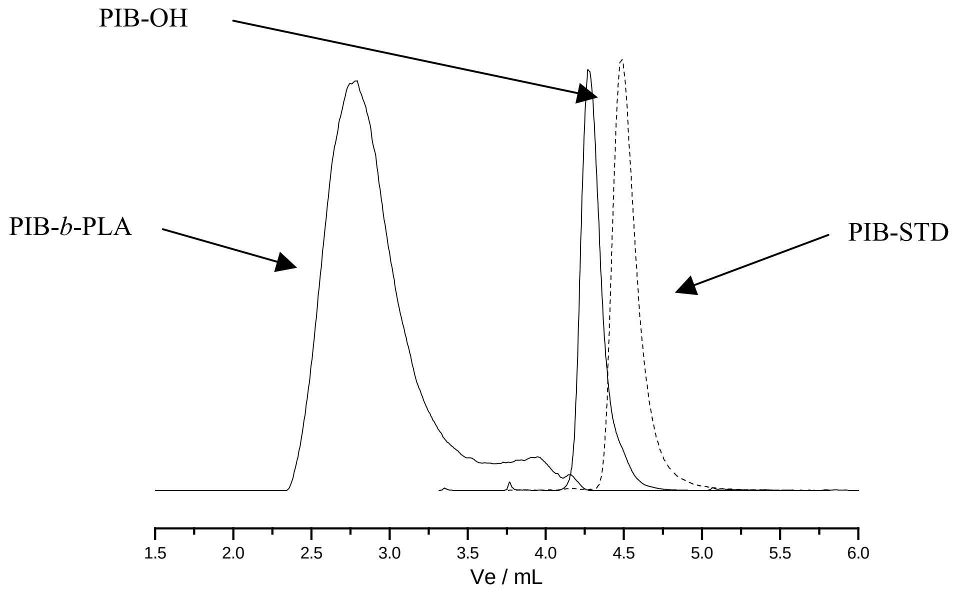


Figure 7. 9. LACCC chromatograms of PIB-*b*-PLA at critical conditions of PIB.

The mass spectra of fractions show that the low molecular weight peak series can be identified as cyclic PLA and linear PLA, while the peak series at higher molar mass belongs to PIB-b-PLA diblock. In agreement with SEC/ MALDI-TOF results the PIB-b-PLA diblock is contamined with cyclic and linear PLA formed at high conversion of the monomer as a result of intra- and intermolecular transesterification.[29]

Figure 7. 11 shows that triblock copolymers can be also separate using the same critical conditions. The peak at 4.2 mL appears to be residual precursor with one OH function.

Figure 7. 10. GPC/ MALDI-TOF of the PIB-b-PLA

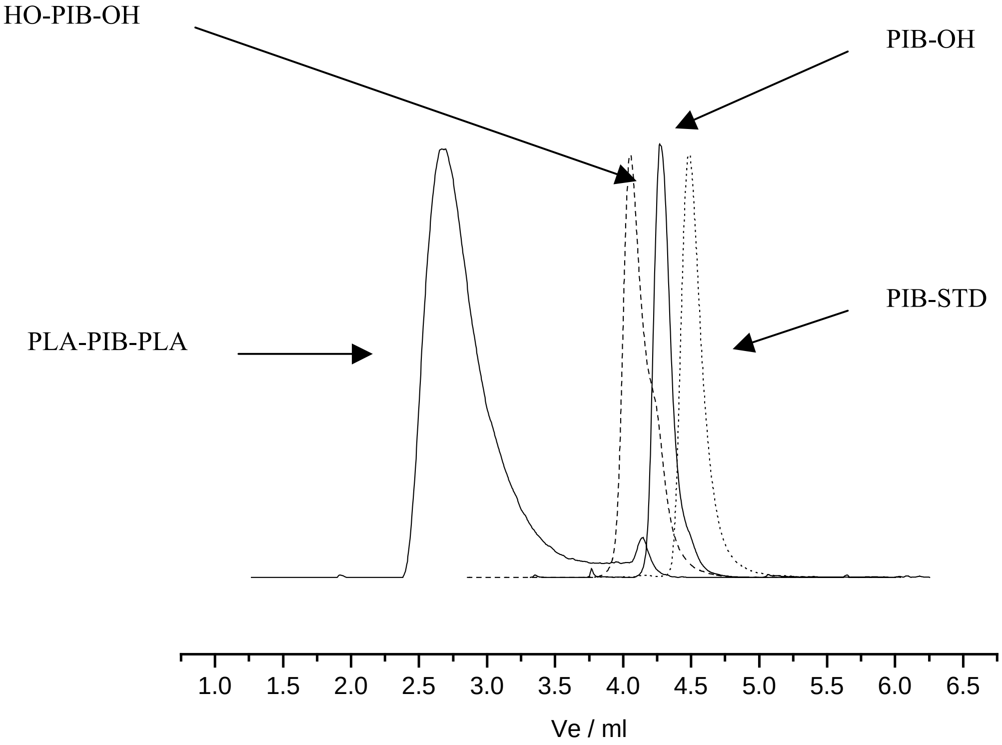


Figure 7. 11. LACCC chromatograms of PLA-*b*-PIB-*b*-PLA at critical conditions of PIB

The formation of the diblock copolymer PIB-b-PLA was also verified by its ^{1}H NMR spectrum shown in Figure 7. 12

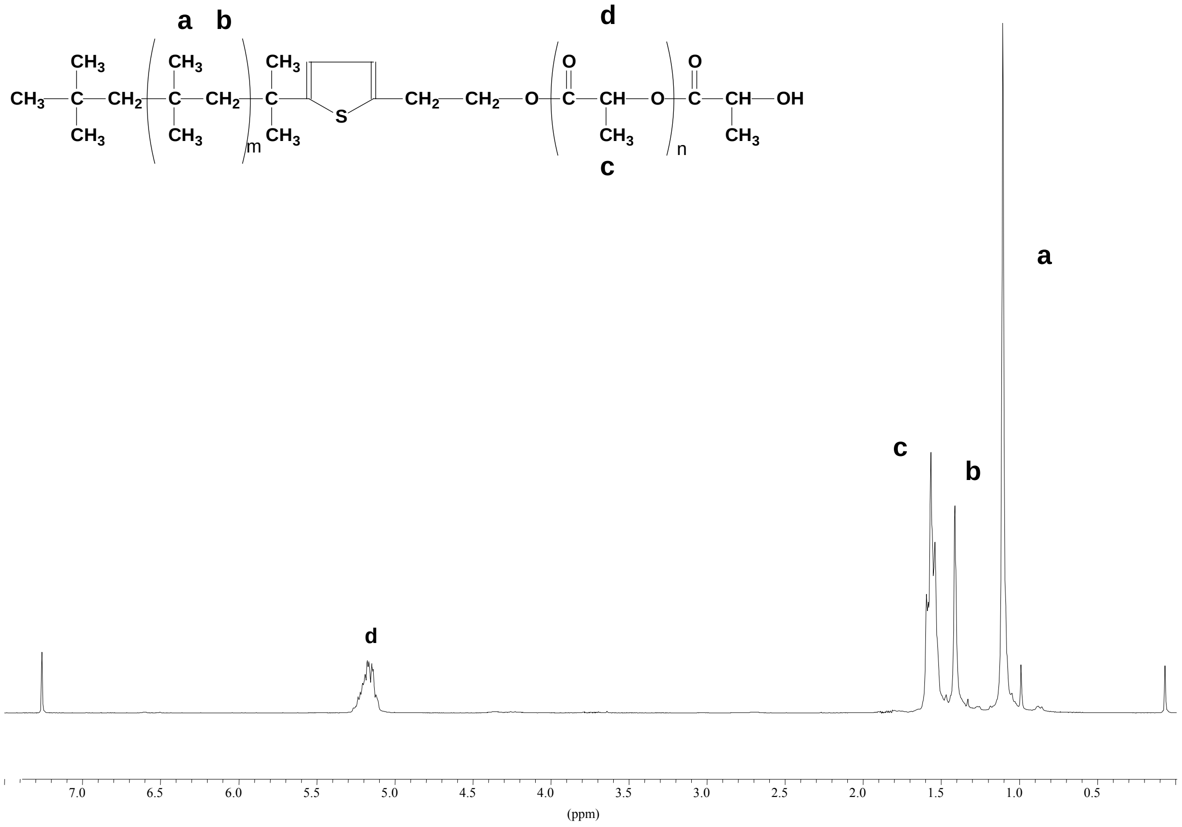


Figure 7. 12. ^{1}H NMR spectrum of the block copolymer PIB-*b*-PLA

Synthesis of PIB-*b*-PεCL

The synthesis of PIB-*b*-PεCL was accomplished by using a similar procedure to that described for the synthesis of PIB-*b*-PLA, however, by limiting the monomer conversion in order to avoid transesterification. In these polymerizations the products were virtually free of unreacted PIB-OH. The SEC trace shown in figure 7. 13. of the resulting diblock copolymer exhibits a monomodal distribution. The results are collected in Table 7. 3.

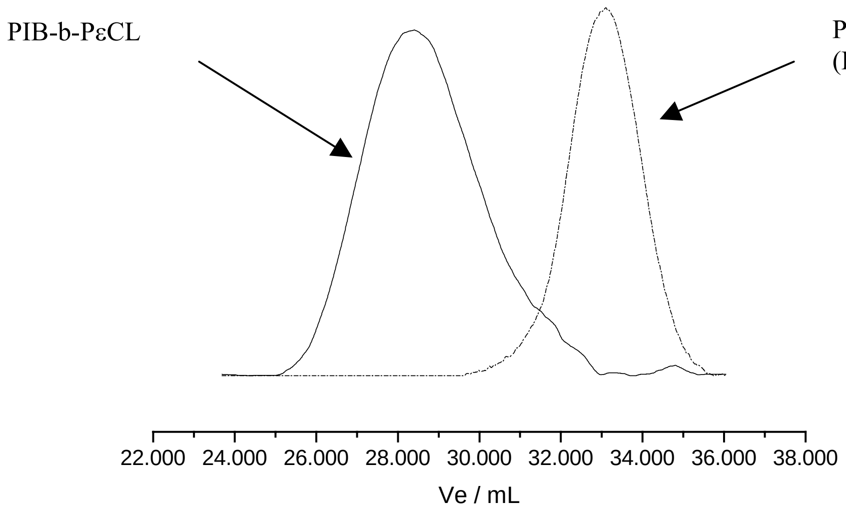


Figure 7. 13. SEC eluograms of the PIB-*b*-PεCL copolymer

The LACCC separation of the diblock copolymer under critical conditions for PIB is shown in Fig. 7. 14. The diblock copolymer and PIB-OH precursor give separate peaks which can be quantified. This suggests that the site transformation technique yields block copolymers with high structural integrity. It is noteworthy that LACCC shows the polymer free of contaminants, indicating that this side reaction can be minimized by limiting the monomer conversion.

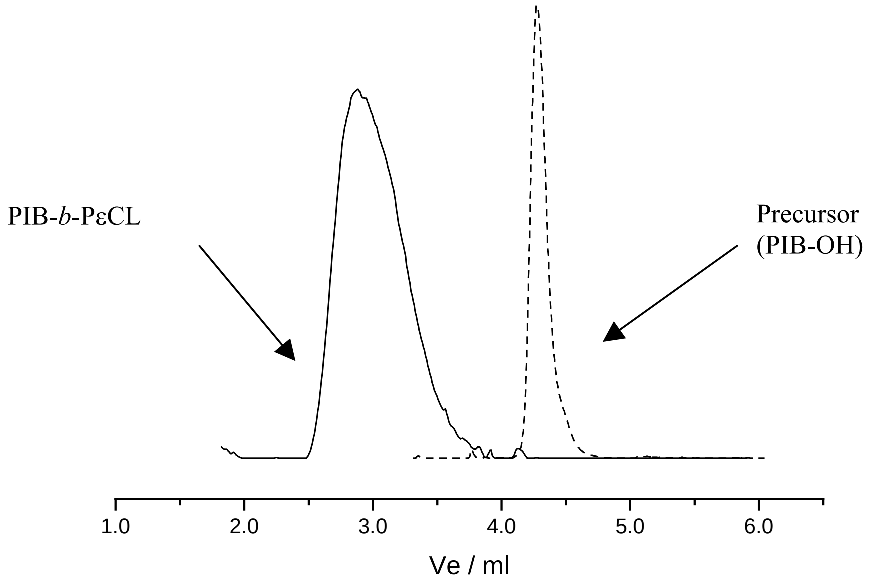


Figure 7. 14. LACCC chromatogram of PIB-*b*-PεCL at critical conditions of PIB

The ^{13}C NMR spectrum of PIB-*b*-PεCL is shown in Figure 7. 15. In addition to the characteristic peaks of PIB, a new set of signals appeared due to the presence of the PεCL block.

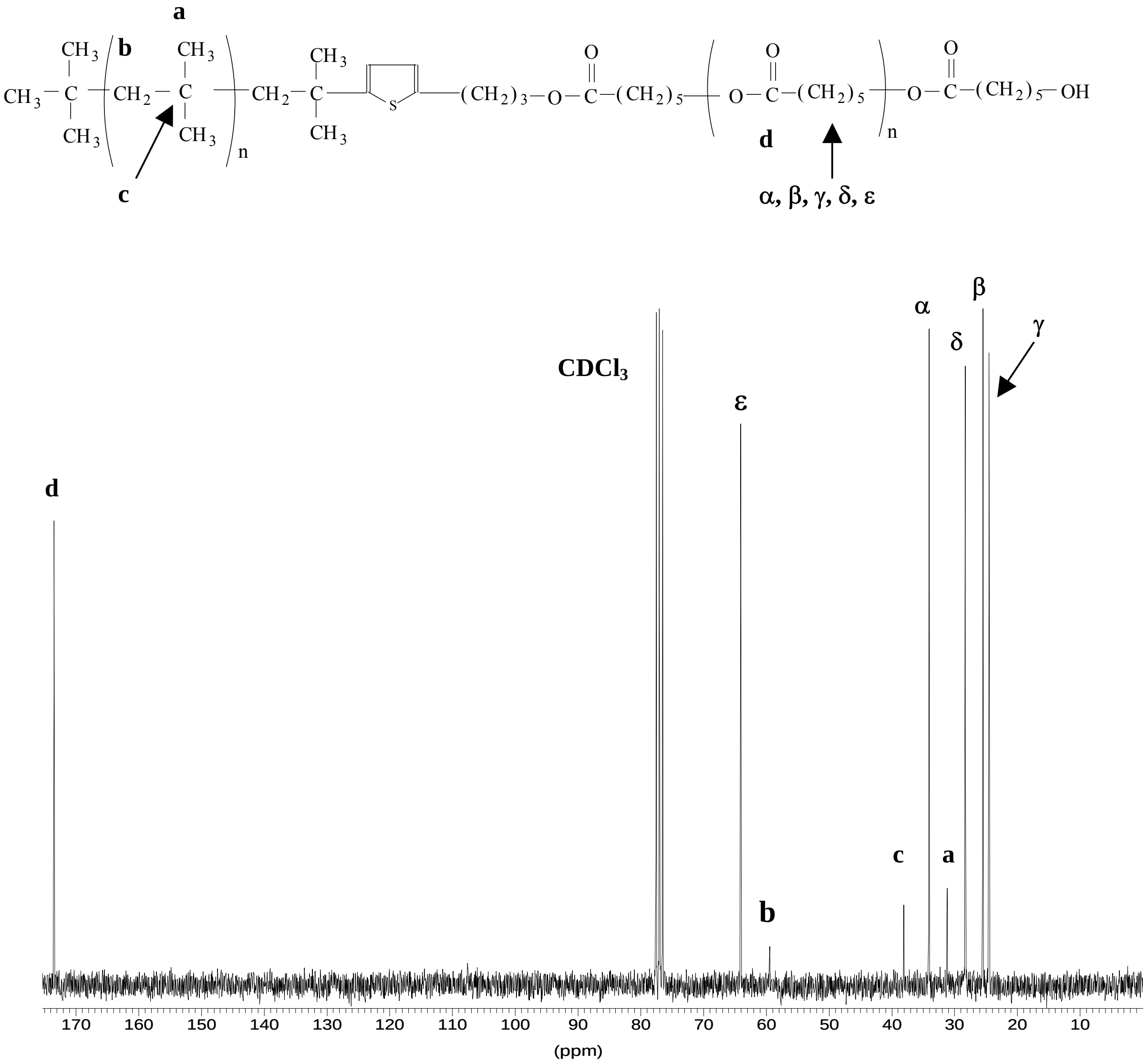


Figure 7. 15. ^{13}C NMR spectrum of PIB-*b*-PεCL.

