1
Anionic Vinyl Polymerization

Durairaj Baskaran and Axel H.E. Müller

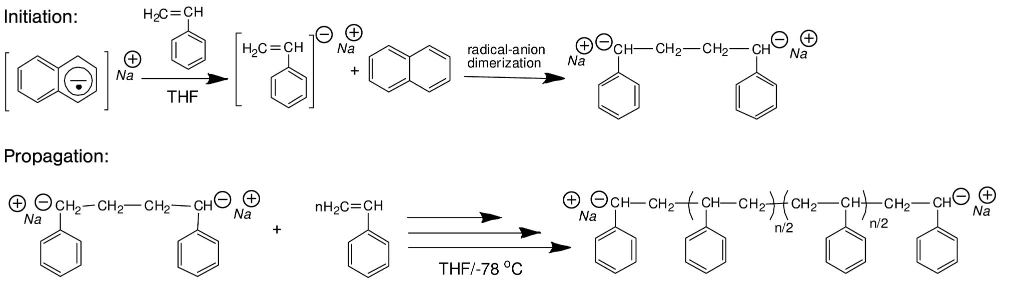
1.1
Introduction

1.1.1
The Discovery of Living Anionic Polymerization

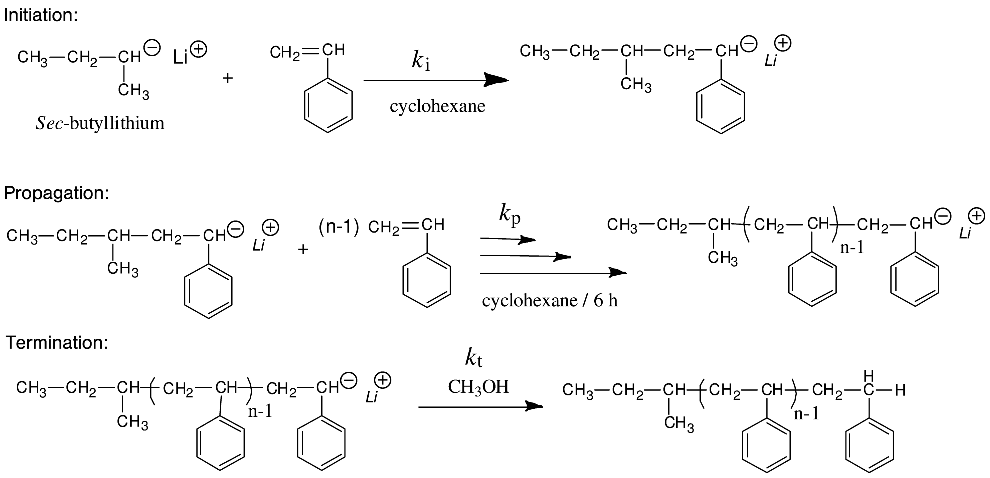
The concept of anionic polymerization was first developed by Ziegler and Schlenk in early 1910. Their pioneering work on the polymerization of diene initiated with sodium metal set the stage for the use of alkali metal containing aromatic hydrocarbon complexes as initiators for various α-olefins. In 1939, Scott and coworkers used for the first time the alkali metal complexes of aromatic hydrocarbon as initiators for the polymerization of styrene and diene. However, in 1956, it was Michael Szwarc who demonstrated unambiguously the mechanism of anionic polymerization of styrene, which drew significant and unprecedented attention to the field of anionic polymerization of vinyl monomers [1, 2]. Michael Szwarc used sodium naphthalenide as an initiator for the polymerization of styrene in tetrahydrofuran (THF). Upon contact with styrene, the green color of the radical anions immediately turned into red indicating formation of styryl anions. He suggested that the initiation occurs via electron transfer from the sodium naphthalenide radical anion to styrene monomer. The styryl radical anion forms upon addition of an electron from the sodium naphthalenide and dimerizes to form a dianion (Scheme 1.1).

After the incorporation of all the monomer, the red color of the reaction mixture persists, indicating that the chain ends remain intact and active for further propagation. This was demonstrated by the resumption of propagation with a fresh addition of another portion of styrene. After determining the relative viscosity of the first polymerized solution at its full conversion, another portion of styrene monomer was added and polymerization was continued. Thus, Szwarc characterized this behavior of the polymerization as *living polymerization* and called the polymers as *living polymers* [2]. Here, the term *living* refers to the ability of the chain ends of these polymers retaining

Controlled and Living Polymerizations. Edited by Axel H.E. Müller and Krzysztof Matyjaszewski
© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-32492-7



Scheme 1.1 Anionic polymerization of styrene using sodium naphthalene as initiator in THF.



Scheme 1.2 Anionic polymerization of styrene using *sec*-butyllithium as initiator.

their reactivity for a sufficient time enabling continued propagation without termination and transfer reactions.

Szwarc's first report of living anionic polymerization of styrene free from termination and transfer reactions in THF marks the beginning of lively research activities in this field [1–5]. Subsequent work on the anionic polymerization of styrene and dienes in hydrocarbons using alkyllithium initiators stimulated interest in this field [6–8]. Scheme 1.2 shows the anionic polymerization of styrene initiated by *sec*-butyllithium.

1.1.2
Consequences of Termination- and Transfer-Free Polymerization

Detailed kinetic measurements confirm that the polymerization of styrene in fact is free from termination and transfer reactions [1, 2]. Assuming a fast

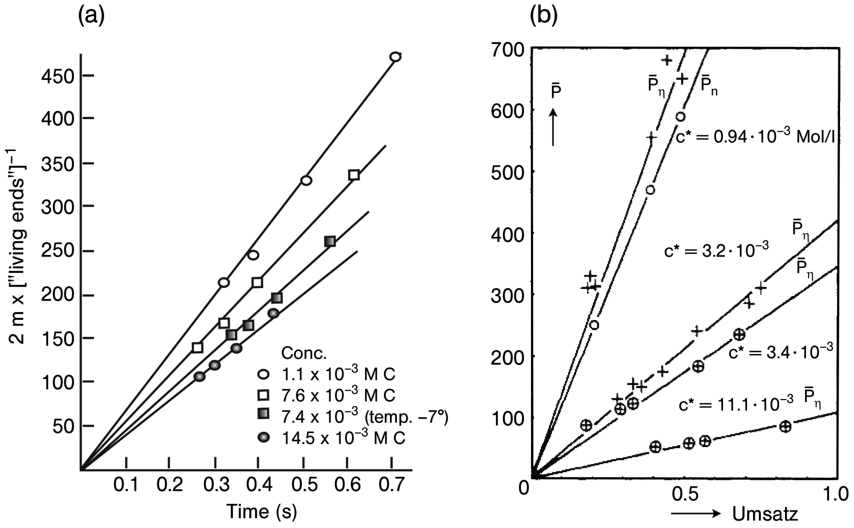


Figure 1.1 (a) Rate of polymerization of polystyrene in THF at 25 °C ('m' corresponds to $[M]_0/[M]_t$) [9]. (b) Number- and viscosity-average degrees of polymerization of polystyrene vs. conversion at various chain-end concentrations, c^* [10]. (Reprinted with permission from Wiley-VCH.)

initiation step, the rate of polymerization is given by

$$R_p = -\frac{d[M]}{dt} = k_p \cdot [P^*] \cdot [M] \tag{1.1}$$

where $[M]$ is the monomer concentration, k_p is the rate constant of propagation, and $[P^*]$ is the concentration of active chain ends. In the absence of termination, $[P^*]$ is constant, and the product $k_\mathrm{p}[P^*] = k_\mathrm{app}$ can be regarded as an apparent first-order rate constant. Introducing monomer conversion, $x_\mathrm{p} = ([M]_0 - [M]_t)/[M]_0$, integration of Eq. (1.1) leads to

$$\ln\frac{[M]_0}{[M]_t} = -\ln(1 - x_\mathrm{p}) = k_\mathrm{p} \cdot [P^*] \cdot t = k_\mathrm{app}t \tag{1.2}$$

Figure 1.1a shows a historic plot of such a first-order time-conversion relation. The linearity indicates that the active center concentration remains constant throughout the polymerization. In case of termination, $[P^*]$ depletes and thus the slope of the first-order plot decreases. It must be noted that this plot does not give evidence for the absence of transfer, since in this case the concentration of active chain ends remains constant.

The absence of transfer can be demonstrated by the linearity of a plot of the number-average degree of polymerization, DP_n, vs. conversion:

$$\overline{\mathrm{DP}}_n = \frac{\text{concentration of consumed monomers}}{\text{concentration of chains}}$$

$$= \frac{[M]_0 - [M]_t}{[P]} = \frac{[M]_0}{[P]} \cdot x_p \tag{1.3}$$

where $[P]$ denotes the *total* number of chains, active and inactive ones, which are generated in the transfer process. In an ideal polymerization $[P] = [P^*] = f[I]_0$, where $[I]_0$ is the initial initiator concentration and f the initiator efficiency. In case of transfer, $[P]$ increases and the slope of the plot decreases. Figure 1.1b shows a historical plot from Schulz *et al.* [10]. This indicated that the propagating anions are free from transfer and the molecular weight of the chains correspond to theoretical molecular weight depending on the monomer conversion [11].

The absence of termination and transfer reactions has two important consequences: (i) the number-average molecular weight, M_n, of the resulting polymer is determined by the amount of consumed monomer and the initiator used for the polymerization[12] and (ii) all the chains at any time, t, propagate at the same rate and acquire the same length after a subsequent time interval, $t + \Delta t$. This leads to a linear growth of polymer chains with respect to the monomer consumption, leading to a narrow distribution of chain lengths characterized by a *Poisson* distribution; the polydispersity index is given by

$$\mathrm{PDI} = \frac{\overline{M}_w}{\overline{M}_n} \approx 1 + \frac{1}{\overline{\mathrm{DP}}_n} \tag{1.4}$$

This distribution had already been derived by Flory in 1940 for the ring-opening polymerization of ethylene oxide [13]. This was experimentally confirmed by Schulz and coworkers who determined the polydispersity index, M_w/M_n, of Szwarc's samples and found that they were in the range of 1.06–1.12 [14].

Monomer resumption experiment is another way to show the absence of termination. Here, a second batch of monomer is added after a certain period has elapsed after full monomer conversion. In case of termination, one will find a bimodal distribution, one peak from the terminated chains and another from the active chains that participated in chain extension with the second batch of monomer.

It is important to note that not all living polymerizations lead to narrow molecular weight distributions (MWDs). First, a *Poisson* distribution is obtained only if the rate of initiation is much faster than that of propagation. Second, as is discussed later, many chain ends in anionic polymerizations (and also in other types of living polymerizations) can exist in various states, e.g., covalent species, aggregates, various types of ion pairs, or free anions, which propagate at different rates or are inactive ("dormant"). Different types of chain ends in anionic polymerization exist in equilibrium with each other and a chain end can change its state depending on the reaction condition such as the polarity of solvent and the temperature. If the rate of exchange between these species is slow compared to the rate of propagation, this can lead to a significant broadening of the MWD.

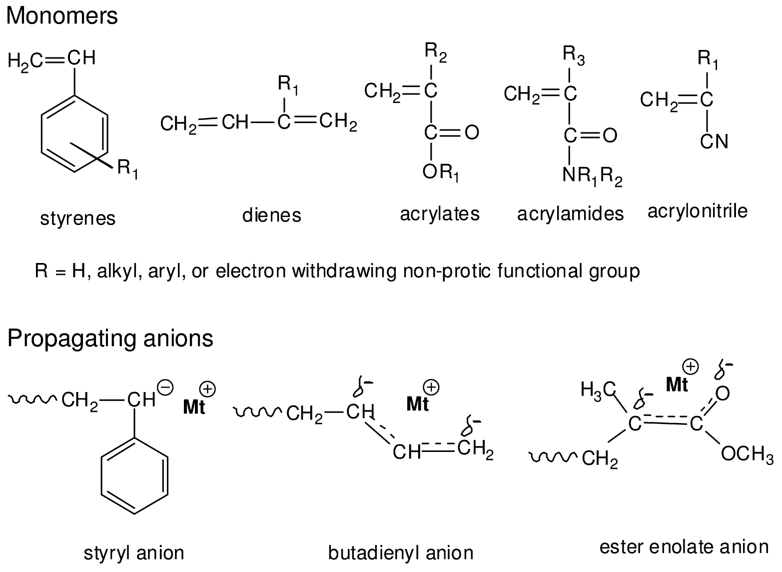


Figure 1.2 Major class of vinyl monomers and their corresponding propagating anions.

1.1.3
Suitable Monomers

A variety of α-olefins substituted with an electron withdrawing group have been subjected to anionic polymerization [15, 16]. Several substituted α-olefin monomers can be polymerized via anionic polymerization except the ones with functional groups bearing acidic protons (or other electrophiles) for the obvious reason that electrophiles react with carbanions and thus either quench the initiator or terminate anionic propagation. However, after appropriate protection, those monomers can be polymerized [17–19]. Hydrocarbon monomers such as dienes and styrene, polar vinyl monomers such as vinyl pyridines, (meth)acrylates, vinyl ketones, acrylonitriles, and cyclic monomers containing oxirane, lactones, carbonates, and siloxanes have been polymerized using anionic initiators [16]. The anionic polymerization of heterocyclic monomers is discussed in Chapter 5. A list of major classes of substituted α-olefin monomers with their corresponding propagating anions is given in Figure 1.2. The reactivity of these propagating anions and their nature of ion pairs are dependent on reaction conditions. The substitution (R_1, R_2, R_3) in the olefin monomers can vary from H, alkyl, aryl, and protected silyl group, leading to numerous monomers that are amenable for anionic polymerization [20, 21]. Various other monomers that are anionically polymerizable with limited control over the polymerization include ethylene, phenyl acetylene, vinyl ketones, and vinyl sulfones and α-olefins with other electron withdrawing group such as $-CN$ and $-NO_2$. A detailed list of monomers for anionic polymerization is given in various books and reviews [21, 22].

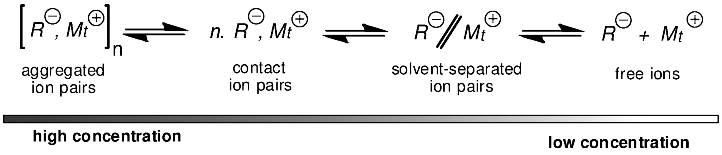
In the following, we first discuss characteristics of carbanions and their ion pairs in different conditions and their function as initiators and chain ends in the anionic polymerization of vinyl monomers. As our intention is to cover the fundamental aspects related to the mechanism of anionic vinyl polymerization in this chapter, the architectural controls using active chain-end manipulations and copolymerization have not been included; they will be covered in other chapters of this book. The existence of different forms of ion pairs in polar and nonpolar solvents and their dynamic equilibrium will be described. Subsequently, the detailed mechanism of anionic polymerization of styrene, dienes, and acrylic monomers in polar and nonpolar solvents will be discussed. Finally, we present some examples of industrial and scientific applications of anionic polymerization.

1.2
Structure of Carbanions

The rate of anionic polymerization of styrene using alkyllithium as initiator strongly depends on the solvent. It is very fast in polar solvents like THF. It is much slower in aromatic hydrocarbons such as benzene and even slower in aliphatic hydrocarbons such as cyclohexane. This is due to the different states of solvation and aggregation of carbanions in these solvents [23, 24]. Therefore, the mechanism of anionic polymerization is complicated due to the contribution of different forms of ion pairs. Thus, we will first examine the various forms of carbanions used in polar and nonpolar solvents before analyzing the mechanisms of initiation and polymerization.

Various factors affect the reactivity of carbanions, and it is important to understand the properties of carbanions that assume different structures depending on the environment. The polarity of the solvent in which anion is prepared and used, the intermolecular ionic interactions, and the size of metallic counterion all dictate the characteristics of a particular carbanion. The stabilization of anions through intermolecular interaction leads to the formation of different associated states called *aggregates*. The nature of anion aggregation is governed by various factors such as the charge density of anion, interionic distances, the dielectric constant, and the donating properties of the solvent [25]. Thus, the aggregated anions always exist in dynamic equilibrium with nonaggregated ones.

Fuoss [26, 27] and Winstein *et al.* [28] independently proposed the existence of two different forms of ion pairs based on the interionic distance. Accordingly, the anion present in solution may be tightly associated with counterion or loosely with solvated counterion. They named a tightly associated anion with cation as contact ion pair and a loosely associated anion with solvent-coordinated cation as solvent-separated ion pair. The different forms of ion pairs that are in equilibrium with each other are shown in Scheme 1.3. Depending on the concentration, the solvent-separated ion pairs can dissociate



Scheme 1.3 Fuoss–Winstein spectrum of anion pairs in a polar solvent.

into free ions and they can also associate intermolecularly to form triple ions. The reactivity of the free ions and solvent-separated ion pairs is very high when compared to that of contact ion pairs. The position of this equilibrium is controlled by the polarity of the solvent as well as the concentration of ion pairs used for the polymerization (Scheme 1.3).

Low temperature favors the formation of solvent-separated ion pairs due to the higher dielectric constant of the solvents at low temperatures. Spectroscopic evidence for the existence of contact- and solvent-separated ion pairs was found by Smid and Hogen-Esch. Two distinct temperature-dependent ultraviolet absorption bands were found for fluorenyl sodium solution in THF [29–31].

The ion pair equilibrium shifts to the formation of free ions, especially at low concentration of ion pairs and in highly solvating media. Although the dissociation of contact- or solvent-separated ion pairs into free ions occurs to a very low extent in polar solvent, their participation in propagation increases the reaction rate tremendously [32, 33]. The participation of free ions during the propagation can be suppressed by addition of a highly dissociating salt containing a common ion, e.g., a tetraphenylborate. The presence of free ions can be identified through conductivity measurement, as the free ions are conductive compared to the nonconductive ion pairs [27, 34].

Although contact ion pair solutions do not show conductance at low concentration, Fuoss found high equivalent conductance at higher concentration [35, 36]. Fuoss and Kraus suggested the formation of a new type of ion pair through intermolecular association called *triple ion* [35–37]. The presence of free anions, ion pairs, triple ions, and aggregated ion pairs plays an important role in anionic polymerization carried out in polar media, as will be seen later.

In nonpolar solvents, the ion pairs exist mostly in the aggregated state in equilibrium with a small amount of contact ion pairs. Of course, initiation and propagation are controlled by the reactive nonaggregated ion pairs irrespective of their concentration as they exist in fast equilibrium with aggregated ones.

1.3
Initiation

In general, the anionic polymerization like in other vinyl polymerization methods consists of three main reactions: (i) initiation, (ii) propagation, and (iii) termination, as described in Scheme 1.2. However, termination is brought about intentionally using a suitable electrophile, which can be useful for end group modification.

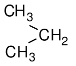
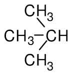
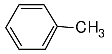
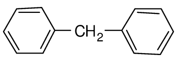
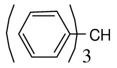
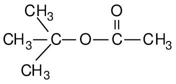
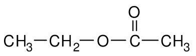
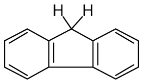
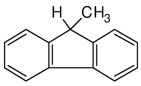
For a well-controlled anionic vinyl polymerization, the initiation reaction is generally fast and is not reflected in the overall rate of the polymerization. The kinetics of the polymerization is predominantly controlled by the propagation step. However, some initiators initiate vinyl monomer slowly over a period of time or with induction period and have significant influence on over all reaction rate as well as affect the MWD of the polymers [38–40]. The kinetics is complicated with the behavior of propagating ion pairs and their association and interaction with solvent molecules (see below). The interaction of propagating ion pairs with functional groups of the vinyl monomer or the polymer chain can affect the propagation rate and in some cases induces side reactions that can cease the polymerization. In a side reaction-free anionic vinyl polymerization, the termination is a simple rapid reaction wherein anions are quenched through acidic hydrogen or another suitable electrophile.

It is important to judiciously choose an appropriate anionic initiator for the polymerization of a particular type of vinyl monomer. This is because the characteristics of carbanions differ significantly by their nucleophilicity and depend on the solvent polarity. The rate of initiation is strongly influenced by the aggregation state of anion and the intermolecular interactions of ion pairs that are formed through opening of the vinyl bond of the monomer and the formation of new propagating species. Hence, it is important to match the reactivity of the initiator with the propagating species in order to have fast and homogeneous initiation. A suitable measure of nucleophilicity is the pK_a value of the corresponding protonated mother compound of the chain end, e.g., butane for butyllithium, ethylbenzene for styrene, or methyl propionate for methyl acrylate polymerization (Table 1.1). Typically, the pK_a of the (protonated) initiator should be comparable to or higher than that of the propagating anion.

1.3.1
Anionic Initiators

Initiators for the anionic polymerization of vinyl monomers can be broadly classified into (i) radical anions, (ii) carbanions, and (iii) oxyanions, including their thio derivatives. As described above, the direct use of radical anions such as sodium naphthalenide in polar solvent for the polymerization of styrene forms dimerized bifunctional anionic propagating species during propagation [2]. Several aromatic hydrocarbons and α-olefins containing aromatic substitution can react with alkali metals to form radical anions. For example, the reaction of sodium metal and 1,1-diphenylethylene (DPE) generates a radical anion in polar solvent, which can be used as initiator for the anionic polymerization [43]. Similarly, the reaction of sodium with α-methylstyrene yields a radical anion in polar solvent, which oligomerizes to the tetramer at room temperature [44, 45]. The general mechanism of the formation of these types

Table 1.1 pK_a values of most important carbon acids related to anionic vinyl polymerization in dimethylsulfoxide solution [41, 42].