7. 4. Conclusions

The monoaddition of ethylene oxide to lithiated PIB-T is demonstrated as a new pathway for the synthesis of hydroxy-functional polyisobutylene (PIB-OH). The degree of functionalization still has to be optimized. However, this is a useful alternative to the tedious procedures used in the literature so far. PIB-OH is a quantitative macroinitiator for the ring opening polymerization of various heterocyclic monomers. Combination of LACCC, SEC and MALDI-TOF MS are convenient methods to obtain more information about the side reactions during the process of polymerization. The resulting products are potential new biodegradable thermoplastic elastomers.

Summary

A new synthetic route for the synthesis of hydroxy-functionalized Polyisobutylene (PIB-OH) and PIB-polyester block copolymers was developed by combining living carbocationic and anionic ring-opening polymerizations. First thiophene end-capped polyisobutylene (PIB-T) was prepared by monoaddition of thiophene to living PIB chains by cationic polymerization catalyzed by $TiCl_4$ in *n*-hexane/CH_2Cl_2 60/40 v/v at –78 °C. Hydroxy-functionalized polyisobutylene (PIB-OH) was obtained by the lithiation of the resulting PIB-T with *n*-BuLi in THF at –40 °C. End-capping with ethylene oxide of $PIB\text{-}T^-,Li^+$ leads to PIB-OH. The resulting PIB-OH was successfully used as a macroinitiator for the ring-opening polymerizations of L-lactide and ε-caprolactone catalyzed by stannous octoate. Characterization of these block copolymers and hydroxy-functionalized polyisobutylene was carried out by Size Exclusion, Liquid Adsorption Chromatography at Critical Conditions, NMR spectroscopy, and MALDI-TOF mass spectrometry.

7. 5. References

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8. Synthesis and Characterization of Terthiophene End-Capped Polyisobutylene and Polythiophene-graft-Polyisobutylene

8. 1. Introduction

Conjugated polymers (polyacetylene, polyaniline, polyphenylene, polypyrrole, polythiophene, polyfluorene, etc.) and oligomers have raised great interest because of their potential electronic applications including light emitting diode (LED) technology, electrochromic materials and sensors[1,2]. Among this class of conductive polymers with π-conjugated electronic structures, polythiophene has been widely studied because of its high magnetic and optical properties, electrical conductivity and environmental stability (both to oxygen and to moisture). Processability, corrosion resistance, and availability of inexpensive starting materials make these polymeric materials important synthetic targets[2]. In particular, polymers obtained from the oxidative polymerization of thiophenes, bithiophenes, and terthiophenes[3] have been intensely studied because of the highly conjugated nature of the resulting materials. Polythiophenes are readily synthesized either by simple chemical oxidation or via electrochemical methods[1] and have been used in the development of electronic devices, energy storage batteries, photochromic devices, sensors, nonlinear optical devices, and in the modification of electrodes. Numerous substituted thiophenes have been reported, ranging from those which make the resulting polymers water soluble and self-doped to those containing transition metals which interact with either the substituents on the polymer backbone or the propagating thienyl units. For a polymer to conduct, it must have a conjugated π system along the backbone, but this adds rigidity to the polymer, which makes processing extremely difficult. These deficient properties, such as poor mechanical properties and processability have considerably limited the common use of conducting polymers. One way to improve the processability of a polymer such as polythiophene is to incorporate processable segments such as polystyrene[4,5], polymethacrylate[6,7], polyacrylate[8] and polydimethylsiloxane[9]. These segments will directly affect the properties of polythiophene. Removal of the segments can leave insoluble polythiophene with a high conductivity. We will use polyisobutylene because of its interesting properties. It is an extremely hydrophobic polymer and it combines a very low Tg with high chemical stability. One disadvantage is that polyisobutylene can only be synthesized by cationic polymerization.

The well-documented fact that not all monomers can be polymerized by every available polymerization mechanism limits the possible combinations of monomers that can be employed in a block copolymers chain. However, synthetic schemes have been devised that allow the polymerization mechanism to be changed appropriately in order to suit the monomers that are going to be incorporated in the same macromolecule. These polymerization processes widen considerably the variety of block copolymers that can be produced.

Active center transformation reactions usually involve the efficient end-functionalization of a polymer chain that is going to comprise one of the blocks of the final copolymer. This concept can be also described as the use of a suitable macromolecular initiator for the polymerization of the second monomer. Transformation of one chain-end followed by the polymerization of the second monomer produces a diblock copolymer, whereas the transformation of both ends of a linear polymer chain results in the formation of an ABA triblock copolymer. Transformation reactions must be

100 % efficient because any unfunctionalized macromolecular chains will not initiate the polymerization of the second monomer and will be present in the final product as a homopolymer impurity. The preparation of well-defined block copolymers requires that every individual step, including the separate polymerization reactions, must be highly efficient and finely controlled. It is obvious that these synthetic strategies involve special care in the design and the application of the chosen synthetic methodology.

In previous chapters, we have described how to obtain some block copolymers comprising a block of polyisobutylene and a polar polymer, i.e. (poly(tert-butyl methacrylate)[10], poly(L-lactide), poly(ε-caprolactone), poly(N,N-dimethylacrylamide)[11]. To that end, thiophene end-capped PIBs were prepared by the capping reaction of living PIB with thiophene. The thiophene-capped PIB was lithiated and then used as a macroinitiator for the polymerization of the second block.

In the course of our continuing investigations into polyisobutylene (PIB)-based block copolymers, we were interested in the introduction of more than one unit of thiophene. In this objective, we report the synthesis and the characterization of terthiophene end-capped PIB (PIB-TT) and polyisobutylene-block-polythiophene (PIB-b-PT). Polyisobutylene was synthesized by cationic polymerization followed by a functionalization with 2-bromothiophene (TBr) or terthiophene (TT). The PIB-TBr was further transformed in order to obtain a polyisobutylene having at one extremity a thiophene unit which has the positions 2 and 5 free, allowing the polymerization of thiophene by oxidative polymerization.

8. 2. Experimental

8. 2. 1. Materials

2,6-Di-*tert*-butylpyridine (D*t*BP, Aldrich, 97%) was purified by distillation from CaH_2. Isobutylene (IB, BASF) was passed through in-line gas purifier columns packed with $CaSO_4$ and no. 13 molecular sieves and condensed at -15 °C prior to polymerization. CH_2Cl_2 was purified by washing it with 10% aqueous NaOH and then with distilled water until neutral and dried over anhydrous $MgSO_4$ overnight. It was refluxed for 24 h and distilled from CaH_2, just before use. n-Hexane was rendered olefin free by refluxing it over concentrated sulfuric acid for 48 h. It was washed with 10% aqueous NaOH and then with deionized water until neutral and stored over $MgSO_4$ for 24 h. It was refluxed over CaH_2 overnight and distilled. Titanium (IV) chloride ($TiCl_4$, Aldrich, 99.9%) was used as received. Thiophene (T, Aldrich, 99%) was distilled the day before use and stored at 4 °C. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared by hydrochlorination of 2,4,4-trimethyl-1-pentene (Fluka, 98 %) with hydrogen chloride gas in dry dichloromethane at 0 °C[12]. The product was dried over $CaCl_2$ and distilled under reduced pressure before use. THF (Merck p.a) was purified first by distillation under nitrogen from CaH_2 and then by refluxing over potassium. Chloroform was distilled over CaH_2, $FeCl_3$ was purchased from ACROS, Terthiophene, Tributyltin chloride, 3-Bromothiophene, Thiophene-3-boronic acid, Tetrakis(triphenylphosphine)palladium and Bis (triphenylphosphine) palladium (II) dichloride were used as received from Aldrich. 2-Methylthiophene and 2-Bromothiophene were purchased from Aldrich and distilled from CaH_2. A solution on *n*-butyllithium (1.6 M in hexane) was purchased from Aldrich and its concentration was titrated by a standard method.

8. 2. 2. Synthesis

Synthesis of Thiophene-Ended PIB (PIB-T)

The synthesis of PIB-T was carried out under a dry nitrogen atmosphere. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added of 120 mL of CH_2Cl_2, 202 mL of n-hexane, and 0.170 mL (0.144 g, 0.75 mmol) of D*t*BP and then the mixture was cooled to -78 °C. 30 mL (18.0 g, 0.32 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring 0.769 mL (0.673 g, 4.53 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 2.0 mL (3.44 g, 0.018 mol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 35.0 mL (37.0 g, 0.44 mol) of T was added to the polymerization system; the color of the solution changed from slightly yellow to red. T was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude product was dissolved in n-hexane and the mixture was filtered in order to remove inorganic precipitates. Then, the hexanes phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was dissolved in a small amount of hexane and precipitated two or three times into acetone in order to remove excess T.

Synthesis of terthiophene-Ended PIB (PIB-TT)

The synthesis of PIB-TT was carried out under a dry nitrogen atmosphere. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added of 240 mL of CH_3Cl, 404 mL of n-hexane, and 0.17 mL (0.144 g, 0.75 mmol) of D*t*BP and then the mixture was cooled to -78 °C. 15 mL (10.57 g, 0.188 mol) of IB was charged to the reactor by a syringe. After 10 min of stirring 0.62 mL (0.55 g, 3.70 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 1.5 mL (2.68 g, 0.014 mol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 8.5 g (34.21 mmol) of Terthiophene (TT) in solution was added to the polymerization system; the color of the solution changed from slightly yellow to red. TT was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude product was dissolved in n-hexane and the mixture was filtered in order to remove inorganic precipitates. Then, the hexanes phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was dissolved in a small amount of hexane and precipitated two or three times into methanol in order to remove excess TT. Nonfunctionalized polymer was separated by column chromatography over activated silica gel. *n*-Hexane and Toluene were used as the eluents. The column was prepared in *n*-hexane. Once the front running polyisobutylene eluted out of the column the eluent was gradually changed to pure toluene to elute the remaining functional polymer. Quantitation of functional and nonfunctional polymer was achieved by LACCC measurements.

Synthesis of 2-(Bromo)-5-(1,1,3,3-tetramethylbutyl)thiophene (TMP-TBr) via the Suzuzki-Miyaura reaction

Model reactions with TMPCl, were carried out under conditions identical to living cationic polymerizations of IB at -78 °C. In a 500 mL three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added 120 mL of CH_2Cl_2, 202 mL of *n*-hexane, and 0.07 mL (0.059 g, 0.312 mmol) of D*t*BP and then the mixture was cooled to -78 C. After 10 min of stirring 5.07 mL (4.43 g, 30 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 6.57 mL (11.38 g, 60 mmol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 20.0 mL (31.8 g, 195.0 mmol) of 2-bromothiophene was added to the system and was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 20 mL (15.7 g, 0.51 mol) of prechilled methanol. Finally, the solvent was removed on a rotary evaporator and the product (TMP-TBr) was dried and distilled under reduced pressure before use.

Synthesis of PIB-TBr

The synthesis of 5-bromothiophene capped PIB was carried out under a dry nitrogen atmosphere. Living polymerizations of IB with TMPCl as initiator were carried out according to the following representative procedure. Into a 1 L three-necked flask equipped with a septum, a magnetic stirrer, and a nitrogen inlet were added of 120 mL of

CH_2Cl_2, 202 mL of n-hexane, and 0.170 mL (0.144 g, 0.75 mmol) of D*t*BP and then the mixture was cooled to -78 °C. 10.4 mL (6.29 g, 0.11 mol) of IB was charged to the reactor. After 10 min of stirring 0.34 mL (0.297 g, 2.00 mmol) of TMPCl was transferred to the reactor by a transfer needle. After 5 min of stirring, 2.0 mL (3.46 g, 0.018 mol) of $TiCl_4$ was transferred to the reactor by a transfer needle. One hour later 40.0 mL (67.36 g, 0.41 mol) of 2-Bromothiophene (TBr) was added to the polymerization system; the color of the solution changed from slightly yellow to red. TBr was allowed to react with the living chain ends for 60 min. Finally, the reaction was quenched by addition of 30 mL (23.55 g, 0.75 mol) of prechilled methanol. The crude product was dissolved in n-hexane and the mixture was filtered in order to remove inorganic precipitates. Then, the hexanes phase was isolated and washed once with NH_3(aq) and subsequently with water until neutral. The organic layer was separated and dried over $MgSO_4$ for about 2 h. Subsequently, the solution was filtered, and the solvent was removed on a rotary evaporator. Then, the polymer was dissolved in a small amount of hexane and precipitated two or three times into acetone in order to remove excess TBr.

Synthesis of 5-(1,1,3,3-tetramethylbutyl)-2,3'-bithiophene (TMP-BT)

Before preparing PIB-BT, orienting model experiments were carried out with TMP-TBr to provide TMP-BT. Under argon atmosphere, a two-necked flask was fed with TMP-TBr (2.05 g, 7.45 mmol), tetrakis (triphenylphosphine) palladium (0.34 g, 0.29 mmol), 50 mL of DME and aqueous sodium carbonate solution (0.74 M). The mixture was vigorously stirred, thiophene-3-boronic acid (1.04 g, 8.2 mmol), was added and the mixture was heated to reflux for 24h, allowed to cool to room temperature, poured into water, and extracted several times with ether. The organic phases were washed with water and dried to yield, after evaporation, a brownish residue. The product was purified by flash chromatography over silica gel with $CHCl_3$/hexane (9/1 v/v) as eluent.

Synthesis of PIB-BT (Stille reaction)

For the synthesis of 5-(2,3'-bithiophene) ended PIB, two-necked flask was fed with PIB-T-Br (M= 3660 g/mol, 2.52 g, 0.69 mmol), tetrakis (triphenylphosphine) palladium (0.03 g, 0.02 mmol), 50 mL of DME and aqueous sodium carbonate solution (0.74 M) under argon atmosphere. The mixture was vigorously stirred, thiophene-3-boronic acid (0.09 g, 0.69 mmol), was added and the mixture was heated to reflux for 24h, allowed to cool to room temperature, poured into water, and extracted several times with ether. The organic phases were washed with water and dried. The product was purified with flash chromatography over silica gel with $CHCl_3$/hexane (9/1 v/v) as eluent.

Synthesis of 2-(Tributylstanny)-5-methyl-thiophene (Me-TSn)

The reaction of lithiated 2- methylthiophene (MeT) with tributyltin chloride was carried out in a 250 mL stirred glass reactor. 200 mL of THF and 3.042 g (30.9 mmol) of MeT were added and then the solution was cooled to -40 °C. After 10 min of stirring 12.71 ml (31.0 mmol) of *n*-BuLi solution were transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with MT for 120 min to form the anion (MeT^-,Li^+). 12.07 g (37.0 mmol) of tributyltin chloride was added and allowed to react with the living chain ends for 60 min. Finally, the solvent was removed on a rotary evaporator and the product (MeT-Sn) was dried and purified.

Synthesis of PIB-T-Sn

The reaction of lithiated PIB-T with tributyltin chloride was carried out in a 250 mL stirred glass reactor. 200 mL of THF and 2.56 g (M= 4270 g/mol, 0.60 mmol) of PIB-T were added and then the mixture was cooled to -40 °C. After 10 min of stirring 0.26 ml (0.65 mmol) of *n*-BuLi solution were transferred to the reactor by a transfer needle. *n*-BuLi was allowed to react with PIB-T for 60 min to form the anion (PIB-T^{-},Li^{+}). 0.234 g (0.72 mmol) of tributyltin chloride were added and allowed to react with the living chain ends for 60 min. Finally, the crude polymer was isolated and dried under vacuum at room temperature.

Synthesis of PIB-BT (Stille reaction)

Under argon atmosphere, a two-necked flask was fed with PIB-TSn (M= 4270 g/mol, 3.82 g, 0.89 mmol), bis(triphenylphosphine) palladium (II) dichloride (0.02 g, 0.03 mmol) and 50 mL of toluene. The mixture was vigorously stirred, added with 3-bromothiophene (0.19 g, 1.16 mmol), was added and the mixture was heated to reflux for 24h, allowed to cool to room temperature and poured into water. The organic phases were washed with water several times and dried. The product was purified with flash chromatography over silica gel with $CHCl_3$/hexane (9/1 v/v) as eluent.

Synthesis of Polyisobutylene-b-Polythiophene (PIB-b-PT)

1.15 g of anhydrous $FeCl_3$ in a 500 mL three-necked flask was stirred under nitrogen atmosphere. The system evacuated and then flashed with dry nitrogen. This procedure was repeated three times to ensure the system was oxygen-free. Then, 70 mL of $CHCl_3$ were added, and a solution of thiophene (0.2 g, 2.4 mmol) and PIB-BT (M=

4270 g/mol, 0.38 g, 0.09 mmol) in $CHCl_3$ was introduced dropwise and stirred at room temperature for 24 hours. The viscous solution was poured into methanol where the polymer precipitated. The crude product was isolated by filtration from the insoluble polythiophene and was washed with water and methanol repeatedly. Further purification was carried out by extraction in a Soxhlet with methanol and then acetone, and dried under vacuum to afford a red polymer.

8. 2. 3. Characterizations

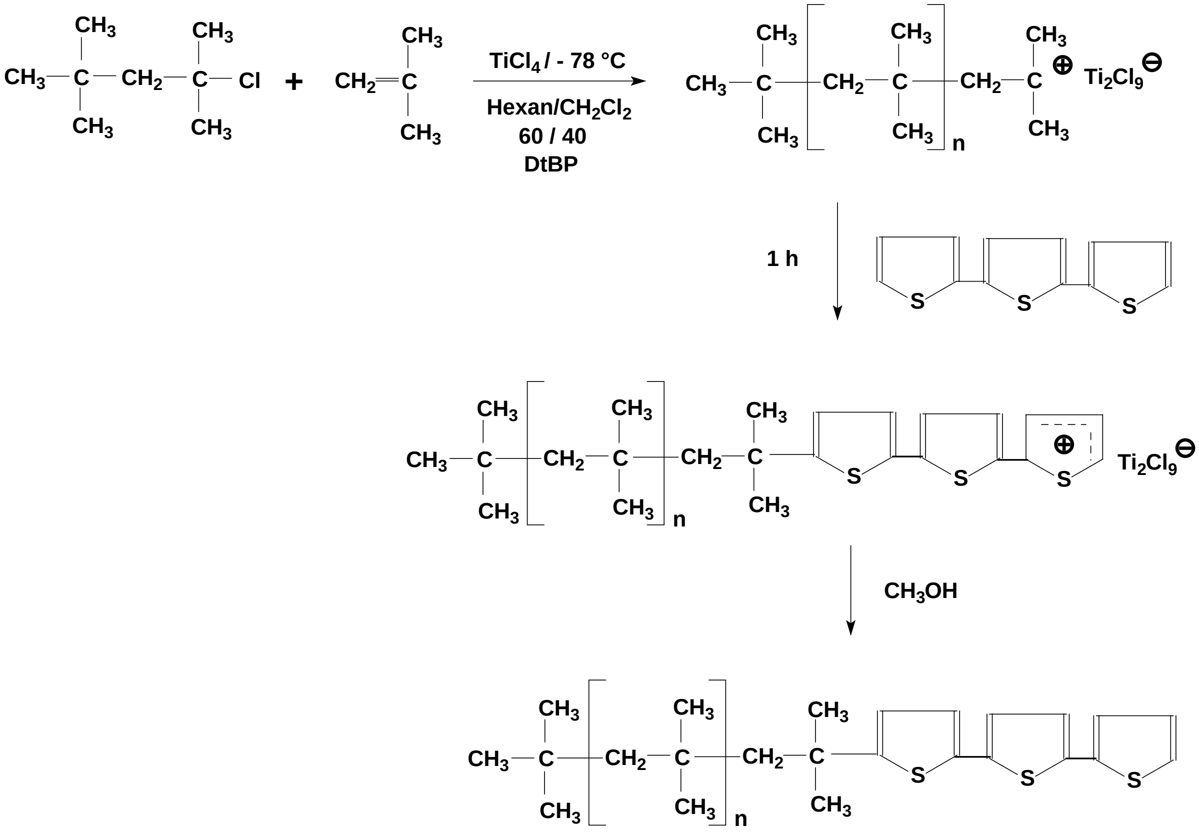
^{1}H-NMR spectroscopy was carried out on a Bruker AC-250 MHz spectrometer at 25 °C in $CDCl_3$ using TMS as an internal standard. *Size Exclusion Chromatography* (SEC) was performed using THF as eluent at a flow rate of 1 ml/min equipped with four 30 cm PSS SDVgel columns (particle size 5 μm, porosity 10^2 - 10^5 Å) heated to 40 °C. Calibration was based on PIB standards (PSS, Mainz). *Liquid adsorption chromatography under critical conditions* (LACCC) was conducted on a TSP HPLC system at a flow rate of 0.5 ml/min. An Evaporative Light Scattering Detector (ELSD, PL-EMD 960) operating at 50 °C with a gas flow rate of 3.5 l/min was used for mass detection. 10 μL of ca. 0.5 wt % polymer solutions were injected. All measurements were carried out at a constant column temperature of 35 °C. Two Reversed Phase columns (YMC, 250 x 4 mm) with 5 μm average particle size, 100 Å and 300 Å pore diameter were used. The critical solvent composition for PIB is THF/Methanol 80.5/19.5 (wt/wt). Premixing of the mobile phase by weight is necessary for a constant and exact composition. UV spectra were recorded on a Perkin-Elmer Lambda15 UV-vis spectrophotometer in the wavelength range from 190 to 700 nm. The spectrum of a

quartz cuvette containg pure solvent was subtracted from sample spectra. *Scanning force microscopy* (SFM) images were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode (free amplitude of the cantilever ≈ 30 nm, set point ratio ≈ 0.98). The samples of PIB-TT were prepared on polished silicon wafers by dip-coating from various solutions (0.5 mg/mL). The sample of PT-g-PIB was prepared on silicon wafer by spin-coating (3000 rpm at room temperature for 20 min) from $CHCl_3$ solution (0.5 mg/mL).

8. 3. Results and Discussion

8. 3. 1. Synthesis of Terthiophene End-Capped Polyisobutylene (PIB-TT)

According to the successful synthesis of thiophene end-capped polyisobutylene (PIB-T) reported previously[10], we decided to apply this synthetic route to the synthesis of the terthiophene end-capped polyisobutylene (PIB-TT). Terthiophene end-quenching of living PIB chain ends initiated by the $TMPCl/TiCl_4$ system took place at –78 °C according to Scheme 8. 1.



Scheme 8. 1. Synthesis of terthiophene end-capped polyisobutylene (PIB-TT)

The details of the capping experiments are given in Table 8. 1. Terthiophene has a poor solubility in most common organic solvents[13]. Since terthiophene is soluble in CH_2Cl_2 but insoluble in *n*-hexane, the functionalization of PIB was conducted by two different methods, in the first experiment we added the terthiophene dissolved in CH_2Cl_2/ *n*-hexane and the efficiency of the end-capping was low. In the second experiment we added the terthiophene dissolved only in CH_2Cl_2 but the efficiency of the end-capping was also low. In general, optimal conditions were not found for this end-capping since terthiophene is soluble in CH_2Cl_2 only at room temperature and only partially soluble at -78 °C.

Exp.No .	$[IB]_o$ mM	$[TMPCl]_o$ mM	$[DtBP]_o$ mM	$[TiCl_4]_o$ mM	$[TT]_o$ mM	$M_n \times 10^{-3}$ g / mol[a]	M_w / M_n	f (NMR)	f (LACCC)
1	220	3.70	0.75	14.0	20	3.69	1.23	0.40	0.45
2	188	3.70	0.75	14.0	34	3.02	1.21	0.50	0.55

[b] determined by SEC with PIB standards in THF.

Table 8. 1. Experimental conditions and results of IB polymerization using TMPCl as initiator and terthiophene endcapping

Liquid chromatography at critical conditions (LACCC). More complex polymers such as monofunctional macromolecules or diblock copolymers have structural units of two different types has been successfully used for the separation according functional groups[14,15]. Figure 8. 1. shows the LACCC chromatogram of a PIB standard and PIB-TT at critical conditions of PIB before and after purification. It is seen that the peaks of the PIB standard and PIB-TT are well-separated. It shows that the end-functionalization of PIB with terthiophene is possible. Preparative purification was possible by chromatography over activated silica gel in hexane/toluene.

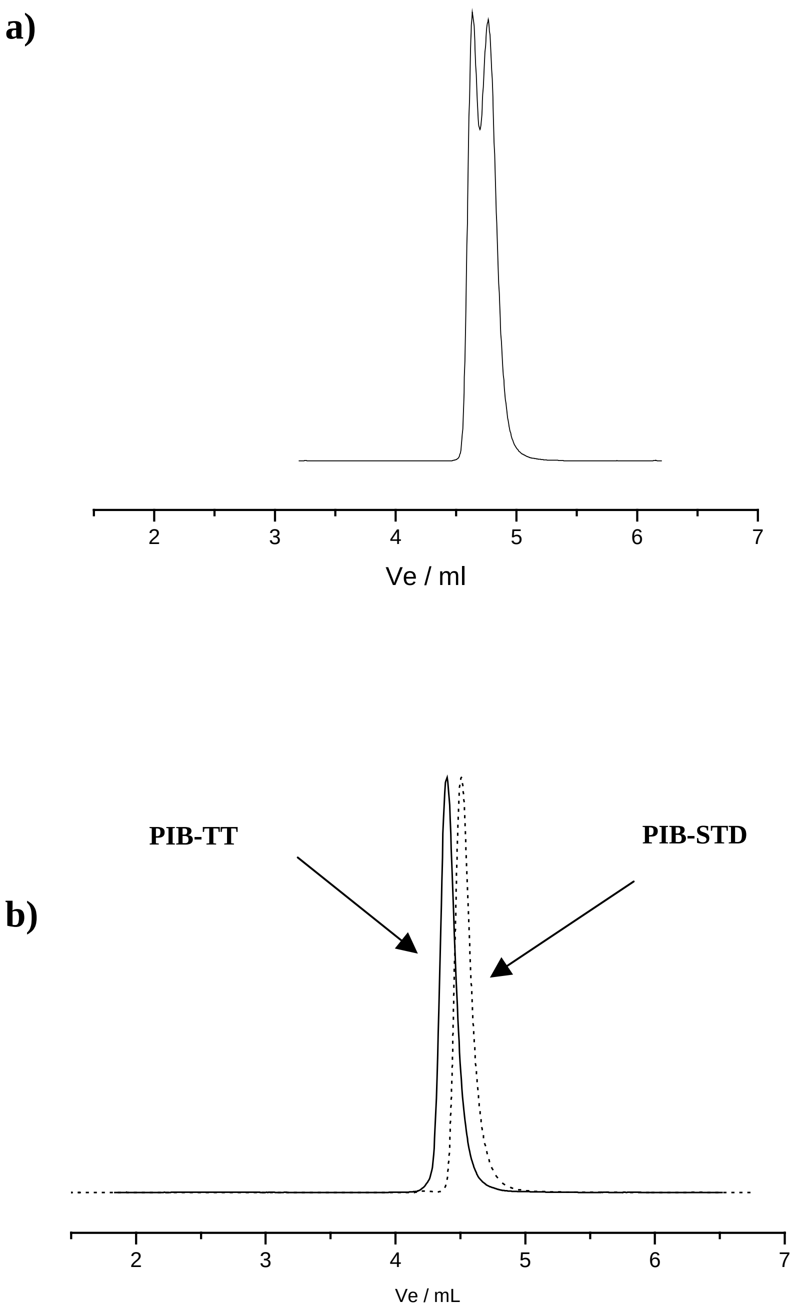


Figure 8. 1. Characterization of terthiophene end-capped polyisobutylene by LACCC, a) before purification, b) after purification

Figure 8. 2 shows the ^{1}H NMR spectrum of the resulting polymer after purification. This spectrum indicates end-functionalization and formation of terthiophene end-capped polyisobutylene (PIB-TT) by this process. The end-capping was indicated by the disappearance of the peaks at 1.9 ppm (PIB-**CH$_2$**-C(CH$_3$)$_2$-Cl) and 1.69 ppm (PIB-CH$_2$-C(**CH$_3$**)$_2$-Cl). A new set of peaks at 1.83, 6.70, 6.6.95, 7.0, 7.15 and 7.20 ppm appeared due to the presence of the terthiophene at the chain end.

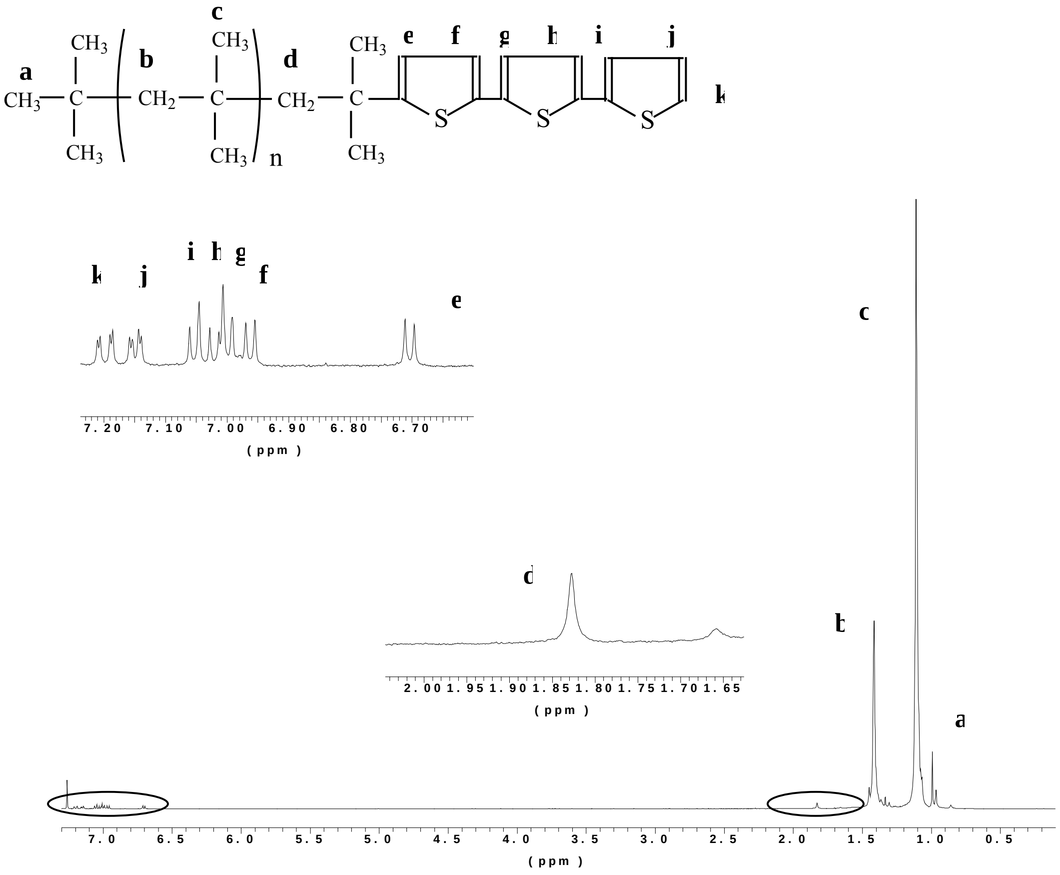


Figure 8. 2. ^{1}H NMR spectrum of the terthiophene end-capped polyisobutylene (PIB-TT)

Figure 8. 3. shows the UV-Visible spectrum of the terthiophene end-capped polyisobutylene in solution. PIB-TT exhibits a maximum of absorption at 360 nm in chloroform solution, which is similar to the maximum of absorption of terthiophene alone[13].