Carbon Acids	pK_a
CH_4	(56)
 $CH_3CH_2CH_3$	(51)[a]
 $(CH_3)_3CH$	(53)[a]
$CH_2{=}CH{-}CH_3$	(44)
	(43)
	32.2
	30.6
	(30.3)
 $CH_3{-}CH_2{-}O{-}C(=O){-}CH_3$	(~30)
	22.6
	22.3

[a] Determined in water.
Values in parenthesis are extrapolated estimates.

of initiators is a transfer of an electron from the surface of the alkali metal to the electron deficient aromatic hydrocarbon or monomer.

Alkali metals were used as initiators for the anionic polymerization of dienes in the past. The synthesis of Buna S rubber is a well-known example for the metal-initiated polymerization [46]. However, metals generate radical anions through electron transfer to the surface adsorbed monomer in a heterogeneous state. The generated monomer radical anions rapidly undergo dimerization to form new dianions, which then initiate monomer to bifunctional anionic propagation. Electron transfer initiators work efficiently in polar solvents providing fast generation of bifunctional growing chains. However, electron transfer is inefficient in nonpolar solvents due to the lack of solvation and it is not possible to prepare radical anions in nonpolar solvents. In the case of polymerization initiated by alkyllithiums in polar solvents, the initiating carbanions and the propagating carbanions are solvated and significantly less aggregated.

Another important class of initiator is simple carbanions; in particular, alkyllithiums derived directly from the reaction of alkylhalide and lithium [7, 8, 47, 48]. Alkyllithiums generally exist in aggregated form in hydrocarbons. The behavior of carbanions and their ion pairs is strictly controlled by their solvation with solvent molecules. The reactivity of carbanions differs significantly depending on the solvent polarity. The structure and reactivity of a carbanion also depend on the size of its counter cation, since it determines the interionic distance in a contact ion pair and the extent of solvation and intermolecular association. Alkyllithiums are highly reactive and unstable in polar solvents and at least the initiation step has to be performed at low temperature (−78 °C).

The intermolecular association of alkyllithium in solid state as well as in solution is well known [49–51]. The extent of aggregation depends strongly on the polarity of the solvent. As alkyllithiums are known to exist in different forms with different degree of intermolecular aggregation, an appropriate initiator should be used for the polymerization in order to have efficient initiation [22, 52–55]. Alkyllithium initiators are especially efficient in nonpolar solvents in the polymerization of hydrocarbon monomers [16].

The aggregation of initiators in nonpolar medium affects the efficiency of initiation of hydrocarbon monomers. The anionic polymerization of styrene and dienes using *n*-butyllithium as initiator in hydrocarbon medium is sluggish and the initiation is often incomplete due to the high degree of aggregation. The highly aggregated *n*-butyllithium shows incomplete initiation of styrene in cyclohexane. At complete monomer conversion, ∼30% and ∼42% of unreacted *n*-BuLi and *t*-BuLi, respectively, present in the polymerization. On the other hand, the less aggregated *sec*-BuLi undergoes fast initiation within a short time enabling proper control of the polymerization [23, 56–58].

In the case of alkyl (meth)acrylate polymerization, less nucleophilic anions should be used (often in conjunction with moderating ligands) to avoid attack of the monomer carbonyl group. Here, the charge distribution over two or three phenyl rings (e.g., 1,1-diphenylhexyl [59] or triphenylmethyl anions [60]) or larger aromatic systems (e.g., fluorenyl anions) [61, 62] attenuates the nucleophilicity enough. However, these initiators are not always nucleophilic enough to efficiently initiate the polymerization of hydrocarbon monomers. (An exception is 1,1-diphenylhexyllithium, which slowly initiates the polymerization of styrene [63, 64].) Ester enolates, which mimic the structure of the chain end, are also good initiators for (meth)acrylates. In conclusion, the selection of an initiator for the polymerization of a particular monomer is very important in order to obtain control of the propagation.

Alkylsodium and alkylpotassium are not frequently used, mostly in the initiation of diene polymerization [65]. However, sodium, potassium, and cesium salts of aromatic anions (e.g., benzyl, cumyl, diphenylmethyl, triphenylmethyl, and fluorenyl) [62, 66, 67] have been used quite frequently to initiate the polymerization of polar monomers such as alkyl(methacryalates). The complexity of the anionic polymerization arises mainly from the charge density of the anionic center in the initiator or in the propagating chain end as they are known to assume multiple configurations and conformations depending on the nature of medium in which they participate in the reaction [68, 69].

1.3.2
Experimental Considerations

Owing to the high nucleophilicity of the carb- or oxyanionic chain ends, the polymerizations must be conducted under inert conditions, i.e., in the absence of moisture or other electrophiles. Oxygen must also be avoided (even in the quenching agent!), since it undergoes electron transfer with carbanions, leading to chain coupling [70]. Thus, monomers, solvents, and reaction vessels must be thoroughly purged and filled with nitrogen or argon. For very high molecular weight polymers (needing very low initiator concentrations), reactions should be performed under high vacuum using special all glass vessels with glass break seals [71]. Some polymerizations proceed extremely fast in polar solvents (half-lives below 1 s). For those, flow-tube reactors with short mixing times have been developed [72]. Alternatively, the monomer should be added very slowly via the gas phase. An overview of experimental details is given by Fontanille and Müller [73].

1.4
Mechanism of Styrene and Diene Polymerization

1.4.1
Polymerization of Styrene in Polar Solvents: Ions and Ion Pairs

The first example of the polymerization of styrene in THF using sodium napthalenide at low temperature proceeded smoothly without any side reaction [1, 2]. Szwarc and his coworkers proved the transfer- and termination-free nature of the propagation through monomer resumption and kinetic experiments (Figure 1.1). They observed a resumption of the polymerization with a second dose of fresh monomer leading to 100% chain extension and also obtained a linear first-order time-conversion plot indicating the absence of termination during the propagation [9]. The observed experimentally determined (apparent) rate constant $k_{p,app} = k_{app}/[P^*]$ (i.e., the slope of the first-order time-conversion plot k_{app} divided by the concentration of active centers $[P^*]$) of the polymerization in THF increased with decreasing concentration of active centers [9]. This suggested the presence of different forms of ion pairs depending on the concentration of initiator.

Subsequently, intensive kinetics studies by Szwarc, Schulz, Ivin, and Bywater revealed that the apparent propagation rate constant of styrene with sodium counterion strongly depends on the ability of the solvent to solvate the counterion, decreasing from dimethoxyethane (DME) over THF and tetrahydropyran (THP) to dioxane [9, 10, 74–81]. This indicated that the structure of the propagating ion pairs of polystyryllithium distinctly depends on the nature of the solvent. It was shown that the experimentally determined rate constant of styrene polymerization, in the presence of various alkali metal counterions, increases linearly with the reciprocal square root of propagating chain-end concentration (Figure 1.3) [10, 82].

This behavior was attributed to the equilibrium of free ions and ion pairs, where the propagation rate constant of free anions, k_-, is much higher than that of the ion pairs, $k_\pm$ (Scheme 1.4). The mole fractions of free ions and ion pairs participating in the propagation are α and $1 - \alpha$, respectively [75, 83–86]. These can be calculated from Ostwald's law, using the dissociation constant, $K_{\text{diss}} = k_i/k_a$, and the total concentration of the ion pairs, $[P^*]$,

$$\frac{\alpha^2}{(1-\alpha)} = \frac{K_{\text{diss}}}{[P^*]} \tag{1.5}$$

Since $K_{\text{diss}} \ll 1$ (typically below 10^{-7} M),

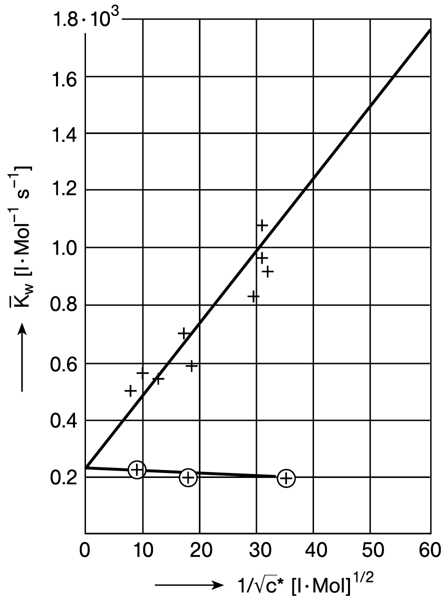
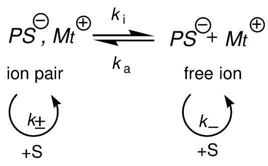


Figure 1.3 Dependence of the experimental rate constant of the anionic polymerization of styrene, $k_{p,\text{exp}}$, in THF with sodium counterion on the concentration of active chain ends, $[P^*]$. Circles denote experiments in the presence of sodium tetraphenylborate [10]. (Reprinted with permission from Wiley-VCH.)



Scheme 1.4 Participation of free ions in the anionic polymerization of styrene in THF.

$$\alpha \approx \sqrt{K_{\text{diss}}/[P^*]} \ll 1 \tag{1.6}$$

The apparent (i.e., experimentally determined) propagation rate constant is

$$k_{\text{p,exp}} = \alpha \cdot k_- + (1 - \alpha) \cdot k_\pm \tag{1.7}$$

leading to

$$k_{\text{p,exp}} = k_\pm + (k_- - k_\pm) \cdot \sqrt{K_{\text{diss}}/[P^*]} \tag{1.8}$$

Thus, the slope of a plot of $k_{\text{p,exp}}$ vs. $[P^*]$ gives $(k_- - k_\pm) \cdot \sqrt{K_{\text{diss}}}$ and the intercept gives the corresponding $k_\pm$ ("Szwarc–Schulz plot"; Figure 1.3) [75, 83–86]. Thus, the equilibrium constant of dissociation determines the apparent rate constant of propagation in anionic polymerization in polar solvents and this depends on the polarity of the solvent. The dissociation of the ion pairs can be efficiently suppressed by adding a common ion salt with higher degree of dissociation, e.g., sodium tetraphenylborate (Figure 1.3) [10, 75]. A plot of $k_{\text{p,exp}}$ vs. $[\text{Na}^+]^{-1}$ according to Eq. (1.9) can also be used to determine the dissociation constant, K_{diss}, independent of conductivity measurements.

$$k_{\text{p,exp}} = k_\pm + (k_- + k_\pm) \cdot (K_{\text{diss}}/[\text{Na}^+]) \tag{1.9}$$

With the knowledge of K_{diss}, the propagation rate constant of free anions was determined and found to be independent of counterion and solvent used, according to expectations [87].

The dynamics of the dissociation equilibrium has a slight effect on the MWD [88]. By analyzing the MWD of polymers obtained in the polymerization of styrene in THF, Figini *et al.* were able to determine the rate constants of dissociation and association separately [83, 88].

In the case of dioxane, a low dielectric medium ($\varepsilon = 2.25$), the propagation rate constants of ion pairs increase with increasing crystal radius of the cation [84, 89], which is attributed to easier charge separation in the transition state for larger cations. It was also expected and confirmed that for a given counterion, the ion pair propagation rate constants depend on the polarity of the solvent due to solvation of the counterion [89]. However, unexpectedly, in THF and in other polar solvents, the propagation rate constants of polystyryl ion pairs follow a reverse order with respect to the size of counterions; cesium ions leading to the slowest propagation. This led to a closer inspection of the nature of the ion pairs involved.

1.4.2
Contact and Solvent-Separated Ion Pairs

Szwarc and Schulz carried out kinetics of the propagation of polystyrylsodium in a variety of polar solvents over a large temperature range. Figure 1.4 shows

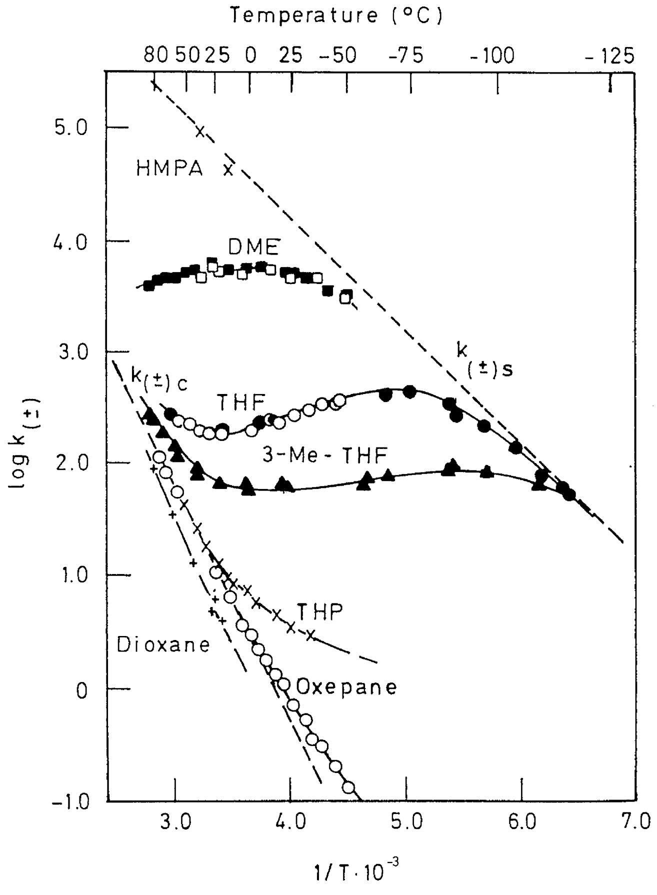
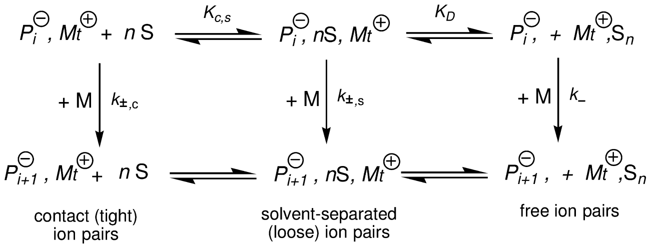


Figure 1.4 Arrhenius plot of the ion pair propagation rate constant in the polymerization of styrene with sodium counterion in polar solvents. (Reprinted with permission from Elsevier [87, 92].)

the Arrhenius plots of the ion pair propagation rate constants, $k_{\pm}$, for various solvents, exhibiting strongly *S-shaped* curves. In DME and THF, the rate constants even increase with decreasing temperature, which would lead to an apparently negative activation energy. Independently, Arest-Yakubovich and Medvedev found that the propagation rate of polybutadienylsodium in THF is independent of temperature below −56 °C and attributed this to a change in the structure of Na^+ solvation [90]. These results suggested the participation of another temperature-dependent equilibrium between two kinds of ion pairs, identified as contact ion pairs and solvent-separated ones [81, 91] (Scheme 1.5). The existence of solvent-separated ion pairs as distinct thermodynamically stable species was already outlined in Section 1.2.



Scheme 1.5 Three-state mechanism of styrene polymerization involving contact- and solvent-separated ion pairs and free anions with $k_{\pm,\mathrm{c}} \ll k_{\pm,\mathrm{s}} < k_-$.

Here, the overall (experimental) ion pair rate constant, $\overline{k_\pm}$, is given by

$$\overline{k_\pm} = \frac{k_{\pm,\mathrm{c}} + K_{\mathrm{c,s}} \cdot k_{\pm,\mathrm{s}}}{1 + K_{\mathrm{c,s}}} \approx K_{\mathrm{c,s}} \cdot k_{\pm,\mathrm{s}} \tag{1.10}$$

where $K_{\mathrm{c,s}}$ is the equilibrium constant for the interconversion of contact(c)- to solvent-separated(s) ion pairs and typically $K_{\mathrm{c,s}} \ll 1$. This interconversion is exothermic since the polarity of the solvent increases with decreasing temperature. Thus, at low temperature, the more reactive solvent-separated ion pairs are favored and the overall rate constant increases until the majority of monomer additions occur via the solvent-separated ion pairs.

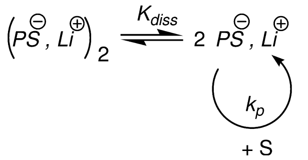
In dioxane, a poorly solvating medium, such a behavior was not observed, whereas in the strongly solvating medium, hexamethylphosphortriamide (HMPA), only solvent-separated ion pairs are found, which supports the above argument that the participation of different types of ion pairs depends on the polarity of the solvent.

In the presence of cesium counterions the participation of *triple ions* was observed in propagation. Results are reviewed by Smid *et al.* [93].

1.4.3
Polymerization of Styrene in Nonpolar Solvents: Aggregation Equilibria

1.4.3.1 Polymerization in Pure Solvents

Initiation and propagation of styrene and diene monomers in hydrocarbon solvent are significantly influenced by the aggregates of alkyllithium compounds [16, 94]. The nature of the alkyl group governs the degree of aggregation. Studies related to the kinetics of polymerization of *styrene* in benzene using *n*-BuLi as initiator began with the work of Worsfold and Bywater in 1960 [95]. The reaction order with respect to propagating anions is 0.5 in benzene, toluene, and cyclohexane [96–99]. This indicated that the growing polystyryllithium anions exist as less reactive dimers in equilibrium with reactive unimers in hydrocarbon solvents. Since the dissociation of lithium ion pairs into free ions is not possible in nonpolar solvent, the assumption



Scheme 1.6 Dimers and unimers in the anionic polymerization of styrene in nonpolar solvent.

of less active dimeric aggregates with coexisting minute amounts of reactive unimer was accepted as a plausible mechanism (Scheme 1.6).

Since the MWD of the polymers is very narrow, the interconversion rate between dimer and unimer must be very high relative to the propagation. As a result, a unimer with high reactivity dominates the propagation in the anionic polymerization of styrene in hydrocarbon solvents. The apparent rate constant of propagation (i.e., the slope of the first-order time-conversion plot) is given as

$$k_{\text{app}} = k_{\text{p,exp}}[P^*] = k_{\text{p}}[\text{P}^-\text{Li}^+] = \alpha k_{\text{p}}[P^*] \tag{1.11}$$

where the fraction of unimers, α, is given as

$$\alpha = \frac{[\text{P}^-\text{Li}^+]}{[(\text{P}^-\text{Li}^+)_2] + [\text{P}^-\text{Li}^+]} \approx \frac{[\text{P}^-\text{Li}^+]}{[P^*]/2} = \sqrt{K_{\text{diss}}/2[P^*]} \ll 1 \tag{1.12}$$

and K_{diss} is the dissociation constant of the dimers to unimers. This leads to

$$k_{\text{app}} = k_{\text{p}}(K_{\text{diss}}/2)^{1/2}[P^*]^{1/2} \tag{1.13}$$

Studies of Morton and coworkers on the viscosity of living polystyryllithium supported the existence of dimeric association [6]. They found that the viscosity of high molecular weight living polystyryllithium solution was 10 times higher as compared to the solution after termination with a drop of methanol. Since the viscosity of a semidilute polymer solution is proportional to $M^{3.4}$, association of two living polymer chains should lead to a viscosity increase by a factor of $2^{3.4}$, ~10.5. Light scattering studies of living and terminated chains confirmed this observation [68, 100].

1.4.3.2 Polymerization in Nonpolar Solvent in the Presence of Ligands

Lewis Bases (σ-Ligands) Owing to their ability to solvate lithium ions, electron donors, such as ethers or amines, have a dramatic effect on the polymerization of styrene in nonpolar solvents. The addition of THF to the polymerization of styrene in benzene strongly increases the rate of polymerization [101, 102]. When adding more than one equivalent of THF, the rates decrease and level off to a level that is higher than the original one (Figure 1.5). This was explained by the formation of two new species, the very reactive monoetherate and a less reactive dietherate, as seen in Scheme 1.7.

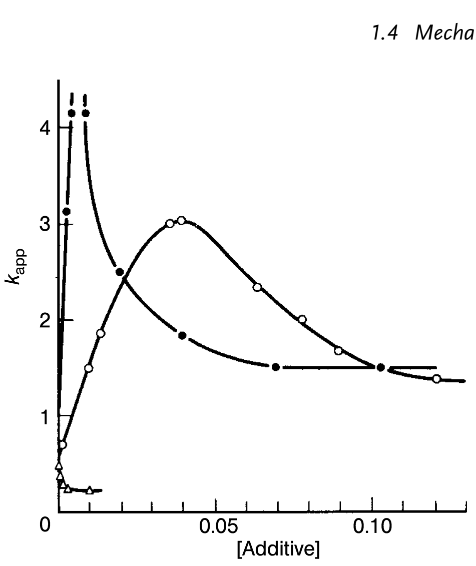


Figure 1.5 Effect of THF (●), 1,4-dioxane (○), and lithium *tert*-butoxide (△) on the polymerization of styrene in benzene, $c = 10^{-3}$ M [102]. (Reprinted with permission from the Canadian Society for Chemistry.)

$$(P\text{-}Li)_2 + 2\,\text{THF} \rightleftharpoons 2\,P\text{-}Li\cdot\text{THF} \xrightleftharpoons{2\,\text{THF}} 2\,P\text{-}Li\cdot 2\,\text{THF}$$

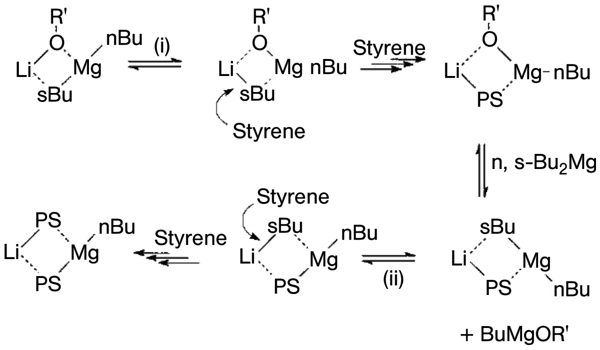
Scheme 1.7 Equilibria in the polymerization of styrene in benzene in the presence of THF.