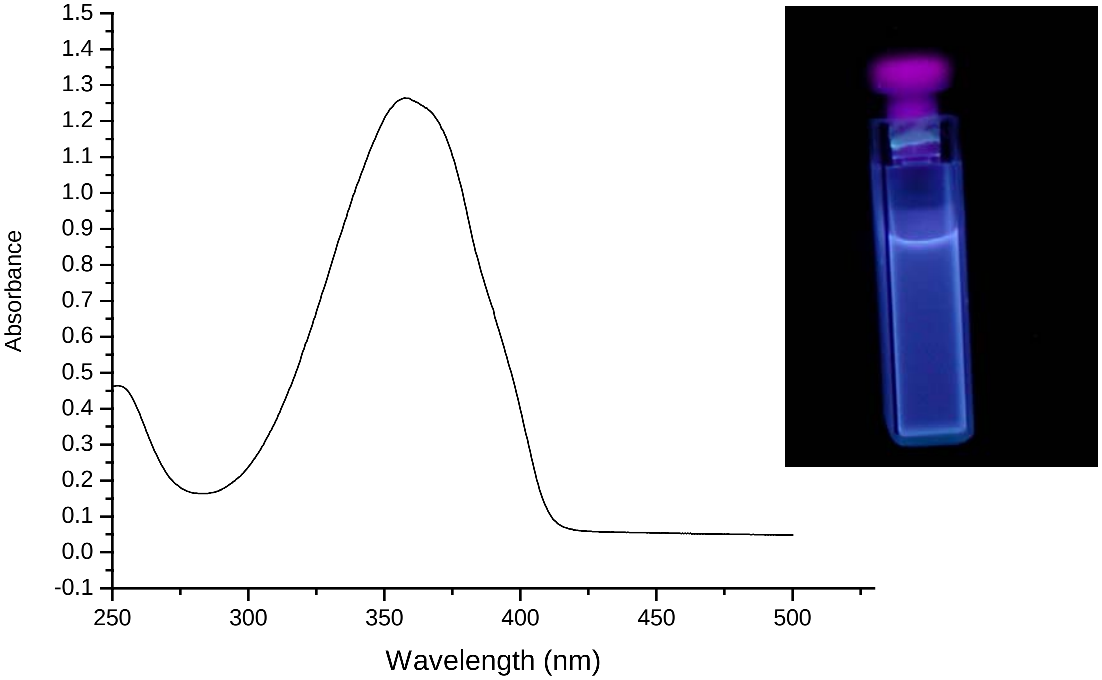
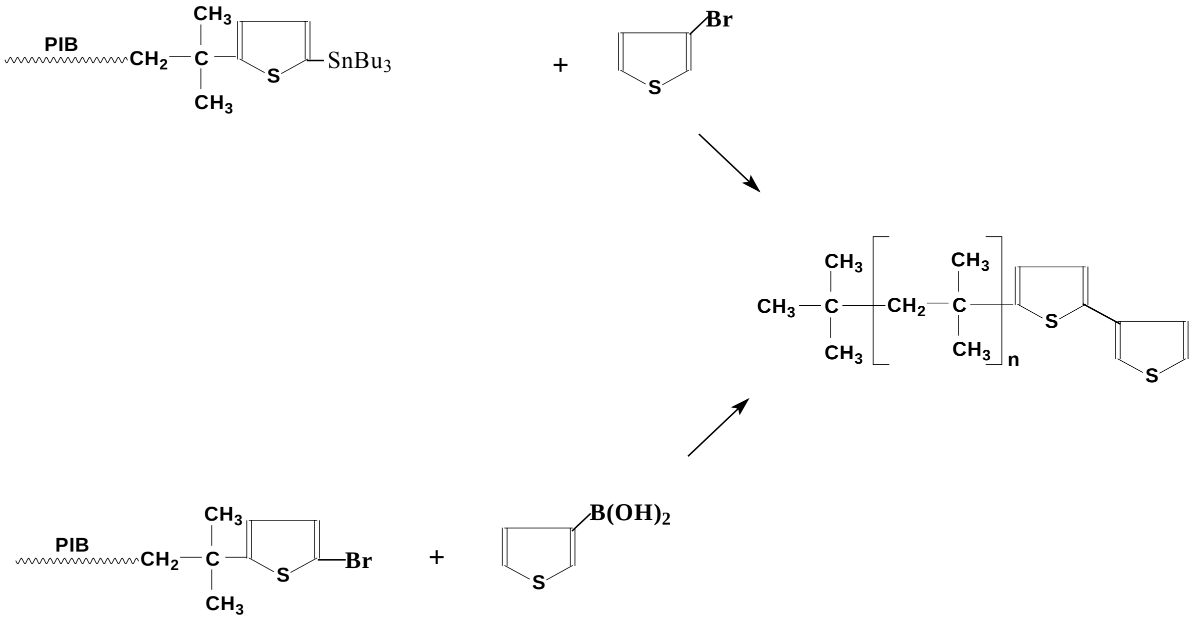


Figure 8. 3. UV-Visible spectrum of terthiophene end-capped polyisobutylene (PIB-TT) in chloroform (Mn = 3.69×10^3)

8. 3. 2. Synthesis of PT-g-PIB

To the best of our knowledge, nothing was known about the transformation from living/controlled cationic polymerization of isobutylene to the oxidative polymerization of thiophene. Therefore, the desired way to solve this problem was to prepare PIB precursors containing endgroups suitable for subsequent oxidative polymerization, in particular having a thiophene group, in which the positions 2 and 5 are free. In order to obtain the desired macromonomer, two possibilities were considered, either the use of Stille coupling or Suzuki-Miyaura coupling[16-19]. Scheme 8. 2. describes the synthetic steps involved in the preparation of PIB-BT.



Scheme 8. 2. Synthetic approaches for the PIB-BT synthesis Top: Stille reaction, bottom: Suzuki-Miyaura reaction.

8. 3. 3. Synthesis of PIB-T-Br

Synthesis of PIB-BT via Suzuki-Miyaura coupling

Orienting experiments were carried out with TMPCl, which mimics the end group structure of *tert*-chloro-terminated PIB and the living chain ends upon addition of $TiCl_4$ as a Lewis acid. These reactions were carried out in order to investigate the end-capping with TBr. The ^{1}H NMR spectrum of 2-(bromo)-5-(1,1,3,3-tetrametylbutyl)thiophene is shown along with the assignments in Figure 8. 4. The resonances identified in the aromatic range at 6.55 (1H on C_d), 6.80 (1H on C_e), confirmed one 2-bromothiophene ring substituted by the TMP residue). In the aliphatic region the ^{1}H NMR spectral assignments are as follows: 0.81 ppm (s, 9H, CH_3), 1.44 ppm (s, 6H, CH_3), 1.73 ppm (s, 2H, CH_2), 6.55 ppm (m, 1H, thiophene CH), 6.80 ppm (m, 1H, thiophene CH).

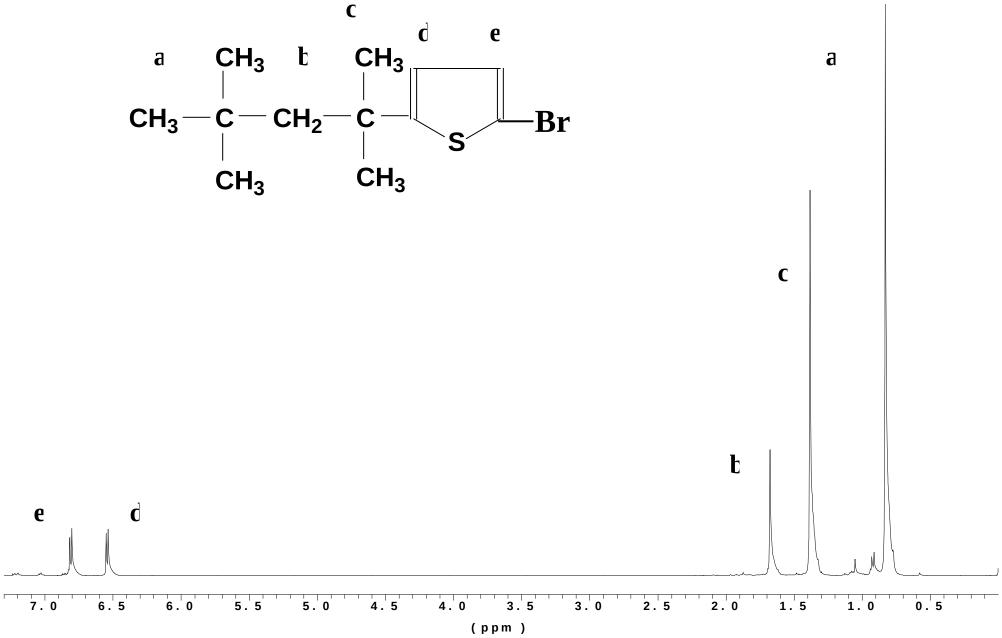
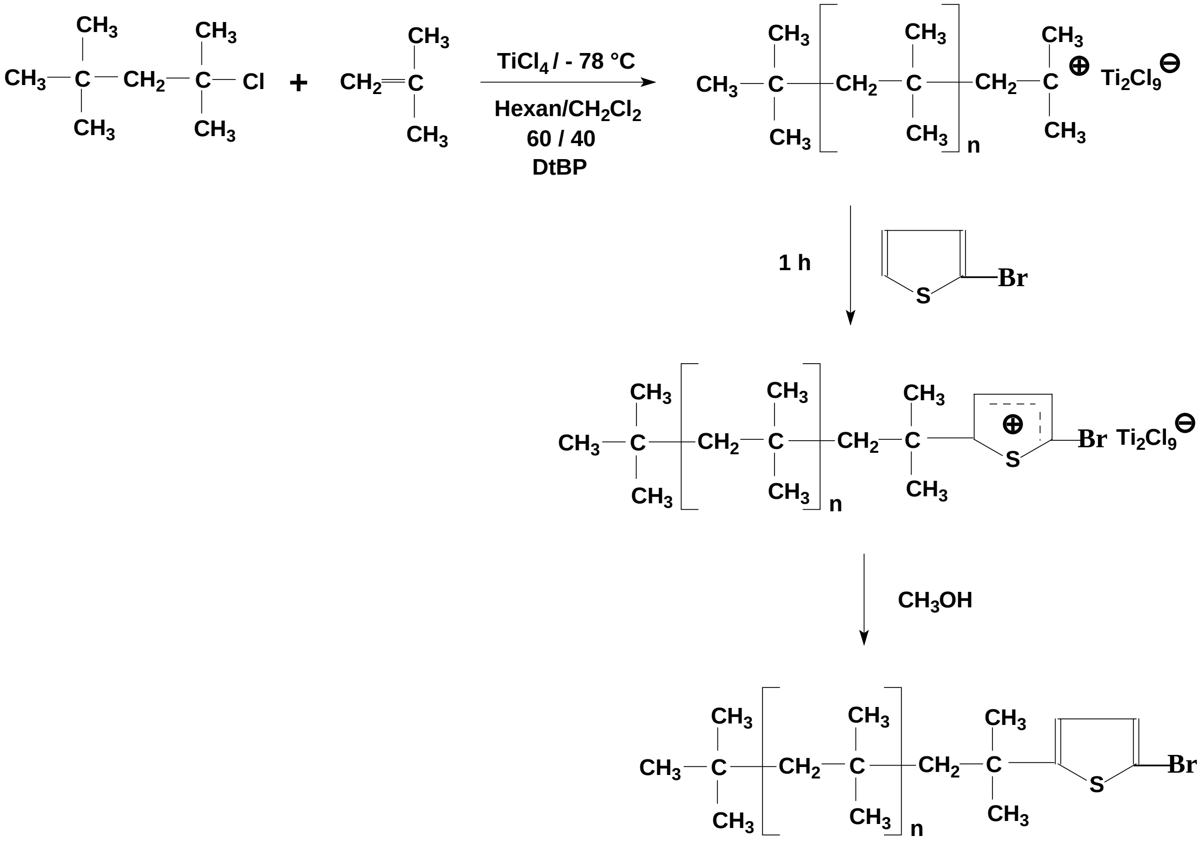


Figure 8. 4. ^{1}H NMR spectrum of 2-(Bromo)-5-(1,1,3,3-tetramethylbutyl)thiophene

It was of interest to determine whether the end-functionalization results obtained with the model compounds could be applied to the synthesis of 2-bromothiophene-ended PIB. 2-Bromothiophene end-quenching of living PIB chain ends initiated by the TMPCl/$TiCl_4$ system took place at –78 °C according to Scheme 8. 3.



Scheme 8. 3. Synthesis of 2-bromothiophene end-capped polyisobutylene (PIB-T-Br)

Table 8. 2. resumes the results obtained from the end-capping of living PIB chain ends initiated by the TMPCl/$TiCl_4$ system with 2-bromothiophene. In the first experiment 50 equivalents of 2-bromothiophene were used for the end-capping, in the second one 200 equivalents of 2-bromothiophene. The results showed that 50 equivalents were not enough for to get high functionalities of the PIB. In contrast to the first experiment, quantitative capping of living PIB with 2-bromothiophene was obtained with 200 equivalents of 2-bromothiophene. It seems that a large excess of 2-bromothiophene is necessary to obtain complete functionality.

Exp.No.	$[IB]_o$ mM	$[TMPCl]_o$ mM	$[DtBP]_o$ mM	$[TiCl_4]_o$ mM	$[TBr]_o$ mM	M_n x 10^{-3} g / mol[a]	M_w / M_n	f (NMR)
1	140	2.66	0.75	10.7	130	3.06	1.12	0.40
2	110	2.0	0.75	18.0	410	3.66	1.09	1.0

[a] determined by SEC with PIB standards in THF.

Table 8. 2. Experimental conditions and results of IB polymerization using TMPCl as initiator and 2-bromothiophene endcapping

Figure 8. 5. shows the ^1H NMR spectrum of the resulting polymer. This spectrum indicates quantitative end-functionalization and formation of 2-bromothiophene end-capped polyisobutylene (PIB-T-Br) by this process. This confirms results obtained with the corresponding model compound. Quantitative addition was indicated by the disappearance of the peaks at 1.9 ppm (PIB-$\mathbf{CH_2}$-$C(CH_3)_2$-Cl) and 1.69 ppm (PIB-CH_2-C($\mathbf{CH_3}$)$_2$-Cl). A new set of peaks at 1.78, 6.55, and 6.82 ppm appeared due to the presence of the 2-bromothiophene ring at the chain end.

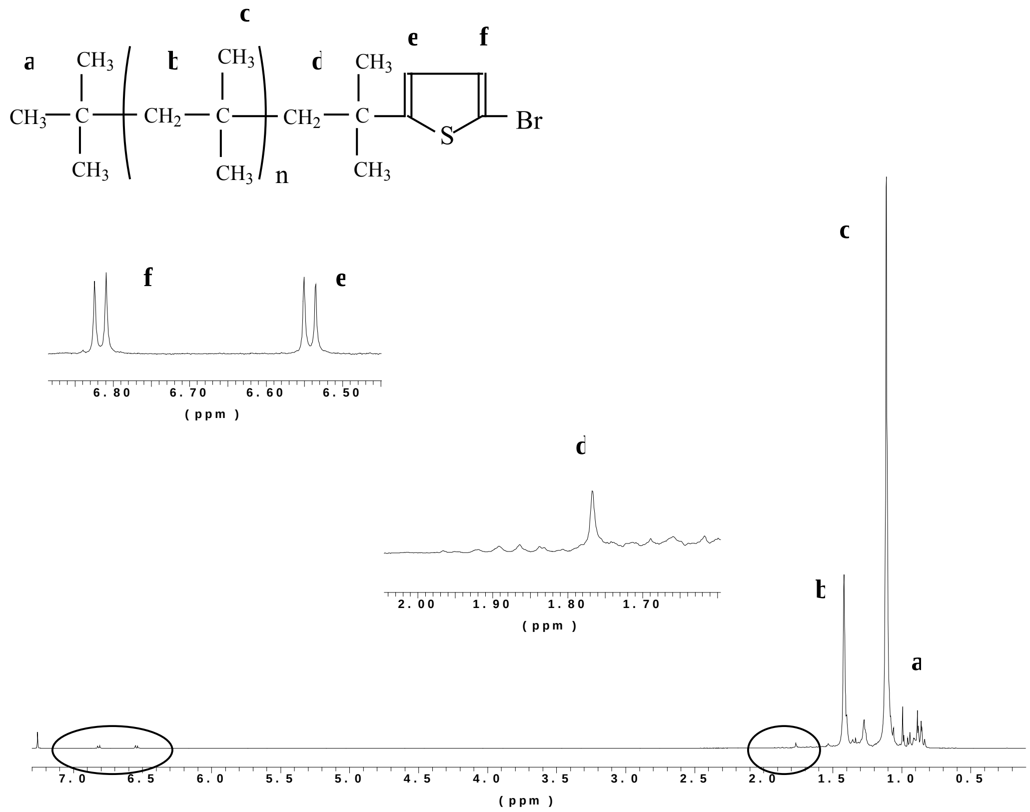


Figure 8. 5. ^{1}H NMR spectrum of the 2-bromothiophene end-capped polyisobutylene (PIB-T-Br).

The UV-Visible spectrum of the 2-bromothiophene end-capped polyisobutylene in chloroform solution exhibits an absorption maximum at 245 nm.

Synthesis of PIB-BT

The synthesis of biaryl and biheteroaryl systems through transition metal catalyzed cross-coupling reactions has been well-studied and developed[16-19]. Among all the possible organometallics used as nucleophilic partners, tin (Stille coupling) and boron derivatives (Suzuki-Miyaura coupling) and, to a lesser extent, organozinc (Negishi coupling) and Grignard reagents (Kumada coupling), have been the most frequently used for cross-coupling reactions of aryl and heteroaryl compounds. The Suzuki-Miyaura cross-coupling reaction, which involves the coupling of an organoboron compound with an electrophile, possesses notable advantages over the other related techniques. Particularly striking is the array of functionality tolerated in the coupling process. The use of organoboron compounds is also valued because the inorganic byproducts of the reaction are nontoxic and can be readily removed by simple workup procedures, while many tin-compounds are toxic, and complete removal of tin-containing byproducts is a well-recognized problem. The synthesis of functionalized thiophene oligomers is generally carried out by reacting thienyl bromides with thienylstannanes or organoboron derivatives, Stille and Suzuky-Miyaura reaction, respectively in the presence of palladium catalysts.

Szuki-Miyaura coupling

Orienting model experiments were carried out with TMP-T-Br, which mimics the end group structure of PIB-T-Br during the Suzuki-Miyaura reaction. These reactions were carried out in order to investigate the formation of TMP-BT. The ^{1}H NMR spectrum of 2-(1,1,3,3-tetrametylbutyl)-2,3'-bithiophene (TMP-BT) is shown along with the assignments in Figure 8. 7. The resonances identified in the aromatic range at 6.70 (1H on C_d), 7.0 (1H on C_e), 7.30 (3H on $C_{f,g,h}$) confirmed 2 thiophene ring substituted by the TMP residue). In the aliphatic region the ^{1}H NMR spectral assignments are as follows: 0.81 ppm (s, 9H, CH_3), 1.44 ppm (s, 6H, CH_3), 1.73 ppm (s, 2H, CH_2), 6.70 ppm (m, 1H, thiophene CH), 7.0 ppm (m, 1H, thiophene CH), 7.30 ppm (m, 3H, thiophene CH).

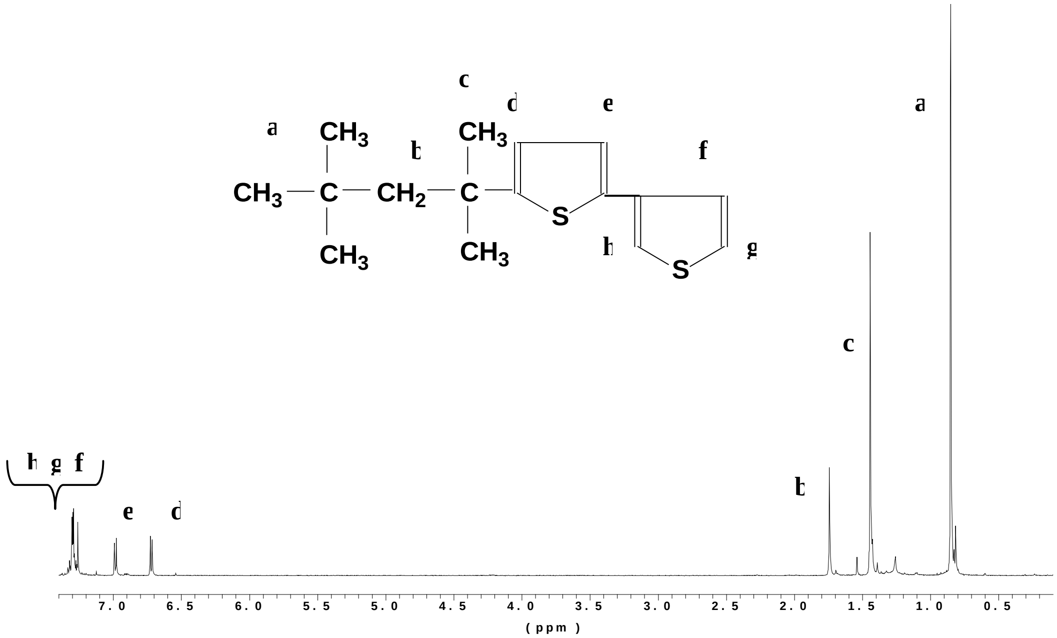
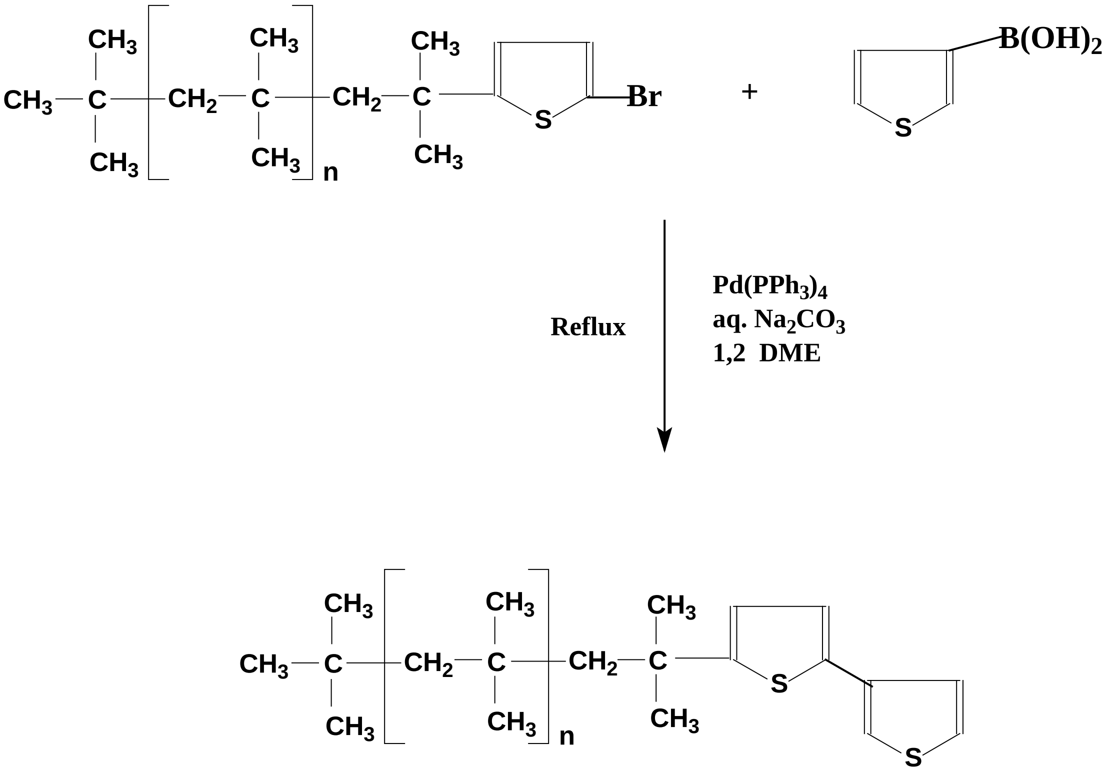


Figure 8. 7. ^{1}H NMR spectrum of 2-(1,1,3,3-tetramethylbutyl)-2,3'-bithiophene (TMP-BT)

Synthesis of PIB-BT

We initiated our study of the Suzuki-Miyaura cross-coupling reaction in order to obtain the PIB-BT due to notable advantages of this reaction over the other related techniques[16]. The results of the Suzuki-Miyaura cross-coupling reaction of TMP-T-Br with 3-thiophene boronic acid showed formation of TMP-BT. It was of interest to determine whether the end-functionalization results obtained with the model compounds could be applied to the synthesis of PIB-BT. Cross-coupling reaction between PIB-TBr and 2-thiophene boronic acid took place according to Scheme 8. 4.



Scheme 8. 4. Synthesis of bithiophene end-capped polyisobutylene (PIB-BT).

Unfortunately, the results showed low yield in this cross-coupling reaction (Table 8. 3). The solubility of PIB-TBr in 1,2-dimethoxyethane is poor, the yield in this case may be reduced because of the insolubility of PIB-TBr under these conditions.

Exp.No.	M_n x 10^{-3} g / mol[a]	M_w / M_n	[PIBTBr]$_o$ mM	[TB(OH)$_2$]$_o$ mM	[Na_2CO_3]$_o$ mM	[Pd(PPh$_3$)$_4$]$_o$ mM	Time hr	f (NMR)
1	3.66	1.09	0.80	0.85	1.35	0.028	24	0.40
2	3.66	1.09	0.69	0.70	1.17	0.02	36	0.50

[a] determined by SEC with PIB standards in THF.

Table 8. 3. Experimental conditions and results of the synthesis of PIB-BT using Suzuki-Miyaura reaction

Since Suzuki-Miyaura cross-coupling reaction gave low yields, we tried to obtain PIB-BT using Stille cross-coupling under another conditions. The Stille reaction is generally carried out by reacting thienyl bromides with thienylstannanes.

Synthesis of PIB-BT via Stille Coupling

Synthesis of PIB-T-$SnBu_3$

Orienting experiments were carried out with 2-methylthiophene (MeT) which mimics the end group structure of PIB-T. These reactions were carried out in order to optimize the reaction of end-capping of PIB-T^-, Li^+ with Tributyltin chloride. The lithiation of MeT was performed at -40 °C, using *n*-BuLi (Scheme 8. 1). After 60 minutes the reaction was quenched with tributyltin chloride at room temperature.

The ^1H NMR spectrum of 2-(tributylstanny)-5-methyl-thiophene is shown along with the assignments in Figure 8. 8. The resonances identified in the aromatic range at 6.95 (1H on C_b), 7.05 (1H on C_c) confirmed one thiophene ring substituted by the TMP residue). In the aliphatic region the ^1H NMR spectral assignments are as follows: 0.90 ppm (m, 9H, CH_3), 1.10 ppm (m, 6H, CH_2), 1.40 ppm (m, 6H, CH_2), 1.60 ppm (m, 6H, CH_2), 2.60 ppm (s, 3H, CH_3), 6.95 ppm (m, 1H, thiophene CH), 7.05 ppm (m, 1H, thiophene CH).

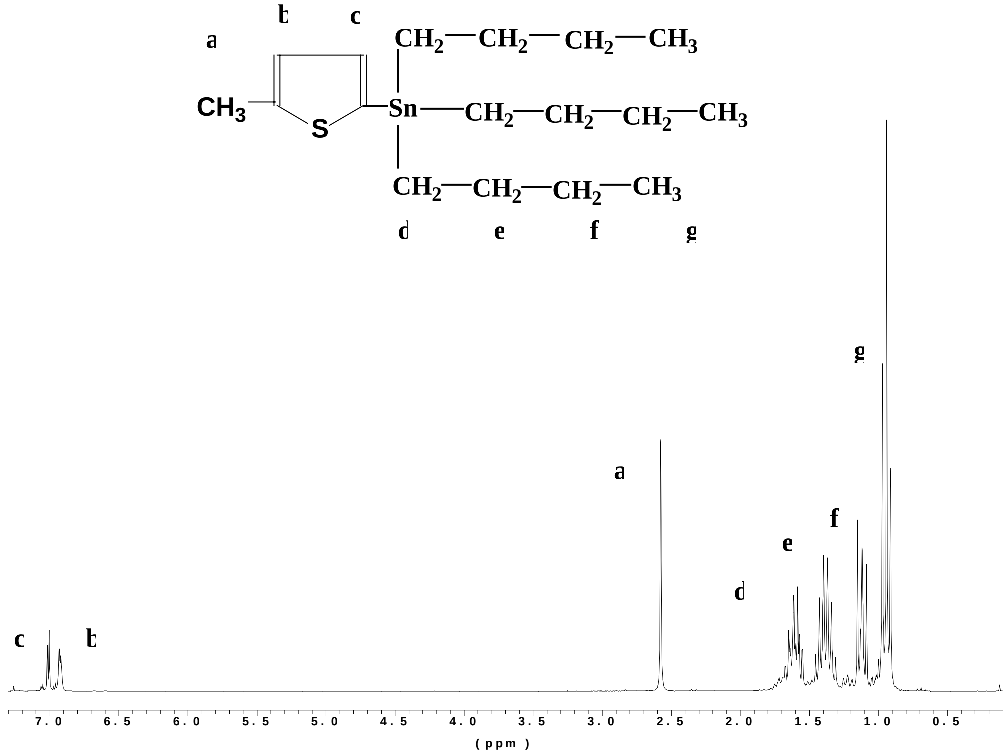
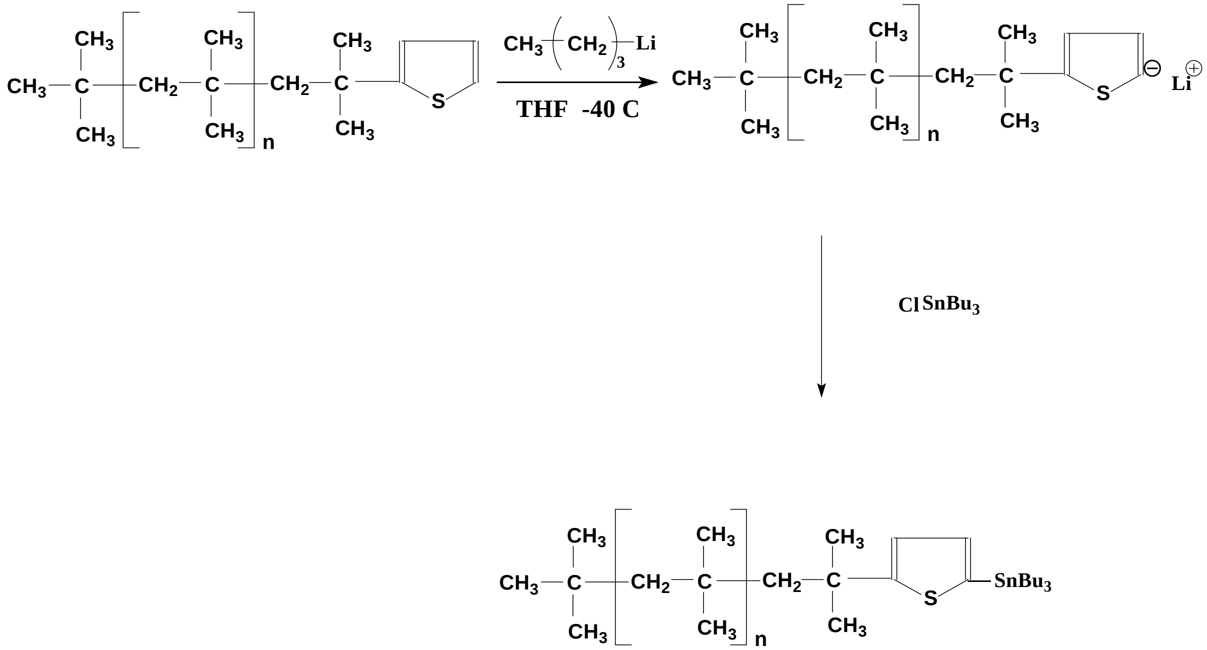


Figure 8. 8. ^{1}H NMR spectrum of 2-(tributylstanny)-5-methyl-thiophene

The model experiment showed high yield in the end-capping of MeT with tributyltin chloride. We next examined the functionalization of PIB with tributyltin. The functionalization took place according to Scheme 8. 5.