Depending on the concentration, tertiary amines such as N, N, N', N'-tetramethylethylenediamine (TMEDA) can lead to an increase or decrease in the rate of polymerization [24, 103]. This is due to the fact that the reaction order in the absence of TMEDA is 1/2, whereas it is unity in its presence. The two lines of a plot of log $k_{\text{p,exp}}$ vs. log c intersect at a certain critical concentration.

Nonpolar ligands with high electron density, such as durene (tetramethylstyrene) or tetraphenylethylene, also affect the aggregation equilibrium and lead to an increase in the rate of polymerization followed by a decrease at higher concentrations. This is explained in terms of the formation of 1 : 1 and 2 : 1 π-complexes with the living chain ends [104].

Lewis Acids (μ-Ligands): Retarded Anionic Polymerization Lewis acids such as alkyl aluminum, alkyl zinc, alkyl magnesium, and lithium alkoxides form mixed aggregates with living chain ends of carbanions and significantly stabilize the ion pairs. In general, the addition of lithium alkoxides and other Lewis acids decreases the rate of polymerization of styrene and dienes (Scheme 1.8) [101, 105–107]. Since lithium alkoxides are even more strongly aggregated than the polystyryllithium chain ends, this leads to the formation of mixed aggregates (μ-complexes).

Addition of lithium chloride leads to a complex behavior, which was explained by the formation of mixed triple ions. These results are reviewed by Smid *et al.* [93].



Scheme 1.8 Mechanism of retarded anionic polymerization of styrene in the presence of dibutylmagnesium [109].

Alkali metal alkoxides (with Li, Na, and K counterions) also strongly affect the stereoregulation of diene polymerization as well as reactivity ratios in the copolymerization with styrene [16, 108].

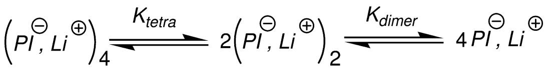
More recently, Deffieux and his collaborators have used a variety of magnesium and aluminum alkyls to retard the polymerization of styrene and at the same time stabilize the chain ends so significantly that they conducted the polymerization in bulk at temperatures of 100 °C and higher [110, 111]. They proposed a mechanism (Scheme 1.8) that involves the formation of mixed aggregates (“ate” complexes). They also showed that a combination of various alkali hydrides and magnesium or aluminum alkyls can be used to efficiently initiate the polymerization of styrene [109, 112, 113] and butadiene [114]. These results present a significant progress, enabling an industrial polymerization of styrene with inexpensive initiators in conventional reactors.

1.4.4
Anionic Polymerization of Dienes in Nonpolar Solvent

1.4.4.1 Kinetics

The anionic polymerization of dienes proceeds without side reactions in hydrocarbon solvents. Kinetic measurements indicated that the propagation is fractional order with respect to the active chain-end concentration [6, 48, 96, 99, 107, 115–119], again supporting the presence of inactive aggregated species. The reaction order with respect to the active center concentration was observed to be in the range of 0.16–0.25 for butadiene [16, 22], indicating hexameric or tetrameric aggregates. Viscosity studies gave ambiguous results, hinting to dimeric aggregates [120].

The aggregation number of living polyisoprenyllithium in benzene depends on the concentration of active centers [121]. The reaction order with respect to active center changes from ~0.25 to ~0.5 with decreasing concentration



$$\left(\overset{\ominus}{PI},\overset{\oplus}{Li}\right)_4 \underset{}{\overset{K_{tetra}}{\rightleftharpoons}} 2\left(\overset{\ominus}{PI},\overset{\oplus}{Li}\right)_2 \overset{K_{dimer}}{\rightleftharpoons} 4\,\overset{\ominus}{PI},\overset{\oplus}{Li}$$

Scheme 1.9 Aggregation equilibrium of polyisopropenyllithium in hydrocarbon solvent.

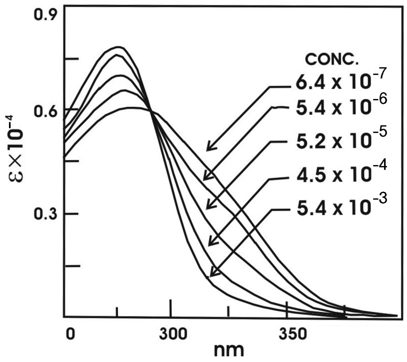


Figure 1.6 UV spectra of living polyisoprenyllithium in benzene solution at various concentrations [123]. (Reprinted with permission from Elsevier.)

[122], indicating a tetramer–dimer aggregation equilibrium (Scheme 1.9). The ultraviolet (UV) spectra of various concentrations exhibit two distinct absorptions at ~275 and ~325 nm with an isosbestic point, indicating a stoichiometric relation between the species formed at high and low concentration (Figure 1.6) [123].

There has been a long-standing, controversial debate in the literature on the nature of the active species in nonpolar solvents based on conflicting evidence from kinetics and direct observation of aggregation by viscosity, light scattering, and small-angle neutron scattering (SANS). SANS results of Fetters and coworkers indicated the existence of huge cylindrical micellar aggregates of polydienyllithium along with dimers and tetramers in dilute solution supporting their claim that dimers are the active species in polymerization [124–127]. These claims were questioned by others [128, 129]. In a recent SANS study, Hashimoto and his coworkers did not find evidence for the presence of such a large aggregates [130].

1.4.4.2 **Regiochemistry**

The regioselection of the diene addition to the ion pairs is controlled by the position of counterion (in particular lithium) and their coordination with incoming monomer, leading to different proportions of 1,2-, 3,4-, and 1,4-addition (the latter in cis or trans). For rubber applications, a high *cis*-1,4 content is important for a low glass transition temperature. This is achieved in nonpolar solvents and low temperatures. Ion pairs with counterions other than lithium have less effect on regiochemistry. The lithium ion undergoes specific solvation due to a short interionic distance compared to bulker metals.

Polar solvents or the addition of Lewis bases in hydrocarbon solvent occupy the coordination sites around the lithium ion and hinder monomer addition to the chain end. Instead, addition in the γ position is favored, leading to an increased fraction of 1,2-units (Scheme 1.10) [16].

The delocalization of ion pairs depends on the extent of solvation of counterion, and hence 1,2-addition of diene increases with increasing concentration of Lewis bases. As an example, equimolar amounts relative to the chain-end concentration of bispiperidinoethane can shift the structure of polybutadiene formed in hexane at room temperature from ~8% 1,2-units to ~99% [131]. More details of the effect of polar additives on the stereochemistry of polydiene and the kinetics of diene polymerization in nonpolar solvent can be found in the textbook of Hsieh and Quirk [16].

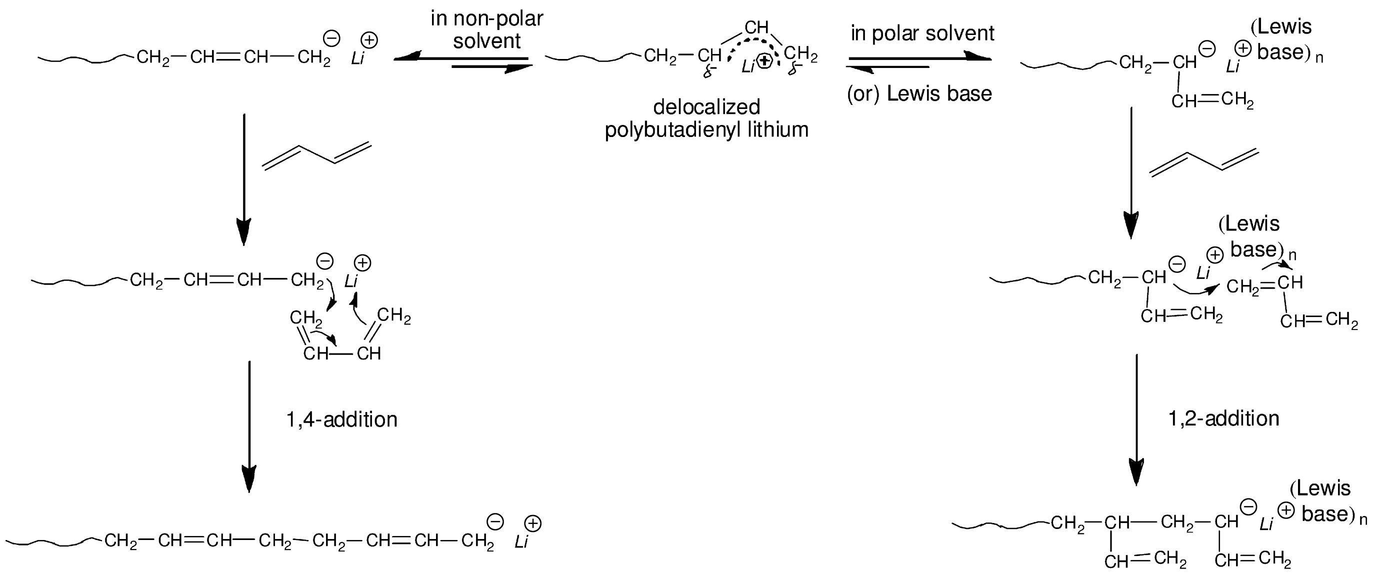
Many more mechanistic details, as well as the regio- and stereochemistry of diene polymerization (mechanism of formation 1,4-*cis* and *trans* isomers), and the kinetics of copolymerization of styrene with dienes can be found in a number of reviews and books [16, 22, 33, 92–94, 132–139].

1.4.5
Architectural Control Using Chain-End Functionalization

Architectural control through coupling of macrocarbanion chain ends opens endless possibilities in anionic vinyl polymerization to produce various type of branched homo or block copolymers (Figure 1.7). Termination of polymeric carbanions, especially, polystyryl and polydienyl, using chlorosilane reagents in nonpolar solvent is an efficient way to produce block and star copolymers. The coupling of chlorosilane with polymeric anion proceeds in a controlled manner through step by step elimination of halogen [140, 141]. Mays and Hadjichristidis and their coworkers pioneered chlorosilane coupling chemistry and synthesized various types of branched polymers, consisting of miktoarm stars, H-shaped polymers, multigrafts, and dendrimers [140, 142–144]. Similarly, Hirao, Quirk, and many others used alkylhalide-functional 1,1-diphenylethylene (DPE) as electrophilic coupling reagent to functionalize polymers to form macromonomers with DPE end group [145–150]. Through successive reinitiation and termination of DPE-functionalized chains, it is possible to synthesize well-defined stars, dendrimers, and hyperbranched polymers and copolymers. More details can be found in Chapter 7.

1.5
Mechanism of Anionic Polymerization of Acrylic Monomers

The most important classes of acrylic monomers are alkyl acrylates and methacrylates. Since some of their polymers, in particular poly(methyl methacrylate) (PMMA), are commercially very important, their polymerization



Scheme 1.10 Anionic propagation of 1,3-butadiene in nonpolar and polar medium and the control of microstructures through delocalization of ion pairs.

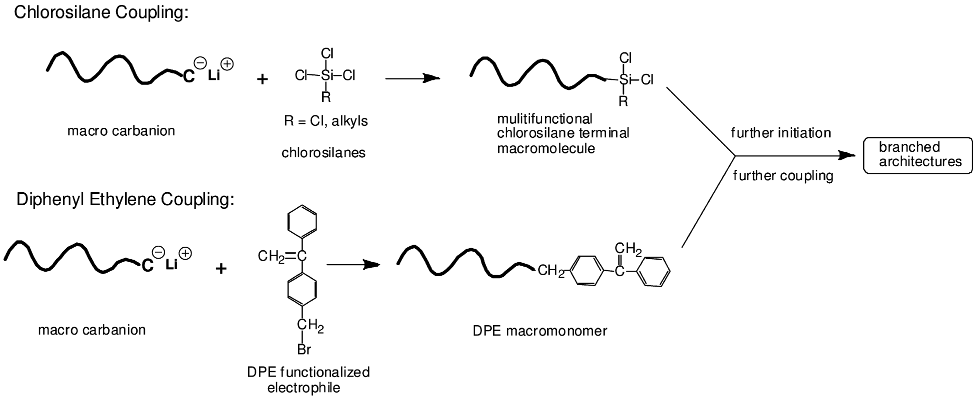


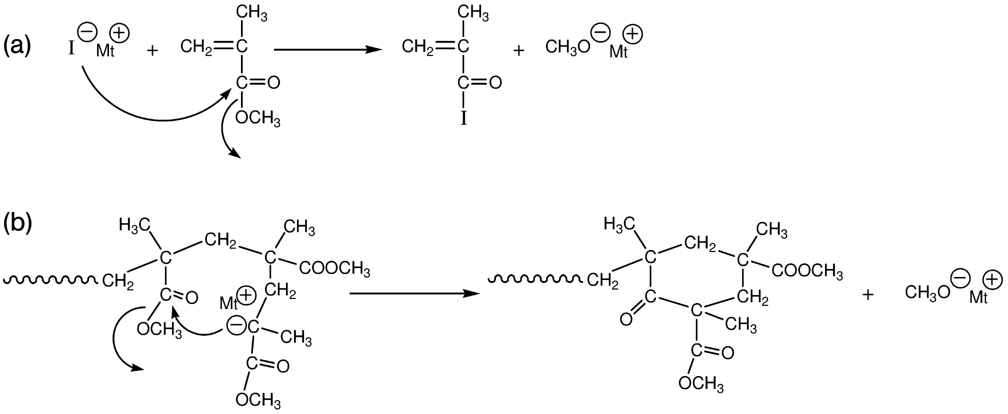
Figure 1.7 Strategies for the synthesis of various branched homo and block copolymer architectures using coupling reactions of multifunctional chlorosilanes and functional diphenylethylenes with polymeric carbanions.

has been investigated in great detail with respect to both kinetics and stereochemistry. More recently, the polymerization of *N*, *N*-dialkylacrylamides has found interest due to the interesting solution properties of the corresponding polymers and their dependence on tacticity.

1.5.1
Side Reactions of Alkyl (Meth)acrylate Polymerization

The initiation of alkyl (meth)acrylates with classical initiators like butyllithium is not straightforward and proceeds with several side reactions, yielding polymers of broad MWD with low conversion [151–158]. The nature of solvent and the size of cation influence the course of alkyl (meth)acrylate polymerization significantly. It proceeds in a controlled way in polar solvents with appropriate initiators (see above) at temperatures below −60 °C. In nonpolar solvents, the polymerization is complicated with incomplete monomer conversion and broad MWD. The occurrence of such side reactions has been experimentally confirmed by many authors [156–167]. The nonideal behavior of alkyl (meth)acrylates is basically due to two facts:

1. Side reactions by the nucleophilic attack of the initiator or the active chain end onto the monomer or polymer ester group, as proposed by Schreiber [152] and Goode *et al.* [61, 154] (Scheme 1.11a) and the intramolecular backbiting reaction (Scheme 1.11b).
2. Aggregation of the active chain ends, having an ester enolate structure. In contrast to nonpolar monomers, this occurs even in polar solvents such as THF and the consequences are discussed below.



Scheme 1.11 Side reactions in the polymerization of methyl methacrylate: (a) Initiator attack onto the monomer ester group and (b) backbiting reaction of propagating enolate anion.

The main termination reaction during *propagation* is the attack of the propagating enolate anion into the antepenultimate ester carbonyl group forming a cyclic β-ketoester (Scheme 1.11b) that was identified by infrared (IR) spectroscopy as a distinct band at 1712 cm^{-1} [154]. Evidence for the formation of vinylketone chain ends, the elimination of unreactive methoxide, and the formation of β-keto cyclic ester through the backbiting reaction was documented by several authors [154, 159–162, 168–172]. The side reactions were substantially reduced by using bulky and delocalized carbanions or Grignard reagents as initiators [161, 173–178]. 1,1′-Diphenylhexyllithium (DPHLi), the addition product of butyllithium and 1,1-diphenylethylene (DPE) [173], a nonpolymerizable monomer, diphenylmethyl [174], triphenylmethyl [60] and fluorenyl [179] anions have been used for the controlled polymerization of (meth)acrylates.

Ester enolates, in particular alkyl α-lithioisobutyrates, were introduced as initiators for methyl methacrylate (MMA) polymerization in polar and nonpolar solvents by Lochmann *et al.* [171, 180, 181]. As these initiators can be considered as a model for the propagating species in the anionic polymerization of alkyl (meth)acrylate, the rate of initiation and propagation was expected to be similar, which, in turn, should lead to polymers with narrow MWD. However, the ester enolate-initiated polymerization of MMA exhibited incomplete initiator efficiency, attributed to the presence of a higher degree of aggregation in both polar and nonpolar solvents [170, 181].

Using delocalized anions and large counterions (e.g., cesium), alkyl methacrylates can be polymerized in polar solvents, especially in THF or DME, at low temperature. However, with lithium as counterion, only moderate control is achieved. This is even worse for alkyl acrylates, in particular *n*-alkyl esters.

Several new initiating systems have been identified during the last two decades for the living polymerization of alkyl (meth)acrylates [182]. There are three main approaches employed for achieving living polymerization:

1. Use of various σ-type (Lewis base) and μ-type (Lewis acid) ligands that can form complexes with the counterion or with the propagating ion pair. This leads to a favorable aggregation dynamics for ligand-complexed ion pairs.
2. Use of nonmetal counterions. This class includes *group transfer polymerization* (GTP) with silyl ketene acetals (silyl ester enolates) as initiators and *metal-free anionic polymerization* using initiators with, e.g., tetrabutylammonium and phosphorous-containing counterions. This suppresses aggregation of ion pairs.
3. Coordinative-anionic systems involving aluminum porphyrin and zirconocene or lanthanocene initiators. This eliminates the ionic character of the propagating enolate and provides control of the polymerization through coordinative monomer insertion.

All these initiating systems enhance the livingness of the alkyl(meth)acrylate polymerization to varying degree to suppress secondary reactions and to achieve manipulations of active chain ends such as chain extension, block copolymerization, and functionalization. In addition, they moderate the position and the dynamics of the association equilibrium. The details of the polymerization of alkyl(meth)acrylates using these new initiating systems have been reviewed in detail by Baskaran [182]. Hence, we will briefly describe the behavior of classical enolate ion pairs, and then examine the newly developed strategies for the advancement of alkyl (meth)acrylate polymerization.

1.5.2
Alkyl (Meth)acrylate Polymerization in THF

1.5.2.1 Propagation by Solvated Ion Pairs

First mechanistic investigations of a living polymerization of MMA were published by Roig *et al.* [183, 184], Löhr and Schulz [185, 186], and Mita *et al.* [187] using sodium or better cesium counterions in THF at low temperature. Schulz, Höcker, Müller, *et al.* studied the effect of different counterions (Li^+, Na^+, K^+, and Cs^+) in the anionic polymerization of MMA in THF [179, 185, 188–191] and found living behavior at low temperatures (indicated by linear first-order time-conversion plots, linear plots of DP_n vs. conversion, and narrow MWD). They also observed a strong dependence of rate constants on the counterion size (except for K^+ and Cs^+; Figure 1.8) and obtained linear Arrhenius plots for the propagation rate constant, much in contrast to the kinetics of styrene polymerization in THF (Figure 1.4). Solvent polarity and

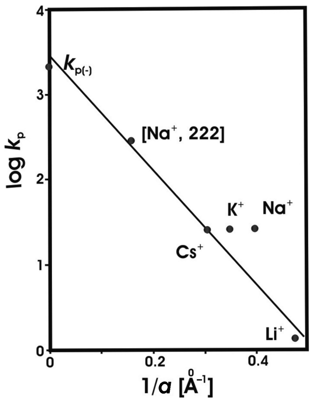


Figure 1.8 Dependence of propagation rate constant on the interionic distance, a, in the anionic polymerization of MMA in THF at −100 °C [191]. (Reprinted with permission from Wiley-VCH.)

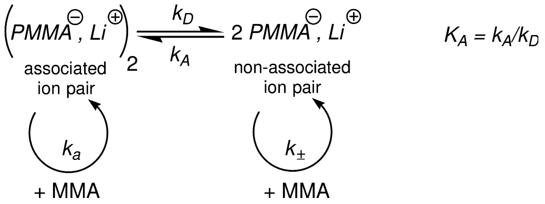
counterion size largely influence the rate of polymerization and affect the tacticity of the methacrylates [192].

The polymerization of MMA exhibits a good control in polar solvents such as THF and DME. *Glusker et al.* and Schulz *et al.* suggested that the polymerization is controlled due to the absence of intramolecular solvation of the counterion. In highly solvating media such as DME, the counterion is externally solvated with solvent coordination, thereby suppressing intramolecular termination via backbiting reaction at low temperature [155, 156, 189, 193]. Their results suggested that only one kind of active species is involved in the MMA polymerization, which they assigned as a peripherally solvated contact ion pair. Owing to a much stronger bond between the enolate oxygen and the counterion, solvent-separated ion pairs were not observed.