Scheme 8. 5. Synthesis of 2-(Tributylstannyl)thiophene end-capped polyisobutylene (PIB-TSn)

The results of the end-capping of PIB-T$^-$, Li$^+$ with Tributyltin chloride are reported in the Table 8. 4. In general, high yields were found in this type of functionalization.

Exp.No.	Mn x 10^{-3} g / mol[a]	Mw / Mn	$[PIB]_o$ mM	$[BuLi]_o$ mM	$[Tributyltin]_o$ mM	f (NMR)
1	4.27	1.20	0.60	0.60	0.72	1.0

[a] SEC molecular weights of polymers were determined with PIB standards in THF.

Table 8. 4. Experimental conditions and results of the synthesis of 2-(Tributylstannyl)thiophene end-capped polyisobutylene (PIB-TSn).

Figure 8. 9 shows the ^{1}H NMR spectrum of the resulting polymer. This spectrum indicates end-functionalization and formation of tributyltin end-capped polyisobutylene (PIB-T-Sn) by this process. The end-capping was indicated by the disappearance of the

peaks at 1.9 ppm (PIB-**CH_2**-$C(CH_3)_2$-Cl) and 1.69 ppm (PIB-CH_2-C(**CH_3**)$_2$-Cl). A new set of peaks at 1.82, 6.91, and 6.94 ppm appeared due to the presence of the tributyltin at the chain end.

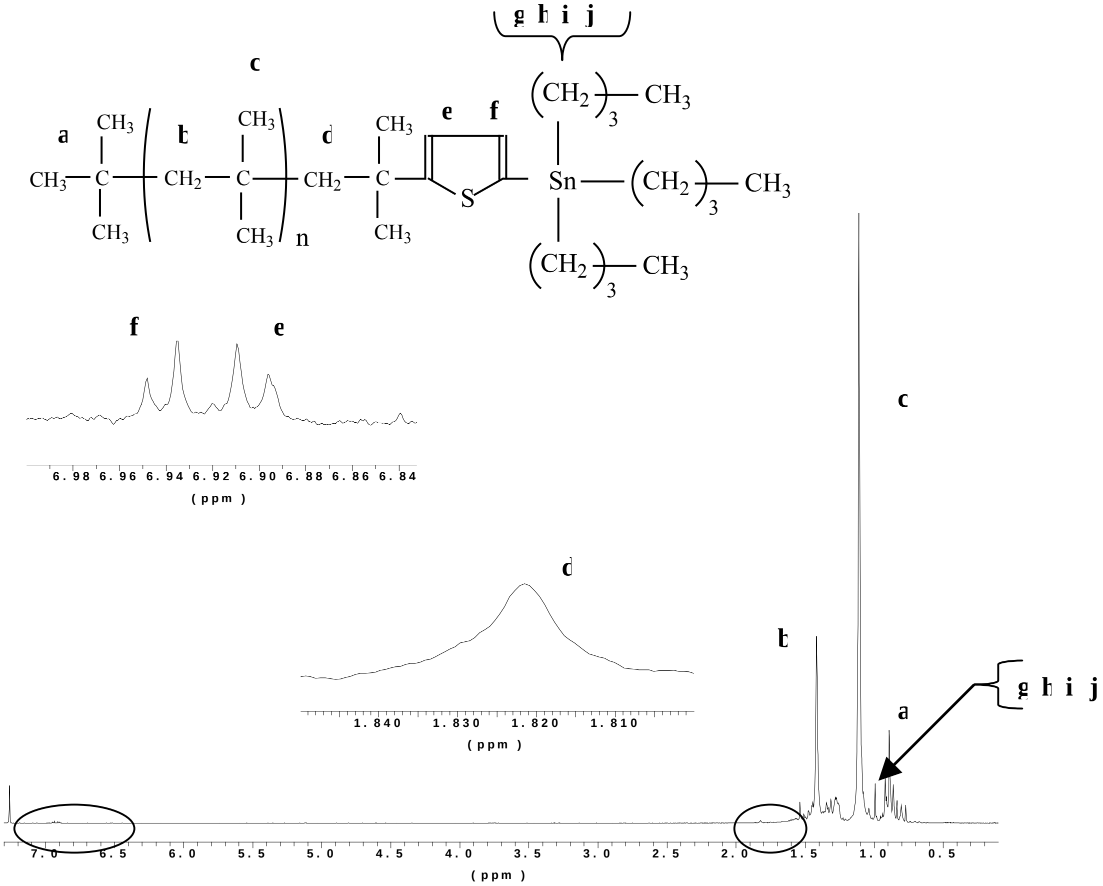


Figure 8. 9. ^{1}H NMR spectrum of the 2-(Tributylstannyl)thiophene end-capped polyisobutylene (PIB-TSn).

Figure 8. 10. shows the UV-Visible spectrum of the 2-(tributylstannyl)thiophene end-capped polyisobutylene in solution. PIB-TSn exhibits a maximum of absorption at 245 nm in chloroform solution.

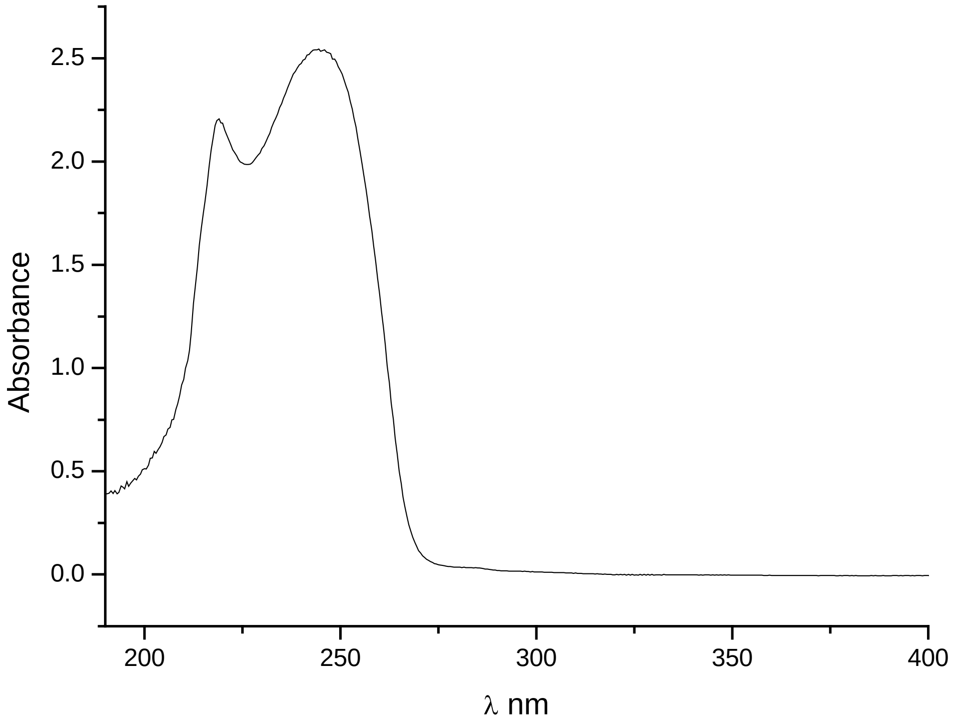
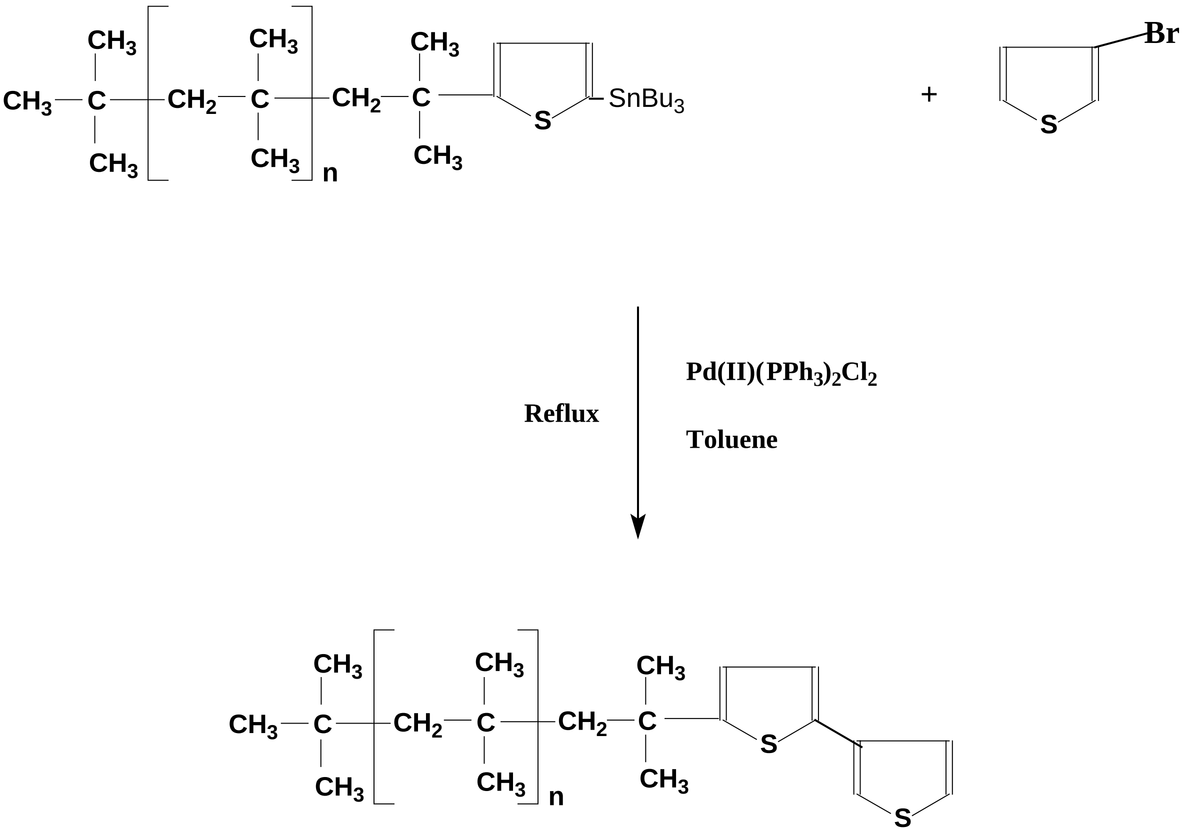


Figure 8. 10. UV-visible spectrum of the 2-(tributylstannyl)thiophene end-capped polyisobutylene (PIB-TSn).

Synthesis of PIB-BT.

The Stille reaction between tributyltin end-capped polyisobutylene and 3-bromothiophene took place according to Scheme 8. 6.



Scheme 8. 6. Synthesis of bithiophene end-capped polyisobutylene (PIB-BT)

70-80 % high yield was obtained in the Stille coupling reaction in toluene, whereas the Suzuki-Miyaura cross-coupling reaction in 1,2-DME showed low yields even after long reaction time. The results are listed in Table 8. 5.

Exp.No.	Mn x 10^{-3} g / mol[a]	Mw / Mn	$[PIBTSn]_o$ mM	$[TBr]_o$ mM	$[Pd(II)(PPh_2Cl_2)_4]_o$ mM	Time hr	f (NMR)
1	4.27	1.20	0.56	0.62	0.021	24	0.70
2	4.27	1.20	0.89	1.0	0.033	36	0.80

[a] SEC molecular weights of polymers were determined with PIB standards in THF.

Table 8. 5. Experimental conditions and results of the synthesis of PIB-BT using Stille reaction

The ^1H NMR spectrum of PIB-BT after purification is shown along with the assignments in Figure 8. 11. The spectrum is similar to that of TMP-BT which was used as a model compound to confirm the assignments (Fig. 8.7.) and that the reported in the literature. A new set of peaks at 1.83, 6.70, 7.0, and 7.30 ppm appeared due to the presence of the bithiophene ring at the chain end.

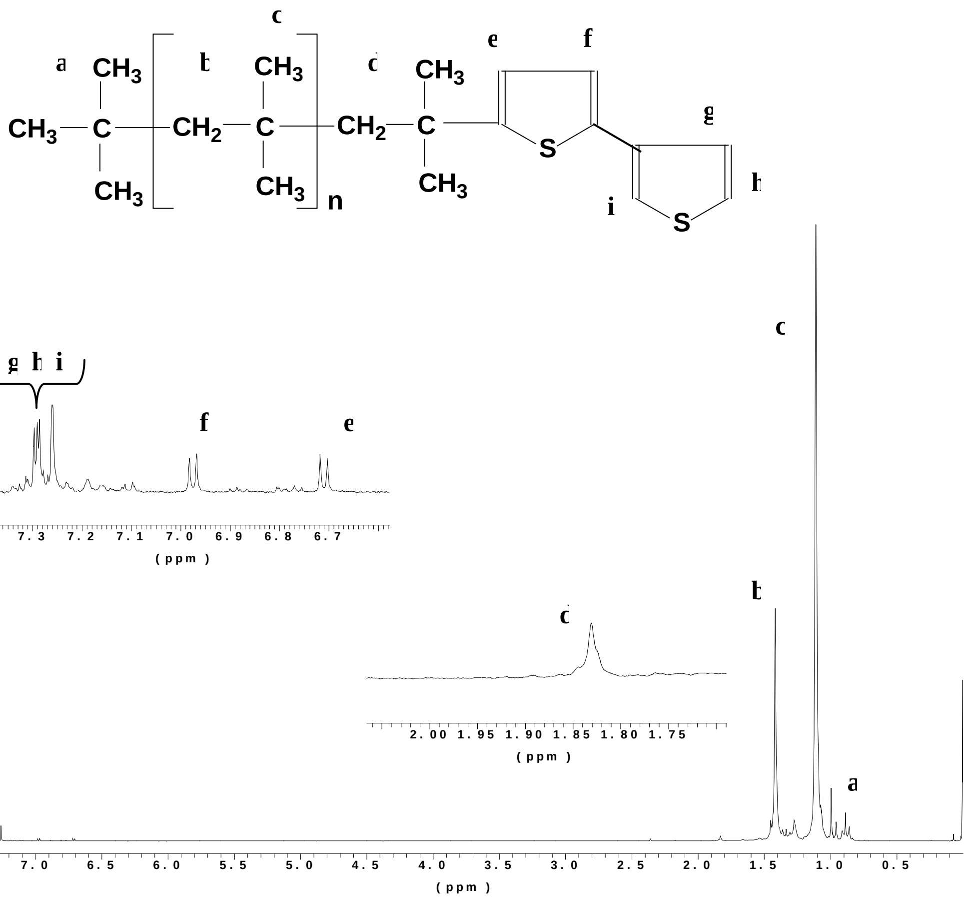


Figure 8. 11. ^1H NMR spectrum of the bithiophene end-capped polyisobutylene (PIB-BT)

Figure 8. 12 shows the UV-visible spectrum of the corresponding PIB-BT in solution. The absorption maximum (λ = 285 nm) is similar to that of BT reported in the literature[21].