1.5.2.2 **Association of Enolate Ion Pairs and Their Equilibrium Dynamics**

The experimentally measured propagation rate constant, $k_{p,exp}$, of the MMA polymerization for Li$^+$ and Na$^+$ counterions was found to decrease with increasing concentration of active centers, [P^*] [194]. The participation of dissociated free enolate ion pairs in the propagation was rolled out as the addition of common ion salt had no or insignificant effect on the rate constants. Thus, the behavior was attributed to the coexistence of associated and nonassociated contact ion pairs propagating at two different rates.

Müller, Tsvetanov, and Lochmann found that the propagation rate constant of associated ion pairs, k_a, is much smaller than that of the nonassociated ion pairs, $k_\pm$, in alkyl (meth)acrylate polymerization (Scheme 1.12). The aggregation of chain ends was further confirmed by quantum-chemical calculations of ester enolates as models of chain ends [170, 195–197]. Aggregation of chain ends in a polar solvent is a feature that differs from the carbanionic ones, which associate only in nonpolar solvents.



Scheme 1.12 Equilibrium between associated and non-associated ion pairs.

The apparent rate constant of propagation, k_{app}, is determined by the rate constants of ion pair, $k_\pm$, the associates, k_a, and the fraction of nonaggregated species, α (Eqs. 1.14–1.16)

$$\begin{aligned} k_{\text{app}} &= [P^*]\left\{\alpha \cdot k_\pm + \frac{1}{2} \cdot (1-\alpha) \cdot k_a\right\} \\ &= [P^*]\left\{\frac{1}{2} \cdot k_a + \left(k_\pm - \frac{1}{2} \cdot k_a\right) \cdot \alpha\right\} \end{aligned} \tag{1.14}$$

and the fraction of nonassociated ion pairs, α, is given by [39, 196]

$$\alpha = \frac{[P_\pm{}^*]}{[P^*]} = \frac{(1 + 8K_A[P^*])^{1/2} - 1}{4 \cdot K_A[P^*]} \tag{1.15}$$

where K_A is the equilibrium constant of association. For $k_a[(P^*)_2] \ll k_\pm[P_\pm{}^*]$, Eq. (1.14) becomes

$$k_{\text{app}} \approx k_\pm[P_\pm] = \alpha k_\pm[P^*] = k_\pm \cdot \frac{(1 + 8 \cdot K_A \cdot [P^*])^{1/2} - 1}{4 \cdot K_A} \tag{1.16}$$

For a limiting case of high chain-end concentration, where $K_A[P^*] \gg 1$, Eqs. (1.15) and (1.16) become

$$\alpha = \frac{1}{\sqrt{2 \cdot K_A \cdot [P^*]}} \propto [P^*]^{-1/2} \tag{1.17}$$

$$k_{\text{app}} = \frac{k_\pm}{\sqrt{2 \cdot K_A}}\sqrt{[P^*]} \tag{1.18}$$

which leads to a reaction order of 0.5 with respect to $[P^*]$. For low chain-end concentrations, $K_A[P^*] \ll 1$, the aggregated ion pairs disappear ($\alpha \approx 1$) and $k_{\text{app}} \approx k_\pm \cdot [P^*]$, leading to a reaction order of unity with respect to $[P^*]$.

In fact, kinetic experiments of polymerization of MMA with lithium counterion in THF at −65 °C showed that the reaction order changes from 0.58 to 0.75 in the concentration range from 2.5 to 0.12 mM [197], allowing for the determination of $k_\pm$ and K_A and proving that aggregation is an important factor in the polymerization of alkyl (meth)acrylates in a polar solvent such as THF.

1.5.2.3 Effect of Dynamics of the Association Equilibrium on the MWD

The rate of interconversion between associated and nonassociated ion pairs in alkyl (meth)acrylate polymerization has a profound effect on the MWD of the polymer synthesized. Although the reactivity of aggregated lithium enolate chain ends is much lower than that of the nonassociated ones, a slow rate of interconversion between active species would allow both species to participate in propagation at two different rates. This leads to the formation of two different populations of polymers with a broad or bimodal MWD depending on the dynamics of the equilibrium. Broad or bimodal MWD was obtained in the polymerization of various (meth)acrylates with lithium counterion at −65 °C (Figure 1.9). Kunkel *et al.* [197] attributed the two peaks in the MWD of poly(*tert*-butyl acrylate) to aggregated and nonaggregated enolate chain ends. They also showed that the high polydispersity is not due to termination but due to the slow association phenomena.

Figini [88, 198] and others [199–202] have shown that, for a two-state mechanism, a slow exchange between various active (or between active and dormant) species leads to a broadening of the MWD (increase of polydispersity index, PDI) as given in Eq. (1.19):

$$\mathrm{PDI} = \frac{M_w}{M_n} = \left(\frac{M_w}{M_n}\right)_{\mathrm{Poisson}} + U_{\mathrm{ex}} \approx 1 + U_{\mathrm{ex}} \tag{1.19}$$

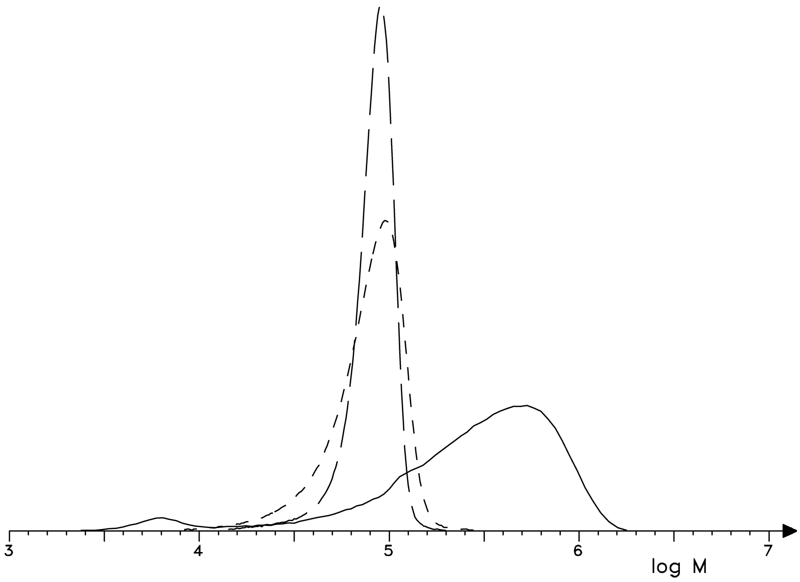


Figure 1.9 MWD obtained in the polymerization of MMA (·····, PDI = 1.3), *tert*-butyl methacrylate (-----; PDI = 1.1), and *tert*-butyl acrylate (——; PDI = 7.9) initiated by methyl α-lithioisobutyrate in THF at −65 °C [197]. (Reprinted with permission from Wiley-VCH.)

where U_{ex} is an additional nonuniformity that depends on the rate of exchange relative to the rate of propagation. The excess term, U_{ex}, is given by [203–205]

$$U_{ex} \cong \frac{2\langle n\rangle}{\overline{\mathrm{DP}}_n} \tag{1.20}$$

where $\langle n\rangle$ is the number of monomer additions between two exchange processes, averaged over the whole polymerization process, and DP_n is the number-average degree of polymerization. At a given conversion, n is identical to the ratio of the rates of polymerization and association [197]:

$$n = \frac{R_p}{R_A} = \frac{k_\pm \cdot [M] \cdot [P^*\pm]}{k_A \cdot [P^*\pm]^2} = \frac{k_\pm \cdot [M]}{k_A \cdot [P^*\pm]} \tag{1.21}$$

Averaging of "n" over the monomer concentrations up to a given monomer conversion, x_p, gives

$$\langle n\rangle = \frac{k_\pm}{2\,k_A \cdot [P^*\pm]} \cdot ([M] + [M]_0) = \frac{k_\pm \cdot [M]_0}{2\,k_A \cdot [P^*\pm]} \cdot (2 - x_p) \tag{1.22}$$

Introducing $\overline{\mathrm{DP}}_n = [M]_0 x_p/[P^*]$ and combining with Eq. (1.20) leads to

$$U_{ex} = \frac{k_\pm}{\alpha k_A}(2/x_p - 1) \tag{1.23}$$

and Eq. (1.19) becomes

$$\frac{M_w}{M_n} = 1 + \frac{k_\pm}{\alpha k_A}(2/x_p - 1) \tag{1.24}$$

For full monomer conversion ($x_p = 1$), Eq. (1.22) becomes

$$\frac{M_w}{M_n} = 1 + \frac{k_\pm}{\alpha k_A} \tag{1.25}$$

Thus, it is required to have high rates of association and high conversions to obtain polymers with narrow MWD in a polymerization system involving associated and nonassociated active species.

Kunkel *et al.* determined all the rate constants involved in this process [197]. They showed that the broad MWD obtained in the polymerization of *tert*-butyl acrylate (*t*BA) is only due to the fact that both the rate constants of association and dissociation are comparable to those for MMA polymerization, but that the rate constant of propagation is 50 times higher.

The concept of slow equilibria between various active and dormant species was later elaborated in more detail (including nonequilibrium initial conditions) and generalized to other kinds of exchange processes by Litvinenko and Müller [39, 206–209]. These calculations have been useful for various other living/controlled processes.

1.5.3
Modification of Enolate Ion Pairs with Ligands: Ligated Anionic Polymerization

The equilibrium dynamics of propagating ester enolate ion pairs in alkyl (meth)acrylates' polymerization both in polar and nonpolar solvents can be modified favorably in the presence of coordinating ligands. Several new ligands capable of coordinating with either the cation or the enolate ion pairs were reported in the literature. In general, the coordination of ligands with enolate ion pairs enhances the rate of interconversion between aggregated and nonaggregated chain ends, thereby altering the kinetics of propagation and to some extent suppressing the side reactions [174, 190, 210–226]. Wang *et al.* [227] have classified the coordination of ligands with enolate ion pairs into the following types:

1. σ-type coordination with Lewis bases such as crown ethers [212, 213], cryptands [190], or tertiary amines [216–219];
2. μ-type coordination with Lewis acids such as alkali alkoxides [228–231], lithium halides [197, 211, 232], lithium perchlorate [215, 233], aluminum alkyls [221–224], boron alkyls [225] and zinc alkyls [174];
3. $\sigma\mu$,-type coordination with alkoxyalkoxides [226, 234–236], aminoalkoxides [237], and silanolates [238].

1.5.3.1 **Lewis Base (σ-Type) Coordination**

The coordination of σ-type ligands such as various *tertiary diamines* (linear and cyclic) and cyclic ethers provides enhanced living character to alkyl (meth)acrylates polymerization through peripheral solvation depending on the sterics and number of coordination sites that are present in the ligand. The influence on the propagation and termination reaction varies on the strength of ligand coordination. For example, the addition of TMEDA was shown to increase the stability of the active centers of MMA polymerization in THF using the monomer resumption method [218] and in kinetic studies [216, 217]. The reaction order with respect to chain ends is 0.5, indicating that chelation of the lithium cation does not effectively perturb the aggregation state of the enolate ion pair. No significant difference in the rate of the polymerization was observed in the presence and in the absence of TMEDA at −20 °C. It was assumed that the chelation only replaces the THF molecules in the dimeric enolate ion pair retaining the peripheral coordination with lithium during propagation.

If a reactive initiator is used, it can metalate the ligand to mediate anionic polymerization. For example, the polymerization of MMA with *n*-butyllithium in pyridine or in a pyridine–toluene mixed solvent leads to monodisperse PMMA indicating a living character from −78 to −20 °C [219, 239, 240]. ^{1}H NMR showed the presence of the dihydropyridine end group in the polymer, indicating that the actual initiator is not the alkyllithium but an adduct with pyridine. In THF, a hindered alkyllithium initiator must be used to maintain molecular weight control.

Various *crown ethers* were used as ligands for the Na^+ counterion in the polymerization of MMA and *t*BA initiated by diphenylmethylsodium in toluene and in THF [212, 213]. The crown ethers substantially increase the monomer conversion, initiator efficiency, and improve the MWD of the resulting PMMA. It is assumed that the crown ether peripherally solvates the counterion, limiting the possibility of backbiting termination. No kinetic studies have been published so far.

Addition of *cryptand* 2.2.2 in the polymerization of MMA with Na^+ counterion in THF increases the propagation rate constants by orders of magnitude, indicating the presence of ligand-separated ion pairs [190].

Quantum-chemical calculations showed that a variety of structures can be formed by the various σ-ligands, including dimers and triple ions [241].

1.5.3.2 Lewis Acid (μ-Type) Coordination

Alkali alkoxides have a significant effect on the polymerization of alkyl (meth)acrylates [228–231]. Lochmann and Müller found that the addition of *lithium t-butoxide* strongly affects the rates of propagation and backbiting termination in the oligomerization of MMA [230] and *t*BA [242, 243] in THF at +20 °C (Figure 1.10). For MMA, the rate constant of propagation is decreased by one order of magnitude, but the termination rate constant is decreased by two orders. Thus, the enolate–alkoxide adduct has a 10 times lower tendency to undergo termination than the noncomplexed ion pair.

However, although *tert*-butoxide increases the livingness of polymerization, the MWD of the resulting polymers becomes broader [243], unless the alkoxide

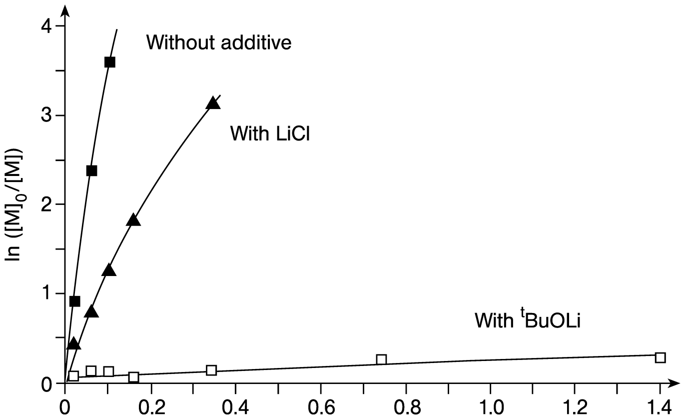


Figure 1.10 First-order time-conversion plots of the anionic polymerization of *tert*-butyl acrylate initiated by *tert*-butyl α-lithioisobutyrate in THF at +20 °C [243]. (Reprinted with permission from Wiley-VCH.)

is added in large (10 : 1) excess [244–246]. This is explained by the existence of various mixed tetrameric (or higher) aggregates in 3 : 1, 2 : 2, and 1 : 3 ratios of the enolate chain end and *t*-butoxide, which are in slow equilibrium with each other. In the 3 : 1 adduct, the degree of aggregation is even higher than in the noncomplexed dimer. Only in the presence of a large excess of alkoxide, the equilibrium is shifted to the side of the 1 : 3 adduct with only one kind of chain end.

Until the late 1980s, the controlled polymerization of alkyl acrylates had not been possible. Incomplete polymerization and very broad MWD (Figure 1.9) were reported. It was assumed that this might be due to both backbiting termination and a transfer reaction between the anion and a hydrogen alpha to an in-chain ester group. However, evidence for the latter has never been reported. In 1987, Teyssié and his coworkers [210, 247] reported for the first time the living anionic polymerization of *t*BA in THF in the presence of an excess of *lithium chloride*, leading to polymers with narrow MWD (Figure 1.11). It was assumed that the beneficial effect of LiCl is due to complexation with chain ends, which suppresses backbiting termination.

Kinetic experiments of Müller and coworkers, however, showed that LiCl affects the rate of propagation, but not the amount of termination [197, 242, 243]. The observed rate constant of propagation passes a slight maximum and then decreases with increasing LiCl/[P^*] ratio (Figure 1.12). Simultaneously, a strong decrease in the polydispersity index was observed with increasing concentration of LiCl. These observations were explained by the formation of 1 : 1 and 2 : 1 adducts of differing activity (Scheme 1.13). Quantum-chemical

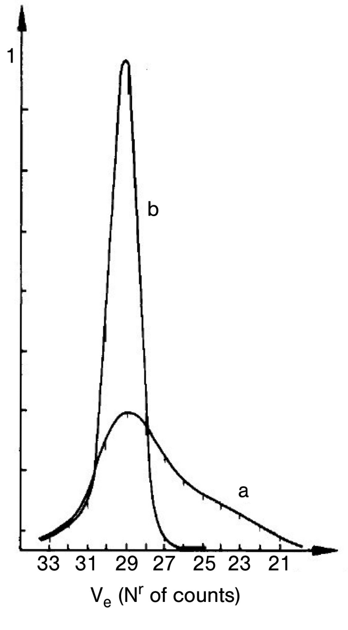


Figure 1.11 Size exclusion chromatography (SEC) traces of poly(*tert*-butyl acrylate) synthesized in the absence (a; PDI = 3.6) and in the presence of excess LiCl (b; PDI = 1.2) in THF using monofunctional α-methylstyryllithium as initiator [210]. (Reprinted with permission from the American Chemical Society.)

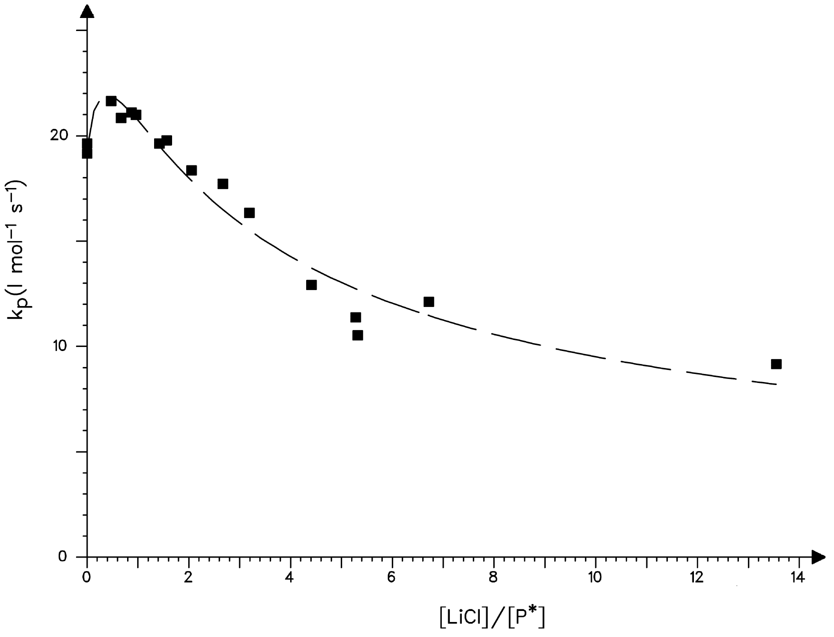


Figure 1.12 Effect of LiCl on the observed rate constant of polymerization in the anionic polymerization of MMA in THF at −65 °C initiated with methyl α-lithioisobutyrate. (Reprinted with permission from Wiley-VCH [197].)

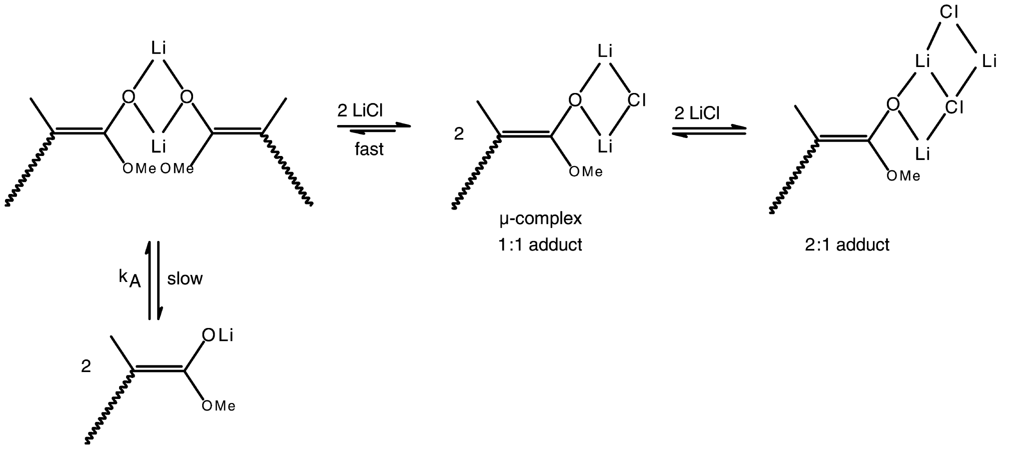
calculations confirmed that the 1 : 1 complex is more stable by 4 kJ mol^{-1} than the noncomplexed dimer [248]. The equilibrium between noncomplexed dimer and unimer is slow, whereas it is faster between the dimer and the LiCl-complexed unimer. The inefficiency of LiCl to control termination is demonstrated by the fact that one cannot control the polymerization on *n*-butyl acrylate (*n*BA) with this ligand. However, aluminum alkyls and σ, μ-ligands can lead to a living polymerization (see below).

Thus, the position of the equilibria between nonassociated, associated, and complexed ion pairs determines the rate of polymerization, whereas the dynamics of interconversion between species governs the polydispersity [197, 242, 243].

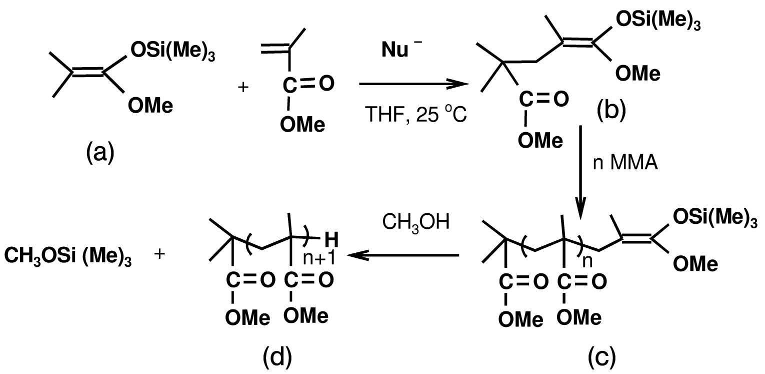
1.5.4
Metal-Free Anionic Polymerization

1.5.4.1 Group Transfer Polymerization (GTP)

In 1983, Webster and coworkers at DuPont demonstrated for the first time that a silyl ketene acetal (silyl ester enolate, Scheme 1.14a) is an initiator for the controlled polymerization of alkyl (meth)acrylates *at room temperature* [249].



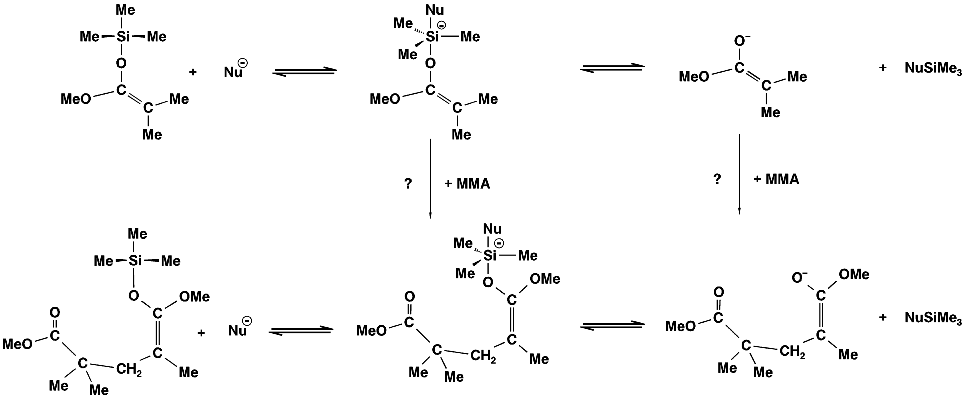
Scheme 1.13 Equilibria in the polymerization of (meth)acrylates in the presence of LiCl.



Scheme 1.14 Group transfer polymerization of MMA with nucleophilic catalyst.

The presence of a small amount of a nucleophilic or Lewis acid catalyst is necessary, leading to poly(alkyl methacrylates) with narrow MWD. The process was called *group transfer polymerization (GTP)* on the basis of the proposed mechanism, which involves the transfer of the trimethylsilyl group coordinated with a nucleophilic catalyst from the initiator or propagating chain end to the carbonyl oxygen of the incoming monomer (Scheme 1.14). It was proposed that the intramolecular transfer takes place via an eight-membered transition state in every insertion of monomer.

Various nucleophilic anions and Lewis acids have been identified as catalysts to promote GTP [249–257]. The relative efficiency of a nucleophilic catalyst strongly depends on the corresponding acidity (pK_a value) of the acid from which it is derived [251, 258, 259]. The Lewis acids are believed to activate monomers by coordination with carbonyl oxygen of acrylates, as indicated by the large amount of Lewis acid necessary (10% based on monomer) for a controlled polymerization [249, 260–262].

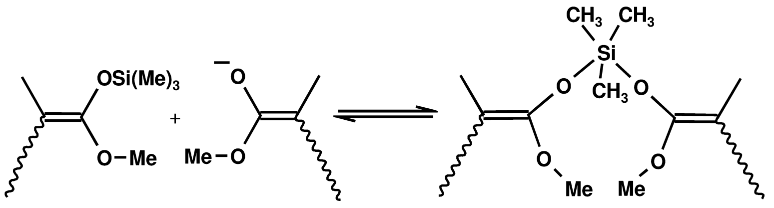


Scheme 1.15 Associative and dissociative mechanisms of GTP of MMA.

There has been a long discussion on the mechanism of GTP, which seems to depend on the type of catalyst used for the polymerization [251, 253, 259, 263–269]. This was originally proposed by Webster and Sogah. Double-labeling experiments supported a direct transfer of the pentacoordinated siliconate from a chain end to the incoming monomer's carbonyl group, named *associative* mechanism [270], though several questions related to this mechanism remained unanswered [271–276]. Kinetic experiments enabled Mai and Müller [259, 266, 277] to propose a modified two-stage associative mechanism in which the monomer adds to the α-carbon of pentacoordinated siliconate chain end and subsequently silyl group migration takes place to the carbonyl oxygen of the monomer. According to this mechanism, a fast exchange of catalyst between the dormant and active chain ends (Scheme 1.15, left equilibrium) is essential to have control on MWD. This exchange is essential because the catalyst concentration is typically in the range of 0.1–10% of that of the initiator concentration. They showed that the rate of polymerization is determined by the concentration of catalyst and the equilibrium constant of activation, whereas the polydispersity, if given by the dynamics of this equilibrium, is very similar to other living polymerization processes.

Quirk proposed a "dissociative" process where the pentacoordinated siliconate dissociates into an ester enolate anion and the corresponding trimethylsilyl–nucleophile compound (Scheme 1.15, right equilibrium) [272, 278]. The two equilibria ensure the necessary exchange of activity between dormant silyl ketene acetal and active enolate chain ends, leading to a control of molecular weight and MWD. Alternately, if dissociation is irreversible, the free enolate anion can exchange activity only in a direct reaction between an active enolate and a dormant silyl ketene acetal (degenerative transfer; Scheme 1.16) [272].

It is very important to note that the mechanism of GTP differs with the type of catalyst used for the polymerization. Moreover, it was found that



Scheme 1.16 Intermolecular activity exchange of an enolate anion with a silylketene acetal [272].

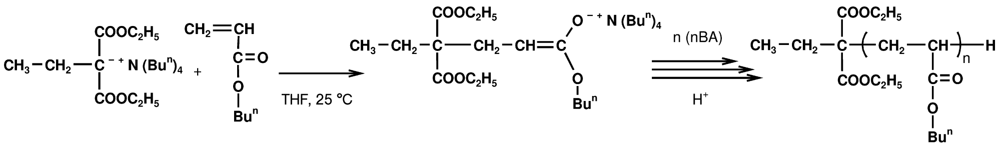
the reaction order with respect to catalyst concentration for the GTP of MMA obtained by different research groups varied depending on the nature of catalyst and its concentration [251, 253, 259, 266, 277]. Comparing the experimental data and the calculations of Müller, Litvinenko let to the conclusion that the mechanism of GTP strongly depends on the nature of the nucleophilic catalyst [39, 206–209, 268]. Catalysts that bind very strongly to silicon, such as bifluoride, seem to undergo an irreversible dissociative (enolate) mechanism, whereas less "silicophilic" catalysts, such as oxyanions, may add via both pathways.

The participation of enolate anions as intermediate during propagation goes along with the backbiting side reaction similar to classical anionic polymerization, although its significance is lower in GTP [279]. It was proposed that the silylalkoxide formed in the backbiting reaction might reversibly open the β-ketoester to reform the active chain end. The active centers of GTP of MMA undergo chain transfer reaction with various carbon acids ($18 < pK_a < 25$) [264, 280], which indicated its higher reactivity analogous to ester enolate active centers ($pK_a \sim 30-31$) (Table 1.1) [42] in the classical anionic polymerization.

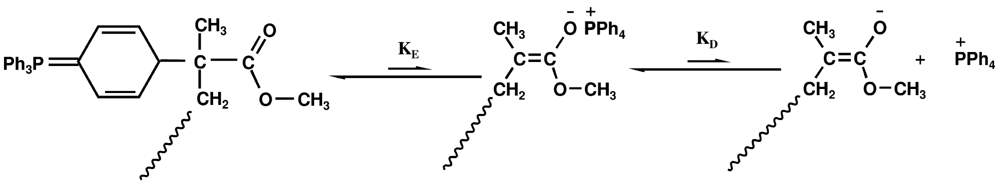
GTP has been used to synthesize a number of structures, including block copolymers [250], macromonomers [281], stars [282, 283], hyperbranched polymers [284, 285], or networks [286]. More detailed discussions on the mechanism and the applications can be found in a number of reviews on GTP [259, 287–290], in particular a very recent one by Webster [291].

1.5.4.2 **Tetraalkylammonium Counterions**

Reetz and coworkers [292–294] first used metal-free carbon, nitrogen, or sulfur nucleophiles as initiators for the controlled anionic polymerization of *n*BA. It was thought that replacing metal counterion in the polymerization would reduce the problem associated with aggregation and improve the control over the polymerization. Tetrabutylammonium salts of malonate derivatives provided poly(*n*-butyl acrylate) (P*n*BA) of relatively narrow MWD at room temperature (Scheme 1.17). Many metal-free initiators for the polymerization of alkyl (meth)acrylates using a variety of anions and cations have been reported [272, 295–299].



Scheme 1.17 Metal-free anionic polymerization of *n*BA with tetrabutylammonium counterions in THF at 25 °C.



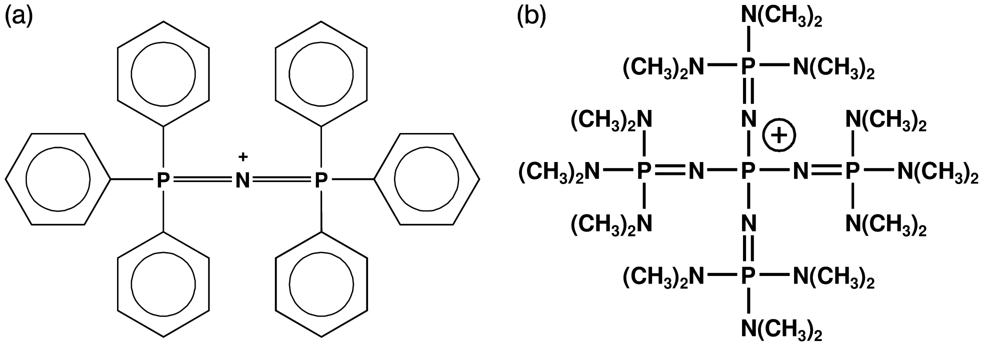
Scheme 1.18 Dynamic equilibrium between ylide, enolate ion pair, and enolate anion.

1.5.4.3 **Phosphorous-Containing Counterions**

Zagala and Hogen-Esch [300] used the tetraphenylphosphonium (TPP^+) counterion in the anionic polymerization of MMA at ambient temperature in THF and produced PMMA in quantitative yield with narrow MWD. Unexpectedly, the reaction solution during the polymerization was characterized by an orange-red color. A detailed kinetic study of the polymerization of MMA using trityl TPP^+ showed that the polymerization is very fast (half-lives at room temperature in the second range); however, the rate constants are two orders of magnitude lower than expected for such a large counterion [301]. It was concluded that the active centers exist in equilibrium with a dormant species. Nuclear magnetic resonance (NMR) and UV investigations on the model compound of the growing PMMA chain end, i.e., methyl tetraphenylphosphonium isobutyrate revealed the existence of a phosphor ylide as dormant species (Scheme 1.18) [302].

This system is different compared to tetrabutylammonium counterion as the phenyl group in the counterion undergoes nucleophilic attack by the enolate ion and forms ylide intermediate. The yilde is unstable and exists in equilibrium with enolate ion pairs. According to the kinetic and spectroscopic data, the fraction of active enolate chain ends is only 1%. The bis(triphenylphosphoranilydene)ammonium (PNP^+) cation (Scheme 1.19a) shows a lower tendency for ylide formation and leads to higher rates [303], whereas the (1-naphthyl)triphenylphosphonium ($NTPP^+$) cation has a strong tendency for ylide formation and propagates extremely slowly [304].

The phosphorous-containing cation that cannot form ylide, the tetrakis[tris (dimethylamino)phosphoranylidenamino] phosphonium ($P_5{}^+$) counterion (Scheme 1.19b) showed fast polymerization with the half-lives that are in the 0.1 s range and the rate constants are in the expected order of magnitude



Scheme 1.19 (a) PNP^+ and (b) $P_5{}^+$ cations.

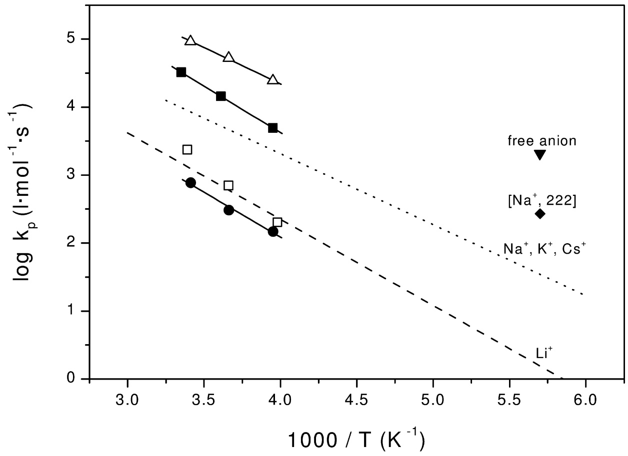


Figure 1.13 Arrhenius plot for the polymerization of MMA in THF with various counterions: (-----) Li^+; (· · · · ·) Na^+, K^+, Cs^+; (●) $Ph_3C^-TPP^+$ (K^+ precursor), (■) $Ph_3C^-PNP^+$ (K^+ precursor), (□) $Ph_3C^-PNP^+$ (Li^+ precursor), (△) $DPH^-P_5{}^+$ (Li^+ precursor) [303, 305]. (Reprinted with permission from Wiley-VCH.)

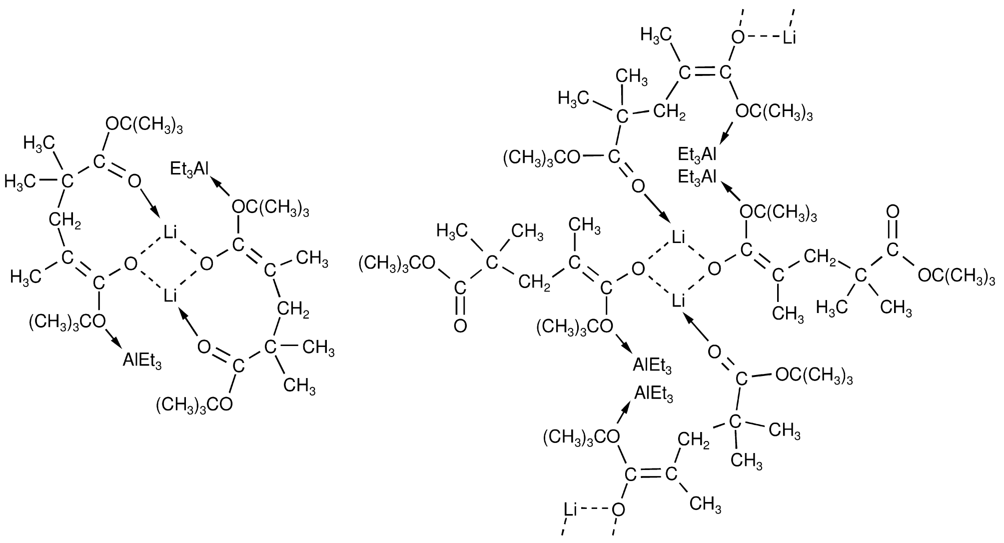
due to the absence of dormant ylide formation [305]. Figure 1.13 shows how these large counterions fit into the Arrhenius plot obtained with various metallic counterions, the cryptated sodium ion and the free anion. Quantum-chemical calculations have confirmed the ylide structure of various phosphorous-containing counterions [306].

1.5.5
Polymerization of Alkyl (Meth)acrylates in Nonpolar Solvents

In nonpolar solvents, the anionic polymerization of alkyl (meth)acrylates is complicated by the slow dynamics of the equilibria between multiple aggregates of ion pairs leading to very broad MWDs. In addition, it leads to more isotactic polymers, which have much lower glass transition temperatures than syndiotactic ones. Thus, a controlled polymerization has only been possible in the presence of ligands.

1.5.5.1 μ-Type Coordination

Hatada and coworkers [221, 307–311] first employed various aluminum alkyls, in particular triethylaluminum, Et_3Al, as additives and *tert*-butyllithium as initiator in the polymerization of MMA in toluene at −78 °C. They obtained syndiotactic polymers with controlled molecular weight and narrow MWD. The complexation of the aluminum compound with the initiator as well as the propagating center is essential to have a proper control of the polymerization. Ballard and his coworkers [222] demonstrated the living nature of MMA polymerization at ambient temperature in the presence of bulky diaryloxyalkyl aluminum. NMR and quantum-chemical investigations [312–314] on the model active center (i.e., ethyl α-lithioisobutyrate, EIBLi) in the presence of MMA and trialkylaluminum confirmed the coordination of the aluminum to the ester oxygen in the dimer of the lithium enolate. The mechanism is complicated by the fact that Et_3Al also forms complexes with the carbonyl groups of the monomer and the polymer. In addition, other carbonyl groups can coordinate with free coordination sites of the lithium atoms (Scheme 1.20). This leads to a physical gel at higher conversion and a downward kink in the time-conversion plot.



Scheme 1.20 Structures of intra- and intermolecular coordination leading to a coordinative network of living polymer chains in the presence of Et_3Al [314].

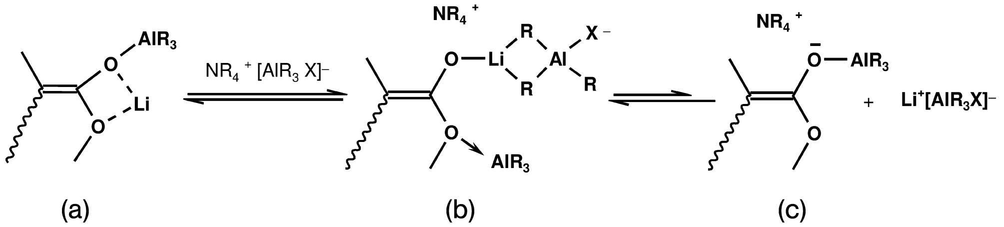
Schlaad *et al.* [223, 315] used several Lewis bases to attach to the free coordination sites of the lithium ion, thus suppressing the network formation during the polymerization. Linear first-order time-conversion plots with higher rates and polymers with much narrower MWD were obtained in the presence of excess methyl pivalate and methyl benzoate. A further improvement was the use of tetraalkylammonium halides as additives, forming a complex with trialkylaluminum, e.g., $NBu_4^+[Al_2Et_6Br]$. They observed linear first-order time-conversion plots using EIBLi as initiator in the presence of high concentration of $NBu_4^+[Al_2Et_6Br]$. The rate of the polymerization is two orders of magnitude higher as compared to the EIBLi/$AlEt_3$ initiating system in toluene/methyl pivalate (3 : 1 v/v) mixed solvent [224, 316]. Similarly, cesium halides can be used as co-ligand [317]. This system combines the advantages of a nonpolar solvent (toluene), convenient temperatures (−20 °C), with easily controllable rates (minutes to hours) and very narrow MWD (PDI < 1.1).

The rather complex kinetics of the process were attributed to an equilibrium between the trialkylaluminum–enolate complex (or its dimer) (Scheme 1.21a), a trialkylaluminum–halide–enolate "ate" complex with tetrabutylammonium counterion (Scheme 1.21b), and a tetraalkylammonium trialkylaluminum enolate (Scheme 1.21c) [314, 316].

This system is also useful for the controlled polymerization of *n*BA below −65 °C, in particular when using cesium fluoride/triethylaluminum as ligand [317, 318]. *n*BA had eluded a controlled anionic polymerization so far, except for the use of lithium alkoxyalkoxides as σ, μ-ligands (see below).

The triethylaluminum system was further modified by Kitayama's group who revived the Ballard system of bulky diphenoxyalkylaluminum ligands and found that these systems lead to a very high control of stereoregularity [319–321]. A further improvement was obtained by Hamada *et al.* by adding multidentate σ-ligands to these systems, allowing for the living polymerization of MMA and even *n*BA at 0 °C [322–325]. At present this system seems to be the most useful one to polymerize *n*-alkyl acrylates in a controlled way.

Recently, Ihara *et al.* reported the use of triisobutylaluminum in combination with potassium *tert*-butoxide for the living anionic polymerization of *t*BA and MMA in toluene at 0 °C [326, 327].



Scheme 1.21 Equilibria between various species in the polymerization of MMA in the presence of trialkylaluminum and tetraalkylammonium halide.