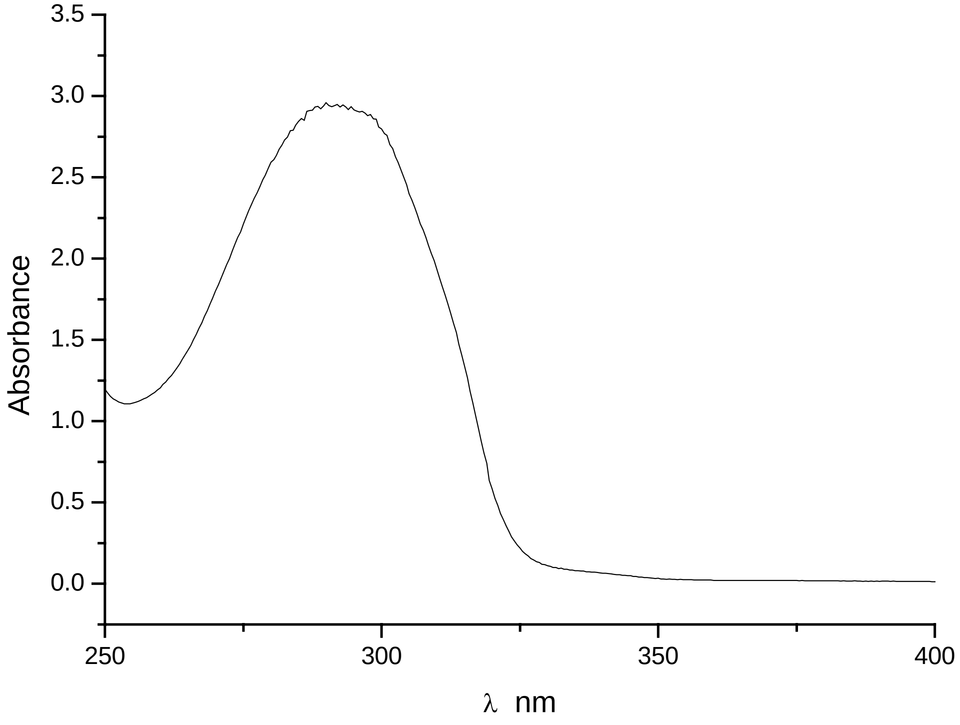
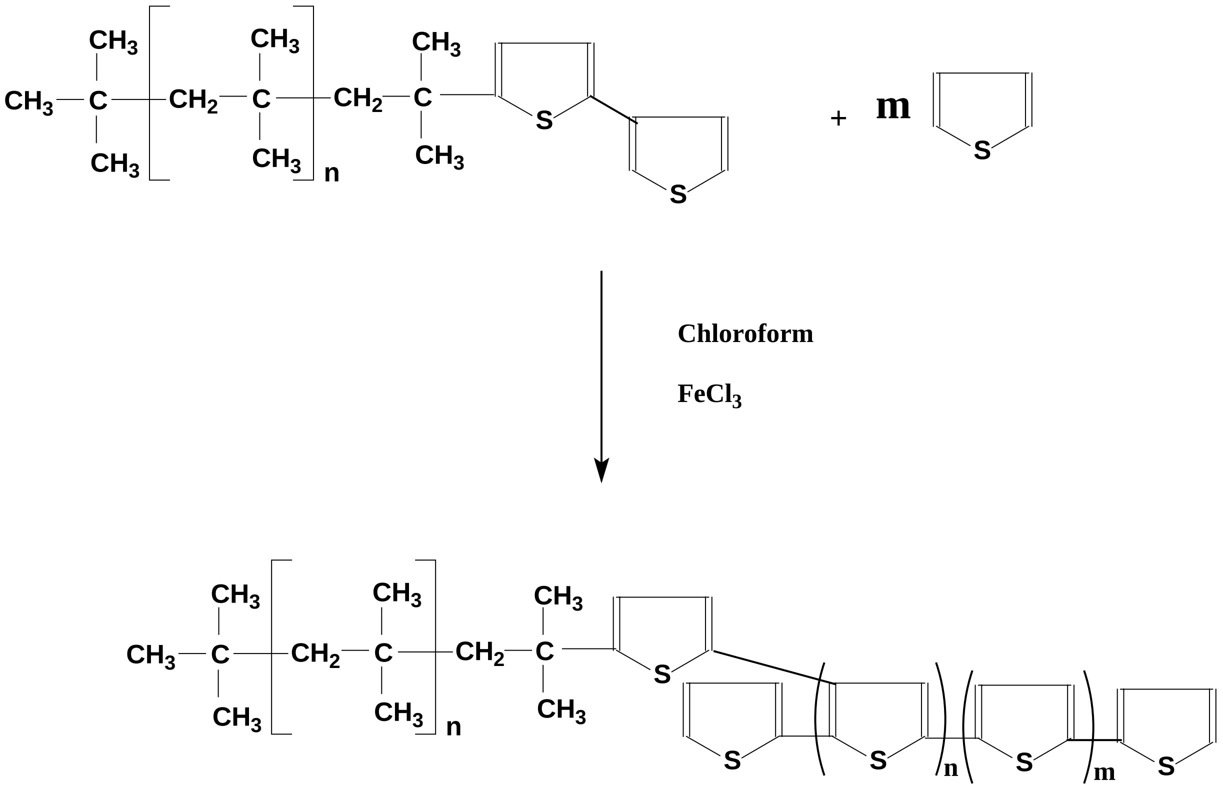


Figure 8. 12. UV-visible spectrum of the bithiophene end-capped polyisobutylene (PIB-BT)

Synthesis of PIB-g-PT

The PIB-BT obtained has a polymerizable group: the thiophene ring with substitution at the 3-position can be employed as a macromonomer in oxidative copolymerization in the presence of $FeCl_3$ as an oxidant[22,23]. The polymerization took place, most probably, at positions 2 and 5 of the thiophene ring (Scheme 8. 7).



Scheme 8. 7. Synthesis of polythiophene-graft-polyisobutylene (PT-g-PIB).

The evidence of successful oxidative copolymerization was given by means of SEC measurements. GPC traces of the macromonomer before and after copolymerization are shown in Figure 8. 13. The peak corresponding to the macromonomer is shifted to higher molecular weight, indicating the successful oxidative polymerization but remains free macromonomer. The molecular weight obtained by calibration with polyisobutylene standards should be taken as apparent values. Figure 8. 13 shows that only a small amount of unreacted macromonomers is left over.

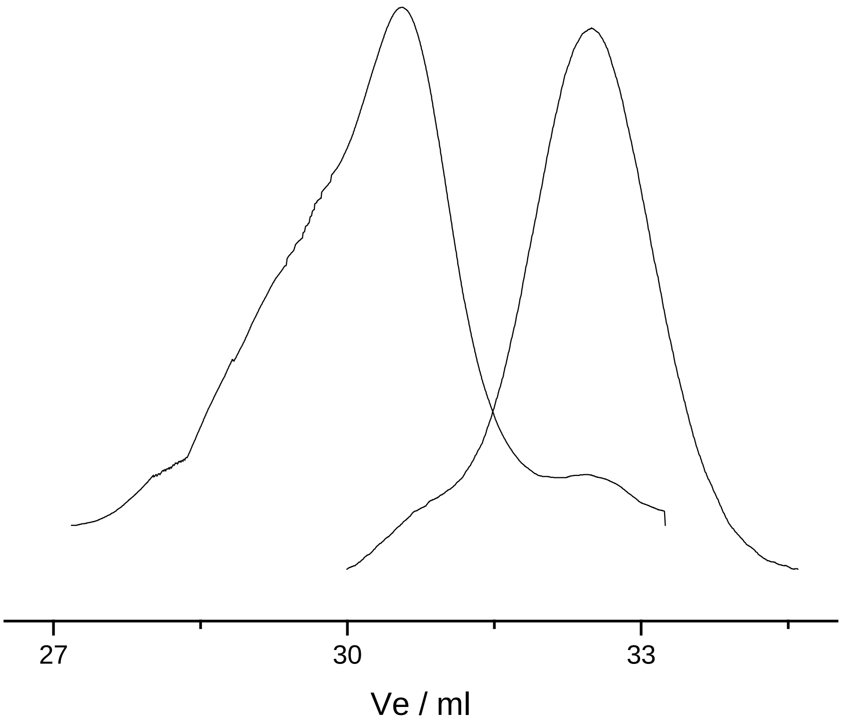


Figure 8. 13. SEC traces (RI detector) of polythiophene-graft-polyisobutylene (PT-g-PIB) and of the PIB-BT macromonomer.

The results of the molecular weight measurements by means GPC are listed in Table 8. 6.

Exp.No.	M_n x 10^{-3} g / mol[a] PIB	M_w / M_n PIB	$[PIB\text{-}BT]_o$ mM	$[T]_o$ mM	S[b]	Mn x 10^{-3} g / mol[a] graftcop.	Mw / Mn graftcop.	mPIB / mT
1	4.27	1.20	0.09	2.37	26	9.74	1.28	1.92
2	4.27	1.20	0.09	5.94	66	18.15	1.42	0.77

[a]determined with PIB standards, molecular weights of block copolymers represent apparent values only, [b]S = theoretical spacing (no. of tumb. between side chains), S = $[T]_0$ / $[PIB\text{-}BT]_0$

Table 8. 6. Experimental conditions and results of the synthesis of PT-g-PIB.

As expected, the maximum of absorption in the UV-visible range of the copolymer in comparison with PIB-BT shifts to higher wavelengths as the as the conjugation length (the number of consecutive thiophene units) increases (Figure 8. 14)[24].

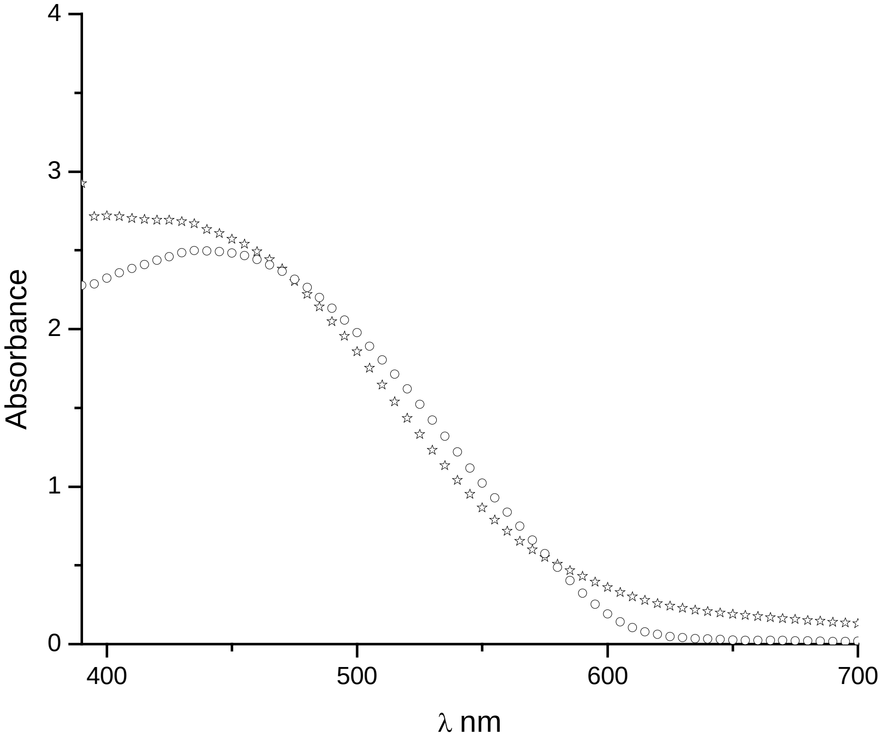


Figure 8. 14. UV-visible spectrum of PT-g-PIB1 (-*-) and PT-g-PIB2 (-o-).

Visualization of assembled structures

Recently, much interest has been devoted to self-assembly of block and graft copolymers consisting of two or more segments with different chemical and physical properties, because of their feasibility to generate nanostructured materials and their numerous potential applications. In particlular, supermolecular assemblies involving conjugated polymer segment is of great interest and might lead to design of new electroactive materials with ordered architectures. Here, we first investigated the morphology of the PIB-TT by scanning force microscopy (SFM), because thiophene oligomers are known to exhibit a variety of interactions, such as der Waals interactions, weak hydrogen bondings, π-πstacking, sulfur-sulfur interactions, all of which are related to the thiophene ring with the high polarizability of sulfur electrons[25]. Hence, PIB containing TT-end group was expected to show characteristic self-assembled structures bsed on the terthiophene interactions. Figure 8. 15. shows tapping mode height SFM images of PIB-TT obtained from different solvents. Both THF and $CHCl_3$ are good solvents for PIB as well as TT. Large spherical morphologies are observed in both cases, suggesting the formation of aggregated structures on silicon wafer. The size of the spherical morphology (height > 50 nm, 1 μ m > diameter > 400 nm) obtained from THF is bigger than that (height > 15 nm, 500 nm > diameter) obtained from $CHCl_3$. The spherical collapsed morphologies (height much lower than diameter) were observed for both cases, which is due to much lower T_g of the hydrophobic PIB than room temperature.

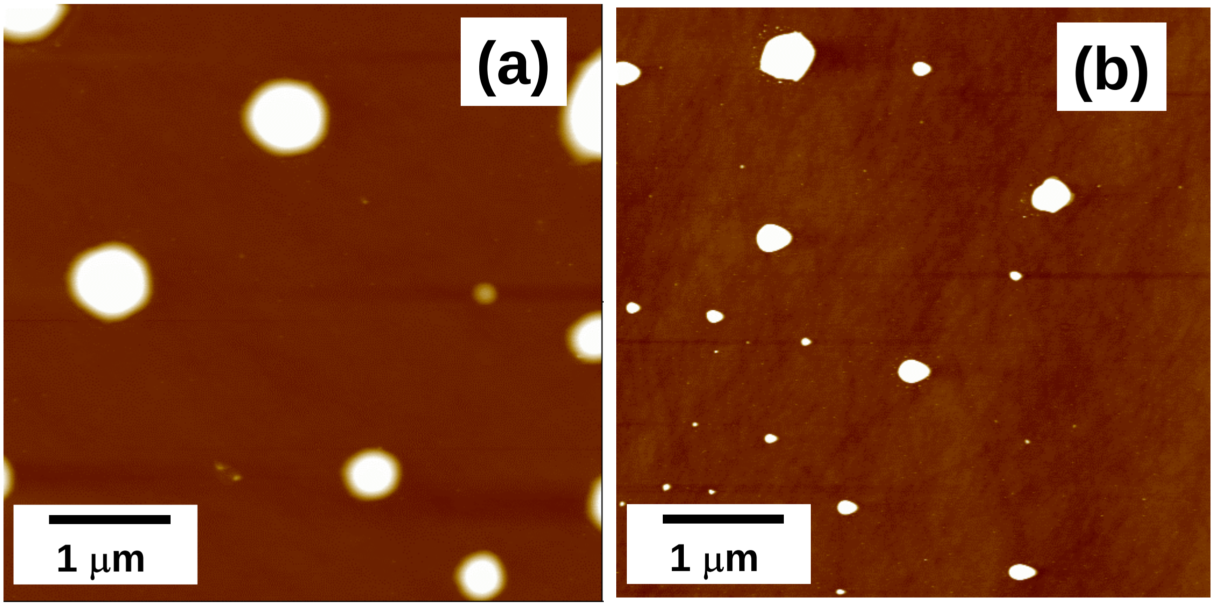


Figure 8. 15. Tapping mode height SFM images of PIB-TT obtained from (a) THF solution, Z range; 50 nm and (b) $CHCl_3$ solution, Z range; 15 nm, respectively

The morphology of the graft copolymer, PT-g-PIB1 was also investigated by SFM, as a step towards the development of novel electronic devices using self-assembly of well-defined block and graft copolymers containing polythiophene segment. The sample was prepared on a silicon wafer by spin-coating from a $CHCl_3$ solution. A typical height image ($5 \times 5\ \mu m^2$) and a high magnification three-dimensional image ($1 \times 1\ \mu m^2$) are shown in Figure 8. 16. These images apparently exhibit the presence of fine structures (height = about 15 nm and diameter = a few hundred nm) with continuous phase. These structures may be related to the assembly of graft copolymers, suggesting the feasibility to produce nanostructured materials with characteristic electroconductive properties.