1.5.5.2 σ, μ-Type Coordination

Polydentate lithium alkoxyalkoxides and aminoalkoxides, as well as dilithium alkoxyalkoxides, have been used as powerful additives in the alkyl (meth)acrylate polymerization [214, 226, 234, 236, 237, 328]. In the presence of these ligands, living polymerization of even primary acrylates proceeded in a controlled manner in THF, in toluene, and in toluene–THF (9:1 v/v) mixed solvent at −78 °C [329]. The rate of MMA polymerization in the presence of lithium 2-methoxyethoxide (LiOEM) in toluene is extremely high ($k_p > 10^4\ \mathrm{l\,mol^{-1}\,s^{-1}}$) [236]. The polymerization proceeds with half-lives in the subsecond range without termination at 0 °C. Baskaran reported the use of dilithium triethylene glycoxide as ligand to achieve control over the living anionic polymerization of MMA using DPHLi as initiator at 0 °C [226], resulting in quantitative conversion, relatively narrow MWD ($1.29 \leq M_w/M_n \leq 1.37$), and high initiator efficiency ($0.81 \leq f \leq 1$). The enhanced living character brought by polydentate dilithium alkoxide ligand was attributed to the formation of a sterically hindered mixed aggregate whose equilibrium dynamics between the complexed ion pairs and uncomplexed ion pairs is high enough to produce narrow MWD PMMA at 0 °C [226, 236]. The complex structure of the chain end, involving tetrameric and hexameric aggregates with coordination of the ether oxygens with lithium, was also confirmed by quantum-chemical calculations [330]. This polymerization has been recently commercialized by Arkema (former Elf-Atochem) to synthesize polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) (SBM), where the PMMA block is synthesized in a flow-tube reactor [331].

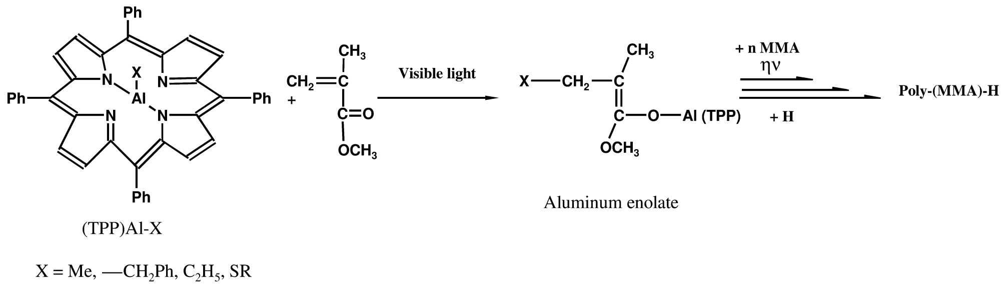
The polymerization of *n*BA is also living at −20 °C in the presence of LiOEM in toluene. The polymerization is so fast (half-lives in the millisecond range) that it can be controlled only in a flow-tube reactor [236].

1.5.6
Coordinative-Anionic Initiating Systems

1.5.6.1 Aluminum Porphyrins

Inoue and his coworkers found that methyl (tetraphenylporphyrinato) aluminum (TPP)AlMe initiates the living polymerization of alkyl (meth)acrylates upon irradiation by visible light (Scheme 1.22) [332]. PMMA was obtained in quantitative conversion and with narrow MWD ($1.06 < M_w/M_n < 1.2$).

The effect of light is observed not only in the initiation step but also in the propagation steps. NMR studies confirmed that the polymerization proceeds via a concerted mechanism, where the MMA coordinates to the aluminum atom leading to the conjugate addition of methyl group of initiator to monomer to form an aluminum enolate. Aluminum enolate once again coordinates with MMA and propagation occurs through a Michael addition process. Visible light accelerates this initiation and propagation to yield quantitative conversion. Later, it was found that the reaction can also be accelerated by Lewis acids,



Scheme 1.22 Aluminum porphyrin-initiated MMA polymerization.

presumably through monomer activation [333–337]. More details can be found in reviews by Aida [138] and Sugimoto and Inoue [338].

1.5.6.2 **Metallocenes**

Metallocenes with various rare earth central atoms, such as $((C_5Me_5)_2SmH)_2$ or the complexes derived from $(C_5Me_5)_2Yb(THF)_2$, show high catalytic activity in the polymerization of MMA in toluene between 40 °C and −78 °C, leading to syndiotactic PMMA with narrow MWD [339–341]. The living nature of the chain ends at room temperature was demonstrated by monomer resumption experiments. The living MMA dimer was crystallized and X-ray diffraction showed that the samarium central atom is coordinated to the enolate oxygen of the chain end and to the carbonyl group of the penultimate monomer unit. Later, it was shown that a living polymerization of acrylates can also be obtained [342]. More details can be found in a review by Yasuda [343]. Zirconocenes have also been used as initiators for the polymerization of (meth)acrylates [344, 345]. A review was recently published by Chen [346].

1.5.7

Polymerization of *N*,*N*-Dialkylacrylamides

Polymers of mono- and dialkylacrylamides are gaining increasing interest due to their thermoresponsive properties in aqueous solution [347, 348]. However, the anionic polymerization of *N*, *N*-dimethylacrylamide (DMAAm) and *N*, *N*-diethylacrylamide (DEAAm) in polar and nonpolar solvents using alkyllithium initiators is complicated due to the presence of slow aggregation dynamics of the propagating amido enolate ion pairs similar to ester enolate ion pairs in alkyl (meth)acrylate polymerization. Attempts were made to use different initiator in combination with coordinating ligands to control the polymerization and only minimum control on molecular weight, MWD, and the stereostructure of the polymers were obtained [349–354].

Major advances were reported by Nakahama *et al.* for the anionic polymerization of DMAAm and DEAAm by the use of organolithium and organopotassium initiators in the presence of Lewis acids (Et_2Zn and Et_3B) in THF [352, 355, 356]. Similarly, Et_3Al was used [353, 357]. The great influence of the system initiator/additive/solvent on the tacticity and the solubility of the resulting polymer was clearly demonstrated. The authors suggested that the coordination of the amidoenolate with the Lewis acid leads to a change of the stereostructure of the final polymer along with the retardation of the polymerization. Highly isotactic poly(*N*, *N*-diethylacrylamide) (PDEAAm) was obtained by using LiCl with organolithium initiator whereas highly syndiotactic and atactic polymers were obtained in the presence of Et_2Zn and Et_3B, respectively. Polymers rich in syndiotactic triads were not soluble in water whereas other microstructures lead to hydrophilic polymers [356]. Ishizone *et al.* reported the successful synthesis of poly(*tert*-butyl acrylate)-*b*-poly(*N*, *N*-diethylacrylamide) in THF at −78 °C. For that purpose, *t*BA was first initiated by an organocesium initiator (Ph_2CHCs) in the presence of Me_2Zn, and DEAAm was then initiated by the poly(*tert*-butyl acrylate)-Cs macroinitiator leading to a well-defined block copolymer ($M_w/M_n = 1.17$) [174].

André *et al.* performed kinetic studies on the polymerization of DEAAm in THF in the presence of triethylaluminum at −78 °C [358]. The kinetics of this process is very complex. It involves two equilibria: activation of monomer and deactivation of chain ends by Et_3Al. These two effects are in a delicate balance that depends on the ratio of the concentrations of Et_3Al, monomer, and chain ends. However, the initiator or blocking efficiencies of these systems remained low ($f < 0.70$). Quantum-chemical calculations on up to trimeric models confirm the various equilibria involved [359]. Et_3Al-coordinated, solvated unimers are the most stable species in the presence of Et_3Al, whereas unimers and dimers coexist in the absence of ligand.

Only one example was reported recently by Kitayama *et al.* for the polymerization of DMAAm in toluene. Living character was observed using a system based on *tert*-butyllithium/bis(2,6-di-*tert*-butylphenoxy)ethylaluminum in toluene at 0 °C [360]. Well-defined block copolymers PDMAAm-*b*-PMMA could be obtained in good yield, but no kinetic studies were performed.

Owing to their acidic proton, the direct anionic polymerization of *N*-monoalkylacrylamides such as *N*-isopropylacrylamide (NIPAAm) is not possible. By using *N*-methoxymethyl-substituted NIPAAm, Ishizone *et al.* synthesized well-defined polymers using organopotassium initiator in the presence of Et_2Zn, but no living character was described [361]. Kitayama *et al.* used *N*-trimethylsilyl-substituted NIPAAm to obtain highly isotactic polymers, but no MWDs were shown due to the poor solubility of the resulting polymers in common solvents [321]. However, these promising methods have opened new synthetic strategies to polymerize *N*-mono-substituted acrylamides with the advantages of anionic polymerization.

1.6
Some Applications of Anionic Polymerization

The application of anionic polymerization to synthesize macromolecular architectures, in particular polymers with various topologies has been reviewed in several reviews and books [16, 145, 362–365]. The polymerization of butadiene by alkali metals had been historically known since the early twentieth century. Synthetic rubberlike product called *Buna* (from the names of the chemicals used in its synthesis: butadiene and Natrium) was made in Germany and in the USSR during World War II using this process [366, 367]. In the 1950s, it was found that the use of lithium in hydrocarbon solvents for the polymerization of butadiene produces high content of *cis*-1,4 microstructure exhibiting better performance [368]. Since then, the anionic homo- and copolymerization of dienes has gained enormous importance in the manufacture of tires and other rubber products.

There is no doubt that the polymer industries and the fields of polymer physics and physical chemistry have benefited immensely from the development of special functional and block copolymers through anionic polymerization. Here, we would like to give some of the important and recent industrial applications of anionic polymerization. More details can be found in the textbook of Hsieh and Quirk [16] and in Chapter 10 of this book.

Various block copolymers consisting of incompatible block segments have been made available commercially by several companies. For example, ABA triblock copolymers of polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) and polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) were made by sequential addition of the monomers to butyllithium in hydrocarbon solvent [369]. These block copolymers and their hydrogenated analogs were sold by Shell under the trade name *Kraton*® and are now sold by Kraton Co. and others. Since the blocks are incompatible, they form microphase-separated structures, where the high-T_g outer polystyrene (PS) blocks form spherical or cylindrical domains in a matrix of the inner low-T_g diene blocks. This material is a thermoplastic elastomer, having rubberlike properties at room temperature, but being processable like a thermoplastic above the T_g of polystyrene. Hydrogenation of the diene block leads to structures resembling polyethylene (PE) or poly(ethylene-*alt*-propylene), which are more stable toward light and oxygen. These thermoplastic elastomers were originally designed to be used in the tire industry, but first applications came in footwear and later in other compounding applications, including automotive, wire and cable, medical, soft touch overmolding, cushions, as well as thermoplastic vulcanizates, lubricants, gels, coatings, adhesives, or in flexographic printing and road marking. Chapter 10 gives an exhaustive review on these materials.

BASF is marketing a variety of polystyrene-*b*-polybutadiene (PS–PB) star-block and star-tapered copolymers made by coupling four living PS–PB chains [370, 371]. With low PB content (*Styrolux*®), this material is used as a high-impact thermoplastic, with high PB content (*Styroflex*®) it is a highly

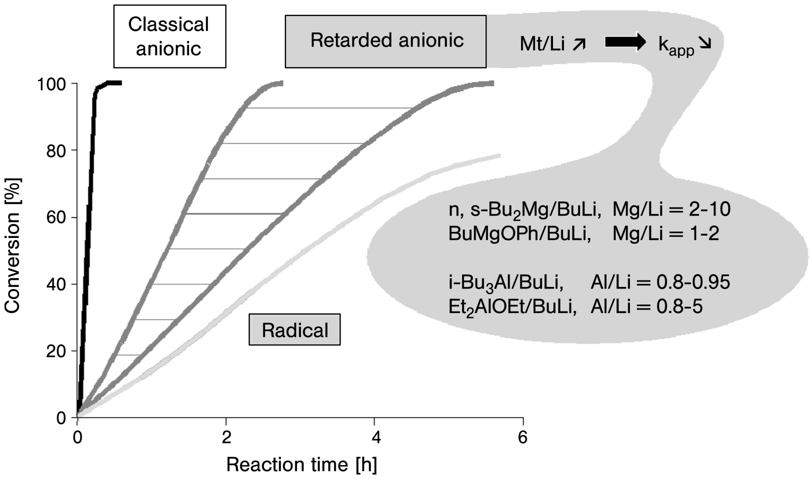


Figure 1.14 Time-conversion plots for a classical anionic (BuLi), retarded anionic and free-radical styrene polymerization: 15% ethylbenzene, $M_W = 450\,000$, $T_{start} = 120\,°C$ (Mt/Li range to reach an appropriate reactivity control) [373]. (Reprinted with permission from Wiley-VCH.)

flexible, transparent wrapping material. Similarly, a polystyrene-*b*-polyisoprene (PS–PI) star-block copolymer is produced by Phillips under the trade name *Solprene®*.

Several intermediate products are prepared by anionic polymerization and used in commercial formulations. For example, low *cis*-polybutadiene rubber is prepared by anionic polymerization (Dow, Mitsubishi, and other companies) and used for manufacturing high-impact polystyrene (HIPS). Recently, Dow has developed a new pentablock copolymer, consisting of hydrogenated PS and PB. Hydrogenation transforms the pentablock copolymer into a new polycyclohexylethylene (PCHE)–PE pentablock copolymer with glassy PCHE as hard blocks and ductile PE as soft blocks (PCHE–PE–PCHE–PE–PCHE). The copolymer has superior mechanical properties with low birefringence, moisture sensitivity, and heat distortion, and is undergoing market testing for optical applications [372].

The "retarded anionic polymerization" of styrene, initiated by lithium alkyls or even hydrides in the presence of aluminum and magnesium compounds (Section 1.4.3.2), patented by BASF, for the first time enables a commercial bulk polymerization of styrene at elevated temperatures above the glass transition temperature, T_g, of polystyrene, which might compete with the present radical process. In these bulk polymerizations, the rate is controlled by the ratio of aluminum or magnesium compounds to lithium (Figure 1.14).

Kuraray offers the ABA triblock copolymer PMMA-*b*-P*n*BA-*b*-PMMA as "LA Polymer". This is synthesized in the presence of diphenoxyalkylaluminum/Lewis acid combination described in Section 1.5.4.1. It is a thermoplastic elastomer and pressure-sensitive adhesive with excellent optical properties that is also used in nanostructure blends with polyesters.

Arkema sells the ABC triblock terpolymer SBM under the trade name *Nanostrength®*. This polymer is synthesized by sequential monomer addition in nonpolar solvent, where the PMMA block is made in the presence of an alkoxyalkoxide in a flow-tube reactor (Section 1.5.4.2). The material is used for the nanostructuring of epoxy blends and other commercial applications. Chapter 10 offers more details on the commercial applications of block copolymers.

In general, diblock copolymers and triblock terpolymers form a multitude of morphologies in the bulk. They have found use as compatibilizers for polymer blends [364]. In selective solvents, they can self-organize into spherical or cylindrical micelles, vesicles, and many more self-organized structures [363–365, 374–378]. The solution properties of various amphiphilic block copolymers have been explored in great detail as surfactants for emulsion polymerization [379], dispersants for pigments [291], drug carriers [380–382], or biomineralization agents [383]. Finally, the nanostructuring of surfaces by self-organization of block copolymers has led to a multitude of applications in nanotechnology [347, 364, 384–389]. These syntheses of various structures using different controlled/living techniques are discussed in detail in Chapter 8 and their properties in bulk and solution are discussed in detail in Chapter 9. In addition, anionic polymerization enables the synthesis of a number of polymer structures with nonlinear topologies, which are described in Chapter 7.

1.7
Conclusions and Outlook

Anionic polymerization is the oldest living/controlled polymerization and (maybe with the exception of some ring-opening polymerizations) the only one, which is living *and* controlled, at least for some monomers. The mechanisms of anionic polymerization of nonpolar and polar monomers are now well understood and an increasing number of monomers are available to be used in a living/controlled fashion; for example, primary acrylates, the polymerization of which had eluded control for more than 30 years. A number of important applications exist, but – except for rubber – not for the mass market, thermoplastic elastomers covering at least a niche market. This is partially due to the necessity of intensive purification of all reagents and low temperatures in some cases. Also, the number of accessible monomers is limited. Anyway, the possibility to construct complicated polymer structures in a well-defined way has inspired theoreticians and experimental physicists for more than 50 years now.

The advent of the other living/controlled techniques has challenged anionic polymerization as being the only mechanism for the synthesis of polymers with controlled structures. All mechanisms have their advantages and drawbacks: for example, controlled radical polymerization is easy to use with little effort for purification; a huge number of standard and functional monomers are accessible to homo- and copolymerization. On the other hand, when it comes to very high molecular weights, very low polydispersity and very precise block copolymer composition, in particular for nanotechnology applications, anionic polymerization is still in the lead. Thus, we hope that the various living polymerization mechanisms that have emerged during the last decades will coexist and help the synthetic chemist to construct even more sophisticated structures for future applications.

References

1. Szwarc, M., Levy, M. and Milkovich, R. (**1956**) *J. Am. Chem. Soc.*, **78**, 2656.
2. Szwarc, M. (**1956**) *Nature (London)*, **178**, 1168.
3. Blomquist, A.T., Tapp, W.J. and Jonson, J.R. (**1945**) *J. Am. Chem. Soc.*, **67**, 1519.
4. Beaman, R.G. (**1948**) *J. Am. Chem. Soc.*, **70**, 3115.
5. Robertson, R.E. and Martion, L. (**1948**) *Can. J. Res.*, **26B**, 657.
6. Morton, M., Bostick, E.E. and Livigny, R. (**1961**) *Rubber Plast. Age*, **42**, 397.
7. Morton, M. and Ells, F.R. (**1962**) *J. Polym. Sci.*, **61**, 25.
8. Morton, M. and Fetters, L.J. (**1967**) in *Macromolecular Reviews*, (ed. A. Peterlin), Vol.2, Interscience, New York, p. 71.
9. Geactinov, C., Smid, J. and Szwarc, M. (**1962**) *J. Am. Chem. Soc.*, **84**, 2508.
10. Hostalka, H., Figini, R.V. and Schulz, G.V. (**1964**) *Makromol. Chem.*, **71**, 198.
11. Brody, H., Ladacki, M., Milkovitch, R. and Szwarc, M. (**1957**) *J. Polym. Sci.*, **25**, 221.
12. Waack, R., Rembaum, A., Coombes, J.D. and Szwarc, M. (**1957**) *J. Am. Chem. Soc.*, **79**, 2026.
13. Flory, P.J. (**1940**) *J. Am. Chem. Soc.*, **62**, 1561.
14. Schulz, G.V. (**1956**) *Z. Elektrochem.*, **60**, 199.
15. Morton, M. (**1969**) Anionic polymerization, in *Vinyl Polymerization* (ed. G.E., Ham), Dekker Inc., New York.
16. Hsieh, H.L. and Quirk, R.P. (**1996**) *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker, Inc., New York, Basel, Hong Kong.
17. Akira, H., Surapich, L. and Takashi, I. (**2002**) *Prog. Polym. Sci.*, **27**, 1399.
18. Seiichi, N. and Akira, H. (**1990**) *Prog. Polym. Sci.*, **15**, 299.
19. Hirao, A. and Nakahama, S. (**1992**) *Prog. Polym. Sci.*, **17**, 283.
20. Hirao, A., Kato, H., Yamaguchi, K. and Nakahama, S. (**1986**) *Macromolecules*, **19**, 1294.
21. Hirao, A., Loykulnant, S. and Ishizone, T. (**2002**) *Prog. Polym. Sci.*, **27**, 1399.
22. Morton, M. (**1983**) *Anionic Polymerization. Principles and Practice*, Academic Press, New York.
23. Roovers, J.E.L. and Bywater, S. (**1975**) *Macromolecules*, **8**, 251.
24. Helary, G. and Fontanille, M. (**1978**) *Eur. Polym. J.*, **14**, 345.
25. Szwarc, M. (ed.) (**1972**) *Ions and Ion Pairs in Organic Reactions*, Vol.1, Interscience, New York.
26. Fuoss, R.M. (**1954**) *J. Am. Chem. Soc.*, **76**, 5905.
27. Fuoss, R.M. (**1958**) *J. Am. Chem. Soc.*, **80**, 5059.
28. Winstein, S., Clippinger, E., Fainberg, A.H. and Robinson, G.C. (**1954**) *J. Am. Chem. Soc.*, **76**, 2597.
29. Hogen-Esch, T.E. and Smid, J. (**1965**) *J. Am. Chem. Soc.*, **87**, 669.
30. Hogen-Esch, T.E. and Smid, J. (**1966**) *J. Am. Chem. Soc.*, **88**, 318.

31. Smid, J. (**1972**) Spectrophotometric studies of ions and ion pairs, in *Ions and ion pairs in organic reactions* (ed. M., Szwarc), Wiley-Interscience, New York, p. 85.
32. Ellingsen, T. and Smid, J. (**1969**) *J. Phys. Chem.*, **73**, 2712.
33. Szwarc, M. (**1983**) *Adv. Polym. Sci.*, **49**, 1.
34. Fuoss, R.M. and Accascina, F. (**1959**) Electrolytic Conductance, Interscience Publishers, Inc., New York.
35. Fuoss, R.M. and Kraus, C.A. (**1933**) *J. Am. Chem. Soc.*, **55**, 2387.
36. Fuoss, R.M. and Kraus, C.A. (**1933**) *J. Am. Chem. Soc.*, **55**, 1019.
37. Fuoss, R.M. and Kraus, C.A. (**1933**) *J. Am. Chem. Soc.*, **55**, 476.
38. Yan, D., Dong, H., Ye, P. and Müller, A.H.E. (**1996**) *Macromolecules*, **29**, 8057.
39. Litvinenko, G. and Müller, A.H.E. (**1997**) *Macromolecules*, **30**, 1253.
40. Mc.Grath, J. E. (ed.) (**1981**) *Anionic Polymerization. Kinetics, Mechanisms, and Synthesis, ACS Symp.Ser.166.*
41. Bordwell, F.G. (**1988**) *Acc. Chem. Res.*, **21**, 456.
42. Bordwell, F.G. and Fried, H.E. (**1981**) *J. Org. Chem.*, **46**(22), 4327.
43. Szwarc, M. (**1983**) *Adv. Polym. Sci.*, **49**, 108.
44. Lee, C.L., Smid, J. and Szwarc, M. (**1962**) *J. Phys. Chem.*, **66**, 904.
45. Richards, D.H. and Williams, R.L. (**1973**) *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 89.
46. US 1859686 (**1932**) I. G. Farbenindustries AG, invs.: E. Tschunkur, W. Bock.
47. Morton, M. (**1964**) Anionic copolymerization, in *Copolymerization* (ed. G.E. Ham), Interscience, New York, p. 421.
48. Morton, M. and Fetters, L.J. (**1964**) *J. Polym. Sci., Part A*, **2**, 3311.
49. Fontanille, M. (**1989**) in *Comprehensive Polymer Science, Vol. 3, Chain Polymerization I* (eds G.C., Eastmond, A., Ledwith, S., Russo and P., Sigwalt), Pergamon, New York, p. 365.
50. Langer, A.W. (**1966**) *J. Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **7**, 132.
51. Langer, A.W. (**1974**) *Polyamine-chelated Alkali Metal Compounds*, Advances in Chemistry Series, Vol.130, American Chemical Society.
52. Schuman, C.M. and Hsieh, H.L. (**1971**) *J. Polym. Sci., Part B*, **9**, 219.
53. Hsieh, H.L. and Glaze, W.H. (**1970**) *Rubber Chem. Technol.*, **43**, 22.
54. Bywater, S. (**1976**) Anionic polymerization of olefins, in *Comprehensive Chemical Kinetics* (eds C.H. Bamford and C.F.H. Tipper), Elsevier, Amsterdam, p. 1.
55. Bywater, S. (**1985**) Anionic polymerization, in *Encyclopedia of Polymer Science & Technology* (eds H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges and J.I. Kroschwitz), Wiley, New York, p. 1.
56. Hsieh, H.L. (**1965**) *J. Polym. Sci.*, **A3**, 163.
57. Fetters, L.J. and Morton, M. (**1974**) *Macromolecules*, **7**, 552.
58. Morton, M. and Fetters, L.J. (**1975**) *Rubber Chem. Technol.*, **48**, 359.
59. Wiles, D.M., Bywater, S. (**1964**), 150.
60. Ishizu, K., Mitsutani, K. and Fukutomi, T. (**1987**) *J. Polym. Sci., Polym. Lett. Ed.*, **25**, 287.
61. Graham, R.K., Dunkelberger, D.L. and Goode, W.E. (**1960**) *J. Am. Chem. Soc.*, **82**, 400.
62. Fox, T.G., Garrett, B.S., Goode, W.E., Gratch, S., Kincaid, J.F., Spell, A. and Stroupe, J.D. (**1958**) *J. Am. Chem. Soc.*, **80**, 1768.
63. Yamagishi, A., Szwarc, M., Tung, L. and Lo, G.Y.-S. (**1978**) *Macromolecules*, **11**, 607.
64. Quirk, R.P. and Lee, B. (**2003**) *Macromol. Chem. Phys.*, **204**, 1719.
65. Arest-Yakubovich, A.A. (**1994**) *Chem. Rev.*, **19**, 1.
66. Asami, R., Levy, M. and Szwarc, M. (**1962**) *J. Chem. Soc., Faraday Trans. 1*, **58**, 361.
67. Hogen-Esch, T.E. and Bannerjee, K.G. (**1993**) *Macromolecules*, **26**, 926.

68. Morton, M., Fetters, L.J., Pett, R.A. and Meier, J.F. (**1970**) *Macromolecules*, **3**, 327.
69. Morton, M. and Fetters, L.J. (**1981**) *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 199.
70. Quirk, R.P. and Chen, W.-C. (**1984**) *J. Polym. Sci., Part A: Polym. Chem.*, **22**, 2993.
71. Uhrig, D. and Mays, J.W. (**2005**) *J. Polym. Sci., Part A: Polym. Chem.*, **43**, 6179.
72. Löhr, G., Schmitt, B.J. and Schulz, G.V. (**1972**) *Z. Phys. Chem. (Frankfurt am Main)*, **78**, 177.
73. Fontanille, M. and Müller, A.H.E. (**1988**) Experimental aspects [of anionic polymerization], in *Comprehensive Polymer Science* (eds G. Allen and J.C. Bevington), Pergamon, Oxford, p. 571.
74. Carvajal, C., Tölle, K.J., Smid, J. and Szwarc, M. (**1965**) *J. Am. Chem. Soc.*, **87**, 5548.
75. Bhattacharyya, D.N., Lee, C.L., Smid, J. and Szwarc, M. (**1964**) *Polymer*, **5**, 54.
76. Dainton, F.S., Harpbell, G.A. and Ivin, K.J. (**1969**) *Eur. Polym. J.*, **5**, 395.
77. Komiyama, J., Böhm, L.L. and Schulz, G.V. (**1971**) *Makromol. Chem.*, **148**, 297.
78. Dainton, F.S., East, G.C., Harpbell, G.A., Hurworth, N.R., Ivin, K.J., La Flair, R.T., Pallen, R.H. and Hui, K.M. (**1965**) *Makromol. Chem.*, **89**, 257.
79. Dainton, F.S., Ivin, K.J. and La Flair, R.T. (**1969**) *Eur. Polym. J.*, **5**, 379.
80. Barnikol, W.K.R. and Schulz, G.V. (**1964**) *Makromol. Chem.*, **68**, 211.
81. Barnikol, W.K.R. and Schulz, G.V. (**1965**) *Z. Phys. Chem. (Frankfurt am Main)*, **47**, 89.
82. Bhattacharyya, D.N., Lee, C.L., Smid, J. and Szwarc, M. (**1965**) *J. Phys. Chem.*, **69**, 612.
83. Figini, R.V., Löhr, G. and Schulz, G.V. (**1965**) *J. Polym. Sci., Part B*, **3**, 485.
84. Bhattacharyya, D.N., Lee, C.L., Smid, J. and Szwarc, M. (**1965**) *J. Phys. Chem.*, **69**, 624.
85. Bhattacharyya, D.N., Lee, C.L., Smid, J. and Szwarc, M. (**1965**) *J. Phys. Chem.*, **69**, 608.
86. Figini, R.V., Hostalka, H., Hurm, K., Löhr, G. and Schulz, G.V. (**1965**) *Z. Phys. Chem. (Frankfurt am Main)*, **45**, 269.
87. Schmitt, B.J. and Schulz, G.V. (**1975**) *Eur. Polym. J.*, **11**, 119.
88. Figini, R.V. (**1964**) *Makromol. Chem.*, **71**, 193.
89. Müller, A.H.E. (**1988**) Carbanionic polymerization: Kinetics and thermodynamics, in *Comprehensive Polymer Science* (eds G. Allen and J.C. Bevington), Pergamon, Oxford, p. 387.
90. Arest-Yakubovich, A.A. and Medvedev, S.S. (**1964**) *Dokl. Akad. Nauk SSSR*, **159**, 1066.
91. Shimomura, T., Smid, J. and Szwarc, M. (**1967**) *J. Am. Chem. Soc.*, **89**, 5743.
92. Böhm, L.L., Chmelir, M., Löhr, G., Schmitt, B.J. and Schulz, G.V. (**1972**) *Adv. Polym. Sci.*, **9**, 1.
93. Smid, J., Van Beylen, M. and Hogen-Esch, T.E. (**2006**) *Prog. Polym. Sci.*, **31**, 1041.
94. Szwarc, M. and Van Beylen, M. (**1993**) *Ionic Polymerization and Living Polymers*, Chapman & Hall, New York.
95. Worsfold, D.J. and Bywater, S. (**1960**) *Can. J. Chem.*, **38**, 1891.
96. Morton, M., Fetters, L.J. and Bostick, E.E. (**1963**) *J. Polym. Sci. Part C*, **1**, 311.
97. Cubbon, R.C.P. and Margerison, D. (**1965**) *Prog. React. Kinet.*, **3**, 403.
98. Hsieh, H.L. (**1965**) *J. Polym. Sci., A*, **153**, 173.
99. Johnson, A.F. and Worsfold, D.J. (**1965**) *J. Polym. Sci., Part A*, **3**, 449.
100. Worsfold, D.J. and Bywater, S. (**1972**) *Macromolecules*, **5**, 393.
101. Welch, F.J. (**1960**) *J. Am. Chem. Soc.*, **82**, 6000.
102. Bywater, S. and Worsfold, D.J. (**1962**) *Can. J. Chem.*, **40**, 1564.
103. Fontanille, M., Helary, G. and Szwarc, M. (**1988**) *Macromolecules*, **21**, 1532.
104. Wang, G. and Van Beylen, M. (**2003**) *Polymer*, **44**, 6457.

105. Roovers, J.E.L. and Bywater, S. (**1966**) *Trans. Faraday Soc.*, **62**, 1876.
106. Hsieh, H.L. and Wang, I.W. (**1986**) *Macromolecules*, **19**, 299.
107. Guyot, A. and Vialle, J. (**1970**) *J. Macromol. Sci., Chem.*, **A4**, 107.
108. Arest-Yakubovich, A.A. (**1994**) *Macromol. Chem. Macromol. Symp.*, **85**, 279.
109. Ménoret, S., Fontanille, M., Deffieux, A., Debois, P. and Demeter, J. (**2002**) *Macromolecules*, **35**, 4584.
110. Desbois, P., Fontanille, M., Deffieux, A., Warzelhan, V., Lätsch, S. and Schade, C. (**1999**) *Macromol. Chem. Phys.*, **200**, 621.
111. Carlotti, S., Me'noret, S., Barabanova, A., Desbois, P. and Deffieux, A. (**2005**) *Polymer*, **46**, 6836.
112. Ménoret, S., Deffieux, A. and Desbois, S. (**2003**) *Macromolecules*, **36**, 5988.
113. Carlotti, S., Ménoret, S., Desbois, P., Nissner, N., Warzelhan, V. and Deffieux, A. (**2006**) *Macromol. Rapid Commun.*, **27**, 905.
114. Labbé, A., Carlotti, S., Shcheglova, L., Desbois, P. and Deffieux, A. (**2006**) *Polymer*, **47**, 3734.
115. Francois, B., Sinn, V. and Parrod, J. (**1963**) *J. Polym. Sci., Part C*, **4**, 375.
116. Margerison, D., Bishop, D.M., East, G.C. and McBride, P. (**1968**) *Trans. Faraday Soc.*, **64**, 1872.
117. Alvarino, J.M., Bello, A. and Guzman, G.M. (**1972**) *Eur. Polym. J.*, **8**, 53.
118. Worsfold, D.J. and Bywater, S. (**1964**) *Can. J. Chem.*, **42**, 2884.
119. Bywater, S. and Worsfold, D.J. (**1967**) *Can. J. Chem.*, **45**, 1821.
120. Morton, M., Pett, R.A. and Fetters, L.J. (**1966**) *Macromol. Symp. Tokyo*, **1**, 69.
121. Bywater, S. and Worsfold, D.J. (**1987**) The effect of molecular weight on association in anionic polymerization, in *Recent Advances in Anionic Polymerization* (eds T.E. Hogen-Esch and J. Smid), Elsevier, New York, p. 109.
122. Sinn, H., Lundborg, C. and Onsager, O.T. (**1964**) *Mackromol. Chem.*, **70**, 222.
123. Roovers, J.E.L. and Bywater, S. (**1973**) *Polymer*, **14**, 594.
124. Fetters, L.J., Balsara, N.P., Huang, J.S., Jeon, H.S., Almadal, K. and Lin, M.Y. (**1995**) *Macromolecules*, **28**, 4996.
125. Stellbrink, J., Willner, L., Jucknischke, O., Richter, D., Lindner, P., Fetters, L.J. and Huang, J.S. (**1998**) *Macromolecules*, **31**, 4189.
126. Niu, A.Z., Stellbrink, J., Allgaier, J., Willner, L., Richter, D., Koenig, B.W., Gondorf, M., Willbold, S., Fetters, L.J. and May, R.P. (**2004**) *Macromol. Symp.*, **215**, 1.
127. Niu, A.Z., Stellbrink, J., Allgaier, J., Willner, L., Radulescu, A., Richter, D., Koenig, B.W., May, R.P. and Fetters, L.J. (**2005**) *J. Chem. Phys.*, **122**, 134906/1.
128. Szwarc, M. (**1982**) *Macromolecules*, **15**, 1449.
129. Arest-Yakubovich, A.A. (**1997**) *J. Polym. Sci., Part A: Polym. Chem.*, **35**, 3613.
130. Tanaka, H., Yamauchi, K., Hasegawa, H., Miyamoto, N., Koizumi, S. and Hashimoto, T. (**2006**) *Physica B: Condens. Matter*, **385–386**, 742.
131. Halasa, A.F., Lohr, D.F. and GHall, J.E. (**1981**) *J. Polym. Sci., Part A: Polym. Chem.*, **19**, 1357.
132. Szwarc, M. (**1968**) *Carbanions Living Polymers and Electron Transfer Process*, Wiley Interscience, New York.
133. Young, R.N., Quirk, R.P. and Fetters, L.J. (**1984**) *Adv. Polym. Sci.*, **56**, 1.
134. Van Beylen, M., Bywater, S., Smets, G., Szwarc, M. and Worsfold, D.J. (**1988**) *Adv. Polym. Sci.*, **86**, 87.
135. Müller, A.H.E. (**1989**) Carbanionic polymerization: kinetics and thermodynamics, in *Comprehensive Polymer Science* (eds G. Allen and J.C. Bevington), Pergamon Press, Oxford, p. 387.
136. Bywater, S. (**1989**) Carbanionic polymerization: polymer configuration and the stereoregulation process, in *Comprehensive Polymer Science* (eds G. Allen and J.C. Bevington), Pergamon Press, Oxford, p. 433.

137. Fontanille, M. (**1989**) Carbanionic polymerization: General aspect and initiation, in *Comprehensive Polymer Science* (eds G. Allen and J.C. Bevington), Pergamon Press, Oxford, p. 365.
138. Aida, T. (**1994**) *Prog. Polym. Sci.*, **19**, 469.
139. Szwarc, M. (**1996**) *Ionic Polymerization Fundamentals*, Hanser/Gardner, Munich.
140. Uhrig, D. and Mays, J.W. (**2002**) *Macromolecules*, **35**, 7182.
141. Hadjichristidis, N., Pitsikalis, M., Pispas, S. and Iatrou, H. (**2001**) *Chem. Rev.*, **101**, 3747.
142. Iatrou, H., Mays, J.W. and Hadjichristidis, N. (**1998**) *Macromolecules*, **31**, 6697.
143. Hadjichristidis, N., Iatrou, H., Pispas, S. and Pitsikalis, M. (**2000**) *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 3211.
144. Zhu, Y., Burgaz, E., Gido, S.P., Staudinger, U., Weidisch, R., Uhrig, D. and Mays, J.W. (**2006**) *Macromolecules*, **39**, 4428.
145. Quirk, R.P., Yoo, T., Lee, Y., Kim, J. and Lee, B. (**2000**) *Adv. Polym. Sci.*, **153**, 67.
146. Quirk, R.P. (**1992**) *Makromol. Chem., Macromol. Symp.*, **63**, 259.
147. Matsuo, A., Watanabe, T. and Hirao, A. (**2004**) *Macromolecules*, **37**, 6283.
148. Hirao, A., Matsuo, A. and Watanabe, T. (**2005**) *Macromolecules*, **38**, 8701.
149. Hirao, A., Higashihara, T., Nagura, M. and Sakural, T. (**2006**) *Macromolecules*, **39**, 6081.
150. Hirao, A., Higashihara, T. and Inoue, K. (**2008**) *Macromolecules*, **41**, 3579.
151. Szwarc, M. and Rembaum, A. (**1956**) *J. Polym. Sci.*, **22**, 189.
152. Schreiber, H. (**1960**) *Makromol. Chem.*, **36**, 86.
153. Goode, W.E., Owens, F.H., Fellwann, R.P., Snyder, W.H. and Moore, J.E. (**1960**) *J. Polym. Sci.*, **46**, 317.
154. Goode, W.E., Owens, F.H. and Myers, W.L. (**1960**) *J. Polym. Sci.*, **47**, 75.
155. Glusker, D.L., Stiles, E. and Yonkoskie, B. (**1961**) *J. Polym. Sci.*, **49**, 297.
156. Glusker, D.L., Lysloff, I. and Stiles, E. (**1961**) *J. Polym. Sci.*, **49**, 315.
157. Glusker, D.L., Gallucio, R.A. and Evans, R.A. (**1964**) *J. Am. Chem. Soc.*, **86**, 187.
158. Krause, S., Defonso, L. and Glusker, D.L. (**1965**) *J. Polym. Sci., Part A*, **3**, 1617.
159. Hatada, K., Kitayama, T., Fujikawa, K., Ohta, K. and Yuki, H. (**1978**) *Polym. Bull. (Berlin)*, **1**, 103.
160. Hatada, K., Kitayama, T., Fumikawa, K., Ohta, K. and Yuki, H. Studies on the anionic polymerization of methyl methacrylate initiated with butyllithium in toluene by using perdeuterated monomer, in *Anionic Polymerization, ACS Symposium Series 166* (ed. J.E. Mc.Grath), Washington, **1981**, p. 327.
161. Hatada, K., Ute, K., Tanaka, K., Kitayama, T. and Okamoto, Y. (**1987**) Mechanism of polymerization of MMA by grignard reagents and preparation of high isotactic PMMA with narrow molecular weight distribution, in *Recent Advances in Anionic Polymerization* (eds T. Hogen-Esch and J. Smid), Elsevier, New York, p. 195.
162. Hatada, K., Ute, K., Tanaka, K. and Kitayama, T. (**1987**) *Polym. J.*, **19**, 1325.
163. Gerner, F.J., Höcker, H., Müller, A.H.E. and Schulz, G.V. (**1984**) *Eur. Polym. J.*, **20**, 349.
164. Kawabata, N. and Tsuruta, T. (**1965**) *Makromol. Chem.*, **80**, 231.
165. Feit, B.A. (**1967**) *Eur. Polym. J.*, **3**, 523.
166. Busfield, W.K. and Methven, J.M. (**1973**) *Polymer*, **14**, 137.
167. Bywater, S. (**1962**) *Pure Appl. Chem.*, **4**, 319.
168. Wiles, D.M. and Bywater, S. (**1963**) *Chem. Ind. (London)*, **1963**, 1209.
169. Wiles, D.M. and Bywater, S. (**1964**) *J. Phys. Chem.*, **68**, 1983.
170. Müller, A.H.E., Lochmann, L. and Trekoval, J. (**1986**) *Makromol. Chem.*, **187**, 1473.
171. Lochmann, L., Rodová, M., Petránek, J. and Lím, D. (**1974**) *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2295.