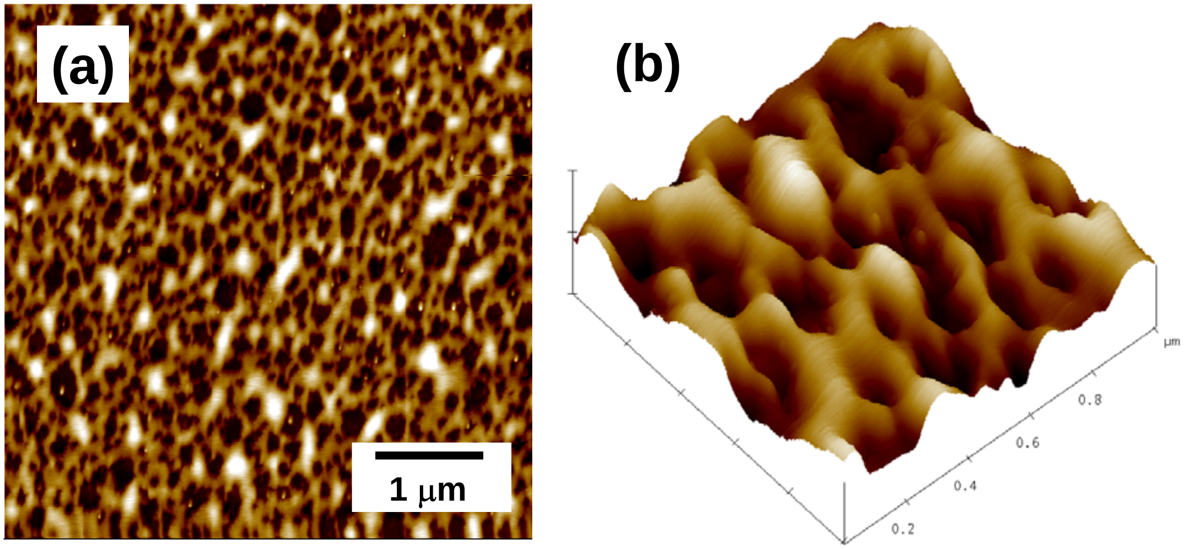


Figure 8. 17. Tapping mode SFM images of PT-g-PIB obtained by spin-coating from $CHCl_3$ solution (a) hight image, Z range; 15 nm and (b) three-dimensional image, Z range; 15 nm, x-y range; 1 x 1 μ m^2.

8. 4. Conclusions

Quantitative functionalization of living PIB with 2-Bromothiophene has been achieved. By lithiation of PIB-T a new, convenient method has been demonstrated for the synthesis of tributyltin end-capped PIB. Furthermore the incorporation of bithiophene or terthiophene moieties into PIB show interesting emissive properties. Moreover, we have demonstrated the chemical synthesis of copolymers consisting of polyisobutylene and polythiophene. Finally, the resulting products are potential new conductive polymers.

Summary

A new synthetic route for the synthesis of terthiophene-functionalized Polyisobutylene (PIB-TT) and Polythiophene-graft-Polyisobutylene (PT-g-PIB) block copolymers was developed by combining living carbocationic and oxidative polymerizations. First terthiophene end-capped polyisobutylene (PIB-TT) was prepared by monoaddition of terthiophene to living PIB chains in conjunction with $TiCl_4$ as Lewis acid in *n*-hexane/CH_2Cl_2 60/40 v/v at –78 °C. PT-g-PIB graft copolymer is obtained in several steps using bithiophene end-capped polyisobutylene (PIB-BT) as a macromonomer: (a) the macromonomer was prepared using either the use of a Stille coupling reaction or a Suzuki-Miyaura coupling reaction, yielding a polyisobutylene end capped with two units of thiophene in which the last unit of thiophene presented its positions 2 and 5 free allowing the oxidative polymerization, (b) the polythiophene backbone of the PT-g-PIB graft copolymer was synthesized using the chemical oxidative polymerization with anhydrous iron(III) chloride ($FeCl_3$) in dry chloroform ($CHCl_3$). Characterization of this graft copolymer and terthiophene-functionalized Polyisobutylene was carried out by Size Exclusion (SEC), NMR, UV, and SFM.

8. 5. References

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9. Summary

The studies presented in this thesis deal with the new block copolymers of isobutylene by combination of cationic and anionic polymerizations, which are new materials with numerous promising potential applications.

A new method for the synthesis of tailored polyisobutylene(PIB)-based block copolymer by combination of controlled / living cationic and anionic polymerizations has been developed. In addition and parallel to these subjects, new synthetic routes for preparation of telechelic PIBs and conductive polymers have been investigated.

The PIB precursors used for subsequent anionic polymerization and other processes were prepared by controlled / living cationic polymerization of isobutylene followed by quenching with thiophene under selected conditions. Quantitative functionalization of living PIB with thiophene (T) has been achieved. The process is complicated by coupling between living PIB and PIB-T formed by in situ deprotonation, By lithiation of PIB-T a new, convenient method has been demonstrated for the synthesis of PIB-based block copolymers, involving anionic initiation of *tert*-butyl methacrylate. A major improvement is that for an industrial process, lithiation by *n*-BuLi is much more convenient than metalation by Na/K alloy, which had to be used in former processes. Block copolymers with narrow and unimodal molecular weight distribution (MWD) were synthesized under well-controlled conditions. The lithiated thiophene-capped PIB was also used to prepare four-armed star PIB via chlorosilane coupling. Using the same method, new amphiphilic block copolymers, namely PIB-b-poly(N,N-dimethylacrylamide) and PIB-b-poly(ethylene oxide) were synthesized.

The anionic polymerization of N,N-dimethylacrylamide (DMAAm) was carried out with a binary initiator system prepared from thienyllithium and the Lewis acids triethylaluminium (Et_3Al), diethylzinc (Et_2Zn) or triethylborane (Et_3B) in THF. Polymerizations proceeded in a homogeneous manner and gave polymers having controlled molecular weights. However, in presence of alkoxides the polymerization results in polymers insoluble in THF, even using Et_3Al. Finally, lithiated PIB-T, in conjunction with Lewis acids, was used to initiate the living anionic polymerization of DMAAm, resulting in the new amphiphilic block copolymer PIB-b-PDMAAm.

The anionic polymerization of ethylene oxide (EO) was carried out with a binary initiator system prepared from thienyllithium and the polyiminophosphazene base tBu-P_4 in THF. Lithilated PIB-T^- in conjunction with tBu-P_4 was used to initiate the living anionic polymerization of ethylene oxide. In a second method, PIB-b-PEO was synthesized using hydroxyl end-capped PIB as macroinitiator in conjunction with tBu-P_4. The aggregation behavior in dilute aqueous solutions of a PIB-*b*-PEO copolymer, produced from the combination of cationic and anionic polymerizations, was investigated by dynamic light scattering in aqueous solution.

The monoaddition of ethylene oxide to lithiated PIB-T is demonstrated as a new pathway for the synthesis of hydroxy-functional PIB (PIB-OH). This is a useful alternative to the tedious procedures used in the literature so far. PIB-OH was successfully used as a macroinitiator for the ring-opening polymerizations of L-lactide and ε-caprolactone catalyzed by stannous octoate. Combination of chromatographic methods and MALDI-TOF ass spectrometry gave information about the side reactions during polymerization.

Quantitative functionalization of living PIB with 2-bromothiophene has been achieved. Using various coupling methods, this polymer was convertet to a macromonomer with a pendant thiophene group, which is accessible in the 1- and 5-position. Oxidative copolymerization with thiophene led to graft copolymers consisting of polythiophene-graft-PIB.

10. Zusammenfassung

In dieser Arbeit wurden neue Blockcopolymere aus Isobutylen untersucht, die durch Kombination von kationischer und anionischer Polymerisation synthetisiert wurden. Sie stellen neue Materialien mit einer Vielzahl vielversprechender potentieller Anwendungen dar.

Es wurde eine neue Synthesemethode zur Darstellung maßgeschneiderter, auf Polyisobutylen (PIB) basierender Blockcopolymere entwickelt, die die kontrolliert / lebende kationische und anionische Polymerisation verbindet. Zusätzlich wurden neue Synthesewege zur Schaffung telecheler PIBs und leitfähiger Polymere untersucht.

Der PIB-Precursor für die darauffolgende anionische Polymerisation sowie andere Reaktionen wurde durch kontrollierte kationische Polymerisation von Isobutylen, gefolgt durch Abbruch mit Thiophen (T) unter ausgewählten Bedingungen hergestellt. Die Funktionalisierung des lebenden PIB mit Thiophen war quantitativ. Als Nebenreaktion wird die Kupplungsreaktion zwischen lebenden PIB-Ketten und PIB-T durch in-situ Deprotonierung beobachtet.

Durch Lithiierung des PIB-T wurde eine neue, bequeme Methode für die Synthese von PIB-basierten Blockcopolymeren eingeführt, der sich die anionische Aktivierung von *tert*-Butylmethacrylat anschließt. Diese Entwicklung vereinfacht industrielle Prozesse, da die Lithiierung über *n*-BuLi wesentlich günstiger ist, als die Metallierung über eine Na/K-Legierung, die in früheren Prozessen benutzt wurde. Blockcopolymere mit enger und monomodaler Molekulargewichtsverteilung (MWD) wurden unter kontrollierten Bedingungen synthetisiert. Das lithiierte Thiophen-funktionalisierte PIB wurde auch benutzt, um vierarmige PIB-Sterne durch Kupplung über Tetrachlorsilan darzustellen.

Mit derselben Methode wurden ebenfalls neue amphiphile Blockcopolymere, PIB-b-poly(N,N-dimethylacrylamid) and PIB-b-polyethylenoxid hergestellt.

Die anionische Polymerisation von N,N-Dimethylacrylamid (DMAAm) wurde unter Verwendung eines binären Initiatorsystems durchgeführt, das aus Thienyllithium und den Lewissäuren Triethylaluminium (Et_3Al), Diethylzink (Et_2Zn) oder Triethylboran (Et_3B) in THF hergestellt wurde. Die homogen katalysierte Polymerisation ergab Polymere mit kontrolliertem Molekulargewicht. In Gegenwart von Alkoxiden wurden trotz Verwendung von Et_3Al in THF unlösliche Polymere erhalten. Letztendlich wurde lithiiertes, mit Lewissäuren konjungiertes PIB-T benutzt, um DMAAm lebend anionisch zu polymerisieren, was das neue, amphiphile Blockcopolymer PIB-b-PDMAAm ergab.

Die anionische Polymerisation von Ethylenoxid (EO) wurde mittels eines binären Initiatorsystems durchgeführt, das aus Thienyllithium und der Polyiminophosphazenbase tBu-P_4 in THF hergestellt wurde. Lithiiertes PIB-T in Verbindung mit tBu-P_4 wurde benutzt, um die lebende anionische Polymerisation von EO zu initiieren. In einer weiteren Syntheseroute wurde PIB-b-PEO unter Verwendung von hydroxyl-funktionalisiertem PIB als Makroinitiator in Verbindung mit tBu-P_4 synthetisiert. Das Aggregationsverhalten in verdünnten wässrigen Lösungen eines PIB-b-PEO Copolymers, das aus der Kombination von kationischer und anionischer Polymerisation hergestellt wurde, wurde mittels dynamischer Lichtstreuung untersucht.

Die Monoaddition von EO an lithiiertes PIB-T wird als neue Möglichkeit aufgezeigt, hydroxy-funktionalisiertes PIB (PIB-OH) herzustellen. Das stellt eine gute Alternative zu den in der Literatur beschriebenen langwierigen Verfahren dar. PIB-OH wurde erfolgreich als Makroinitiator für die ringöffnende, durch Zinnoctanoat katalysierte Polymerisation von L-Lactid und ε-Caprolactam eingesetzt. Eine Kombination von chromatographischen Methoden sowie MALDI-TOF Massenspektrometrie erlaubte Rückschlüsse auf bei der Polymerisation auftretende Nebenreaktionen.

Quantitative Funktionalisierung lebender PIB-Ketten mit 2-Bromthiophen wurde erzielt. Unter Verwendung verschiedener Kupplungsmethoden wurde aus diesem Polymer ein Makromonomer mit anhängender Thiophengruppe hergestellt, die an Position 1 und 5 angreifbar ist. Oxidative Copolymerisation mit Thiophen führte zu Pfropfcopolymeren mit der Struktur Polythiophen-graft-PIB.

Danksagung

An dieser Stelle möchte ich mich bei all denen bedanken, die mit ihrer Unterstützung zum Gelingen dieser Arbeit beigetragen haben.

Besonderer Dank gilt Prof. Dr. Axel H. E. Müller für die sehr interessante Themenstellung, für seine stete Unterstützung und für sein Vertrauen, mir den Freiraum zur Verwirklichung eigener Ideen zu lassen. Vielen Dank für die Möglichkeit, einige Monate an der University of Massachusetts zu verbringen. Die Erfahrungen dort gingen weit über fachliche Erkenntnise hinhaus. Muchas Gracias.

Mein besonderer Dank gilt auch Dr. Michael Lanzendörfer für die Diskussionen, in deren Mittelpunkt nicht immer nur Fragestellungen der kationischen Polymerisation standen.

Thanks to the Cationic people down under at University of Massachusetts at Lowell: Prof. Dr. Rudolf Faust, Dr. Methin H. Acar and Dr. Young Kwon for their help and the very good atmosphere during my stay in USA. Thank you very much for always having an answer to my questions.

Mein besonderer Dank gilt auch Dr. Hideharu Mori für die Hilfestellung bei der Durchführung der AFM und der Interpretation der Ergebnisse, sowie für eine Vielzahl anregender Diskussionen. Darüber hinaus möchte ich ihm danken, dass er auch in nicht-chemischen Angelegenheiten immer ein kompetenter Ansprechpartner war.

Sehr herzlich bedanke ich mich bei Xavier André, der nicht nur stets Zeit für anregende Gespräche fandet, sondern auch für seine Hilfe. Merci beaucoup de t'avoir eu à mes cotés pendant ma thèse et pour l'amitié que tu m'as offert.

Besonders möchte ich auch mich bei Annette Krökel, für die vielen praktischen Ratschläge bedanken und dafür, dass sie unser Labor so gut gehalten hat. Muchas gracias, sin ti este doctorado no hubiera sido posible.

Grösser Dank gilt auch Adriana Boschetti für die Durchführung der DSC-Messungen. Gracias mujer por toda tu ayuda, no solo en quimica y los buenos momentos que pudimos pasar riendo.

Bei Mingfu Zhang und Markus Burkhardt möchte ich mich ganz herzlich für die Durchführung der DLS-Messungen sowie die Diskussion der Ergebnisse bedanken. Viele mühevolle Stunden waren notwendig, um die Messungen zum Laufen zu bringen.

Dr. Dmitry Pergushov (Universität Moskow) danke ich für die Durchführung der Fluoreszenz-Messungen und der Interpretation der Ergebnisse.

Zu Dank verpflichtet bin ich Dr. Markus Hartenstein für die Mithilfe beim 2D-Chromatographie.

Bei Sabine Wünder bedanke ich mich herzlich für die Durchführung zahlreicher GPC-Messungen. Gracias por hacerme reir, fue muy agradable trabajar contigo.

Ferner gilt mein Dank Chih-Cheng Peng für die Betreuung des Computernetzwerkes, Gabi Rösner-Oliver für die kleinen Hilfen im Umgang mit der fränkischen Bürokratie.

Danken möchte ich auch allen jetzigen und ehemaligen Arbeitskreismitgliedern für die angenehme Atmosphäre und die gute Zusammenarbeit. Insbesondere danke ich Christine Schilli, Andreas Walter, Evis Pennot (te deseo mucha suerte mujer y muchas gracias por tu ayuda), Thomas Lorenzo (la persona que siempre soportaba mi mal caracter) und Sasha.

Weiterhin danke ich allen Französinen des Lehrstuhles für Makromolekulare Chemie II, Delphine, Nolwenn und Sandie für die Freundschaft und das angnehme Laborklima.

Meiner Familie gebührt ganz besonderer Dank für die grosse Unterstützung, nicht nur in finanzieller Hinsicht, während dem Studium und der Promotion.

Dem Deutschen Akademischen Austauschdienst (DAAD) danke ich für die Gewährung eines Doktorandenstipendiums.