172. Janata, M., Lochmann, L. and Müller, A.H.E. (**1990**) *Makromol. Chem.*, **191**, 2253.
173. Wiles, D.M. and Bywater, S. (**1965**) *Trans. Faraday Soc.*, **61**, 150.
174. Ishizone, T., Yoshimura, K., Hirao, A. and Nakahama, S. (**1998**) *Macromolecules*, **31**, 8706.
175. Hatada, K., Nakanishi, H., Ute, K. and Kitayama, T. (**1986**) *Polym. J.*, **8**, 581.
176. Nishioka, A., Watanabe, H., Yamaguchi, I., Abe, K. and Sono, Y. (**1960**) *J. Polym. Sci.*, **48**, 241.
177. Ando, I., Chujo, R. and Nishioka, A. (**1970**) *Polym. J.*, **1**, 609.
178. Miyamoto, T., Tomoshige, S. and Inagaki, H. (**1975**) *Makromol. Chem.*, **176**, 3035.
179. Warzelhan, V., Höcker, H. and Schulz, G.V. (**1978**) *Makromol. Chem.*, **179**, 2221.
180. Lochmann, L. and Lím, D. (**1973**) *J. Organomet. Chem.*, **50**, 9.
181. Lochmann, L., Rodová, M. and Trekoval, J. (**1974**) *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2091.
182. Baskaran, D. (**2003**) *Prog. Polym. Sci.*, **28**, 521.
183. Roig, A., Figueruelo, J.E. and Llano, E. (**1965**) *J. Polym. Sci., Part B*, **3**, 171.
184. Roig, A., Figueruelo, J.E. and Llano, E. (**1965**) *J. Polym. Sci., Part C*, **16**, 4141.
185. Löhr, G. and Schulz, G.V. (**1973**) *Makromol. Chem.*, **172**, 137.
186. Löhr, G. and Schulz, G.V. (**1974**) *Eur. Polym. J.*, **10**, 121.
187. Mita, I., Watanabe, Y., Akatsu, T. and Kambe, H. (**1973**) *Polym. J.*, **4**, 271.
188. Löhr, G., Müller, A.H.E., Schulz, G.V. and Warzelhan, V. (**1973**) *Preprints, 24th IUPAC International Congress Hamburg*, p. 12.
189. Kraft, R., Müller, A.H.E., Warzelhan, V., Höcker, H. and Schulz, G.V. (**1978**) *Macromolecules*, **11**, 1095.
190. Johann, C. and Müller, A.H.E. (**1981**) *Makromol. Chem., Rapid Commun.*, **2**, 687.
191. Jeuck, H. and Müller, A.H.E. (**1982**) *Makromol. Chem., Rapid Commun.*, **3**, 121.
192. Bywater, S. (**1989**) in *Comprehensive Polymer Science* (eds G.C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt), Pergamon Press, Elmsford, p. 433.
193. Kraft, R., Müller, A.H.E., Höcker, H. and Schulz, G.V. (**1980**) *Makromol. Chem., Rapid Commun.*, **1**, 363.
194. Warzelhan, V. and Schulz, G.V. (**1976**) *Makromol. Chem.*, **177**, 2185.
195. Weiss, H., Yakimansky, A.V. and Müller, A.H.E. (**1996**) *J. Am. Chem. Soc.*, **118**, 8897.
196. Tsvetanov, C.B., Müller, A.H.E.S. and Schulz, G.V. (**1985**) *Macromolecules*, **18**, 863.
197. Kunkel, D., Müller, A.H.E., Lochmann, L. and Janata, M. (**1992**) *Makromol. Chem., Macromol. Symp.*, **60**, 315.
198. Figini, R.V. (**1967**) *Makromol. Chem.*, **107**, 170.
199. Coleman, B.D. and Fox, T.G. (**1963**) *J. Polym. Sci., Part C*, **4**, 345.
200. Coleman, B.D. and Fox, T.G. (**1963**) *J. Am. Chem. Soc.*, **85**, 1214.
201. Gee, G., Higginson, W.C.E. and Merrall, G.T. (**1959**) *J. Chem. Soc.*, 1345.
202. Szwarc, M. and Hermans, J.J. (**1964**) *J. Polym. Sci., Part B*, **2**, 815.
203. Böhm, L.L. (**1970**) *Z. Phys. Chem. [Frankfurt am Main*, **72**, 199.
204. Böhm, L.L. (**1974**) *Z. Phys. Chem. [Frankfurt am Main*, **88**, 297.
205. Puskas, J.E., Kaszas, G. and Litt, M. (**1991**) *Macromolecules*, **24**, 5278.
206. Müller, A.H.E., Zhuang, R., Yan, D.Y. and Litvinenko, G. (**1995**) *Macromolecules*, **28**, 4326.
207. Müller, A.H.E., Yan, D.Y., Litvinenko, G., Zhuang, R. and Dong, H. (**1995**) *Macromolecules*, **28**, 7335.
208. Müller, A.H.E., Yan, D.Y. and Litvinenko, G. (**1996**) *Macromolecules*, **29**, 2339.
209. Müller, A.H.E., Yan, D.Y. and Litvinenko, G. (**1996**) *Macromolecules*, **29**, 2346.
210. Fayt, R., Forte, R., Jacobs, R., Jérôme, R., Ouhadi, T., Teyssié, P. and Varshney, S.K. (**1987**) *Macromolecules*, **20**, 1442.

211. Varshney, S.K., Hautekeer, J.-P., Fayt, R., Jérôme, R. and Teyssié, P. (**1990**) *Macromolecules*, **23**, 2618.
212. Wang, J.-S., Jérôme, R., Bayard, P., Baylac, L., Patin, M. and Teyssié, P. (**1994**) *Macromolecules*, **27**, 4615.
213. Varshney, S.K., Jérôme, R., Bayard, P., Jacobs, C., Fayt, R. and Teyssié, P. (**1992**) *Macromolecules*, **25**, 4457.
214. Bayard, P., Jerome, R., Teyssié, P., Varshney, S.K. and Wang, J.S. (**1994**) *Polym. Bull.*, **32**, 381.
215. Baskaran, D. and Sivaram, S. (**1997**) *Macromolecules*, **30**, 1550.
216. Baskaran, D., Chakrapani, S. and Sivaram, S. (**1995**) *Macromolecules*, **28**, 7315.
217. Baskaran, D., Müller, A.H.E. and Sivaram, S. (**2000**) *Macromol. Chem. Phys.*, **201**, 1901.
218. Marchal, J., Gnanou, Y. and Fontanille, M. (**1996**) *Makromol. Chem., Macromol. Symp.*, **107**, 27.
219. Gia, H.-B. and McGrath, J.E. (**1987**) Pyridine-mediated anionic homo- and copolymerization of alkylmethacrylate, in *Recent Advances in Anionic Polymerization* (eds T., Hogen-Esch and J., Smid), Elsevier, New York, p. 173.
220. Hatada, K., Ute, K., Tanaka, K., Okamoto, Y. and Kitayama, T. (**1986**) *Polym. J.*, **18**, 1037.
221. Kitayama, T., Shinozaki, T., Sakamoto, T., Yamamoto, M. and Hatada, K. (**1989**) *Makromol. Chem., Suppl.*, **15**, 167.
222. Ballard, D.G.H., Bowles, R.J., Haddleton, D.M., Richards, S.N., Sellens, R. and Twose, D.L. (**1992**) *Macromolecules*, **25**, 5907.
223. Schlaad, H., Schmitt, B., Müller, A.H.E., Jüngling, S. and Weiss, H. (**1998**) *Macromolecules*, **31**, 573.
224. Schlaad, H., Schmitt, B. and Müller, A.H.E. (**1998**) *Angew. Chem., Int. Ed. Engl.*, **37**, 1389.
225. Ishizone, T., Yoshimura, K., Yanase, E. and Nakahama, S. (**1999**) *Macromolecules*, **32**, 955.
226. Baskaran, D. (**2000**) *Macromol. Chem. Phys.*, **201**, 890.
227. Wang, J.S., Jérôme, R. and Teyssié, P. (**1995**) *J. Phys. Org. Chem.*, **8**, 208.
228. Lochmann, L., Doskocilova, D. and Trekoval, J. (**1977**) *Collect. Czech. Chem. Commun.*, **42**, 1355.
229. Lochmann, L., Kolarik, J., Doskocilova, D., Vozka, S. and Trekoval, J. (**1979**) *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 1727.
230. Lochmann, L. and Müller, A.H.E. (**1990**) *Makromol. Chem.*, **191**, 1657.
231. Vlcek, P., Lochmann, L. and Otoupalova, J. (**1992**) *Macromol. Chem., Rapid Commun.*, **13**, 163.
232. Varshney, S.K., Bayard, P., Jacobs, C., Jérôme, R., Fayt, R. and Teyssié, P. (**1992**) *Macromolecules*, **25**, 5578.
233. Baskaran, D., Müller, A.H.E. and Sivaram, S. (**1999**) *Macromolecules*, **32**, 1356.
234. Wang, J.-S., Jérôme, R., Bayard, P., Patin, M. and Teyssié, P. (**1994**) *Macromolecules*, **27**, 4635.
235. Wang, J.S., Jérôme, R., Bayard, P. and Teyssié, P. (**1994**) *Macromolecules*, **27**, 4908.
236. Maurer, A., Marcarian, X., Müller, A.H.E., Navarro, C. and Vuillemin, B. (**1997**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **38**(1), 467.
237. Marchal, J., Fontanille, M. and Gnanou, Y. (**1998**) *Macromol. Symp.*, **132**, 249.
238. Zundel, T., Zune, C., Teyssié, P. and Jérôme, R. (**1998**) *Macromolecules*, **31**, 4089.
239. Braun, D., Herner, M., Johnsen, U. and Kern, W. (**1962**) *Makromol. Chem.*, **51**, 15.
240. Anderson, B.C., Andrews, G.D., Arthur, Jr, P., Jacobson, H.W., Melby, L.R., Playtis, A.J. and Sharkey, W.H. (**1981**) *Macromolecules*, **14**, 1599.
241. Yakimansky, A.V. and Müller, A.H.E. (**2001**) *J. Am. Chem. Soc.*, **123**, 4932.
242. Janata, M., Lochmann, L. and Müller, A.H.E. (**1993**) *Makromol. Chem.*, **194**, 625.
243. Janata, M., Lochmann, L., Vlcek, P., Dybal, J. and Müller, A.H.E. (**1992**) *Makromol. Chem.*, **193**, 101.
244. Dvoranek, L. and Vlcek, P. (**1993**) *Polym. Bull.*, **31**, 393.
245. Dvoranek, L. and Vlcek, P. (**1994**) *Macromolecules*, **27**, 4881.

246. Vlcek, P., Dvoranek, L., Otoupalova, J. and Lochmann, L. (**1995**) *Polym. Bull.*, **34**, 1.
247. Jérôme, R., Forte, R., Varshney, S.K., Fayt, R. and Teyssié, P. (**1987**) The anionic polymerization of alkyl acrylates: A challenge, in *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization* (eds M., Fontanille and A., Guyot), D. Reidel, Dordrecht, Netherlands, p. 101.
248. Yakimansky, A.V., Müller, A.H.E. and Van Beylen, M. (**2000**) *Macromolecules*, **33**, 5686.
249. Webster, O.W., Hertler, W.R., Sogah, D.Y., Farnham, W.B. and RajanBabu, T.V. (**1983**) *J. Am. Chem. Soc.*, **105**, 5706.
250. Sogah, D.Y., Hertler, W.R., Webster, O.W. and Cohen, G.M. (**1987**) *Macromolecules*, **20**, 1473.
251. Brittain, W.J. (**1988**) *J. Am. Chem. Soc.*, **110**, 7440.
252. Schubert, W., Sitz, H.-D. and Bandermann, F. (**1989**) *Makromol. Chem.*, **190**, 2193.
253. Schubert, W. and Bandermann, F. (**1989**) *Makromol. Chem.*, **190**, 2721.
254. Schmalbrock, U. and Bandermann, F. (**1989**) *Makromol. Chem.*, **190**, 2713.
255. Schubert, W. and Bandermann, F. (**1989**) *Makromol. Chem.*, **190**, 2161.
256. Dicker, I.B., Hertler, W.R., Cohen, G.M., Farnham, W.B., Del Laganis, E. and Sogah, D.Y. (**1987**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **28**(1), 106.
257. Dicker, I.B., Cohen, G.M., Farnham, W.B., Hertler, W.R., Laganis, E.D. and Sogah, D.Y. (**1990**) *Macromolecules*, **23**, 4034.
258. Schmalbrock, U. and Bandermann, F. (**1993**) *Makromol. Chem.*, **194**, 2543.
259. Müller, A.H.E. (**1990**) *Makromol. Chem., Macromol. Symp.*, **32**, 87.
260. Hertler, W.R., Sogah, D.Y., Webster, O.W. and Trost, B.M. (**1984**) *Macromolecules*, **17**, 1415.
261. Zhuang, R. and Müller, A.H.E. (**1995**) *Macromolecules*, **28**, 8035.
262. Zhuang, R. and Müller, A.H.E. (**1995**) *Macromolecules*, **28**, 8043.
263. Brittain, W.J. and Dicker, I.B. (**1989**) *Macromolecules*, **22**, 1054.
264. Hertler, W.R. (**1987**) *Macromolecules*, **20**, 2976.
265. Hertler, W.R., Reddy, G.S. and Sogah, D.Y. (**1988**) *J. Org. Chem.*, **53**, 3532.
266. Mai, P.M. and Müller, A.H.E. (**1987**) *Makromol. Chem., Rapid Commun.*, **8**, 247.
267. Doherty, M.A., Gores, F., Mai, P.M. and Müller, A.H.E. (**1988**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **29**(2), 73.
268. Müller, A.H.E. (**1994**) *Macromolecules*, **27**, 1685.
269. Sitz, H.D. and Bandermann, F. (**1987**) Group transfer polymerization of methyl methacrylate with basic catalysts, in *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization* (eds M. Fontanille and A. Guyot), D. Reidel, Dordrecht, Netherlands, p. 41.
270. Farnham, W.B. and Sogah, D.Y. (**1986**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **27**(1), 167.
271. Bywater, S. (**1993**) *Makromol. Chem., Macromol. Symp.*, **67**, 339.
272. Quirk, R.P. and Bidinger, G.P. (**1989**) *Polym. Bull. (Berlin)*, **22**, 63.
273. Matyjaszewski, K. (**1990**) *New Polym. Mater.*, **2**, 115.
274. Quirk, R.P. and Ren, J. (**1992**) *Macromolecules*, **25**, 6612.
275. Webster, O.W. (**1993**) *Makromol. Chem., Macromol. Symp.*, **67**, 365.
276. Quirk, R.P. and Kim, J.S. (**1995**) *J. Phys. Org. Chem.*, **8**, 242.
277. Mai, P.M. and Müller, A.H.E. (**1987**) *Makromol. Chem., Rapid Commun.*, **8**, 99.
278. Quirk, R.P., Ren, J. and Bidinger, G. (**1993**) *Makromol. Chem., Macromol. Symp.*, **67**, 351.
279. Brittain, W.J. and Dicker, I.B. (**1993**) *Makromol. Chem., Macromol. Symp.*, **67**, 373.
280. Hertler, W.R. (**1987**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **28**(1), 108.
281. Asami, R., Kondo, Y. and Takaki, M. (**1987**) Synthesis of poly(methyl methacrylate) macromonomer by

group transfer polymerization, and polymerization of the macromonomer, in *Recent Advances in Anionic Polymerization* (eds T.E. Hogen-Esch and J. Smid), Elsevier, Amsterdam, pp. 381.

282. Simms, J.A. and Spinelli, H.J. (**1987**) *J. Coat. Technol.*, **59**, 742.
283. Sogah, D.Y. (**1988**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **29**(2), 3.
284. Sakamoto, K., Aimiya, T. and Kira, M. (**1997**) *Chem. Lett.*, 1245.
285. Simon, P.F.W., Radke, W. and Müller, A.H.E. (**1997**) *Makromol. Chem., Rapid Commun.*, **18**, 865.
286. Simmons, M.R., Yamasaki, E.N. and Patrickios, C.S. (**2000**) *Macromolecules*, **33**, 3176.
287. Webster, O.W. (**1992**) *Makromol. Chem., Macromol. Symp.*, **60**, 287.
288. Webster, O.W. (**1992**) *Makromol. Chem., Macromol. Symp.*, **53**, 307.
289. Webster, O.W. (**1993**) *Makromol. Chem., Macromol. Symp.*, **70/71**, 75.
290. Webster, O.W. (**2000**) *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 2855.
291. Webster, O.W. (**2004**) *Adv. Polym. Sci.*, **167**, 1.
292. Reetz, M.T., Knauf, T., Minet, U. and Bingel, C. (**1988**) *Angew. Chem.*, **100**, 1422.
293. Reetz, M.T. and Ostarek, R. (**1988**) *J. Chem. Soc., Chem. Commun.*, 213.
294. Reetz, M.T. (**1988**) *Angew. Chem.*, **100**, 1026.
295. Sivaram, S., Dhal, P.K., Kashikar, S.P., Khisti, R.S., Shinde, B.M. and Baskaran, D. (**1991**) *Macromolecules*, **24**, 1698.
296. Sivaram, S., Dhal, P.K., Kashikar, S.P., Khisti, R.S., Shinde, B.M. and Baskaran, D. (**1991**) *Polym. Bull.*, **25**, 77.
297. Raj, D.J.A., Wadgaonkar, P.P. and Sivaram, S. (**1992**) *Macromolecules*, **25**, 2774.
298. Bandermann, F., Beckelmann, D., Broska, D., Fieberg, A., Roloff, T. and Wolters, D. (**1995**) *Macromol. Chem. Phys.*, **196**, 2335.
299. Sivaram, S. and Khisti, R.S. (**1991**) *Makromol. Chem., Rapid Commun.*, **12**, 435.
300. Zagala, A.P. and Hogen-Esch, T.E. (**1996**) *Macromolecules*, **29**, 3038.
301. Baskaran, D. and Müller, A.H.E. (**1997**) *Macromolecules*, **30**, 1869.
302. Baskaran, D., Müller, A.H.E., Kolshorn, H., Zagala, A.P. and Hogen-Esch, T.E. (**1997**) *Macromolecules*, **30**, 6695.
303. Konigsmann, H., Jüngling, S. and Müller, A.H.E. (**2000**) *Macromol. Rapid Commun.*, **21**, 758.
304. Dimov, D.K., Warner, W.N., Hogen-Esch, T.E., Juengling, S. and Warzelhan, V. (**2000**) *Macromol. Symp.*, **157**, 171.
305. Baskaran, D. and Müller, A.H.E. (**2000**) *Macromol. Rapid Commun.*, **21**, 390.
306. Weiss, H., Steiger, S., Juengling, S., Yakimansky, A.V. and Müller, A.H.E. (**2003**) *Macromolecules*, **36**, 3374.
307. Kitayama, T., Shinozaki, T., Masuda, E., Yamamoto, M. and Hatada, K. (**1988**) *Polym. Bull.*, **20**, 505.
308. Kitayama, T., Masuda, E., Yamaguchi, M., Nishiura, T. and Hatada, K. (**1992**) *Polym. J.*, **24**, 817.
309. Ikeda, M., Hirano, T. and Tsuruta, T. (**1971**) *Makromol. Chem.*, **150**, 127.
310. Abe, H., Imai, K. and Matsumoto, M. (**1968**) *J. Polym. Sci., Part C*, **23**, 469.
311. Matsuzaki, K., Kanai, T., Ichijo, C. and Yazawa, M. (**1984**) *Makromol. Chem.*, **185**, 2291.
312. Schlaad, H., Kolshorn, H. and Müller, A.H.E. (**1994**) *Macromol. Rapid Commun.*, **15**, 517.
313. Schlaad, H. and Müller, A.H.E. (**1995**) *Macromol. Symp.*, **95**, 13.
314. Schmitt, B., Schlaad, H., Müller, A.H.E., Mathiasch, B., Steiger, S. and Weiss, H. (**2000**) *Macromolecules*, **33**, 2887.
315. Schlaad, H. and Müller, A.H.E. (**1996**) *Macromol. Symp.*, **107**, 163.
316. Schlaad, H. and Müller, A.H.E. (**1998**) *Macromolecules*, **31**, 7127.
317. Schmitt, B., Stauf, W. and Müller, A.H.E. (**2001**) *Macromolecules*, **34**, 1551.
318. Schmitt, B. and Müller, A.H.E. (**2001**) *Macromolecules*, **34**, 2115.
319. Hirano, T., Kitayama, T. and Hatada, K. (**1998**) *Polym. J. (Tokyo)*, **30**, 736.

320. Kitayama, T., Zhang, Y. and Hatada, K. (**1994**) *Polym. J. (Tokyo)*, **26**, 868.
321. Tabuchi, M., Kawauchi, T., Kitayama, T. and Hatada, K. (**2002**) *Polymer*, **43**, 7185.
322. JP 99–236,445; EP 1,078,942 A1. (**1999**) Kuraray Co. Ltd., Japan, invs.: K. Hamada, K. Ishiura, M. Kato, S. Yaginuma.
323. Ruckdäschel, H., Sandler, J.K.W., Altstädt, V., Rettig, C., Schmalz, H., Abetz, V. and Müller, A.H.E. (**2006**) *Polymer*, **47**, 2772.
324. EP. 1 489 116 A1 (**2004**) Kuraray Co., Ltd., invs.: Y. Morishita, K. Hamada, S. Sasaki.
325. EP. 1 580 206 A1 (**2005**) Kuraray Co., Ltd., invs.: T. Kurihara, K. Hamada.
326. Ihara, E., Ikeda, J. and Inoue, K. (**2002**) *Macromolecules*, **35**, 4223.
327. Ihara, E., Ikeda, J., Itoh, T. and Inoue, K. (**2004**) *Macromolecules*, **37**, 4048.
328. Marchal, J., Gnanou, Y. and Fontanille, M. (**1997**) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **38**(1), 473.
329. Wang, J.-S., Bayard, P., Jérôme, R., Varshney, S.K. and Teyssié, P. (**1994**) *Macromolecules*, **27**, 4890.
330. Yakimansky, A.V. and Müller, A.H.E. (**1999**) *Macromolecules*, **32**, 1731.
331. Navarro, C., Marcarian, X. and Vuillemin, B. (**1998**) *Macromol. Symp.*, **132**, 263.
332. Kuroki, M., Aida, T. and Inoue, S. (**1987**) *J. Am. Chem. Soc.*, **109**, 4737.
333. Adachi, T., Sugimoto, H., Aida, T. and Inoue, S. (**1993**) *Macromolecules*, **26**, 1238.
334. Sugimoto, H., Kuroki, M., Watanabe, T., Kawamura, C., Aida, T. and Inoue, S. (**1993**) *Macromolecules*, **26**, 3403.
335. Sugimoto, H., Aida, T. and Inoue, S. (**1994**) *Macromolecules*, **27**, 3672.
336. Aida, T., Sugimoto, H., Kuroki, M. and Inoue, S. (**1995**) *J. Phys. Org. Chem.*, **8**, 249.
337. Takeuchi, D., Watanabe, Y., Aida, T. and Inoue, S. (**1995**) *Macromolecules*, **28**, 651.
338. Sugimoto, H. and Inoue, S. (**1999**) *Adv. Polym. Sci.*, **146**, 41.
339. Yasuda, H., Yamamoto, H., Yokota, K., Miyake, S. and Nakamura, A. (**1992**) *J. Am. Chem. Soc.*, **114**, 4908.
340. Yasuda, H., Yamamoto, H., Yamashita, M., Yokota, K., Nakamura, A., Miyake, S., Kai, Y. and Kanehisa, N. (**1993**) *Macromolecules*, **26**, 7134.
341. Yasuda, H., Yamamoto, H., Takemoto, Y., Yamashita, M., Yokota, K., Miyake, S. and Nakamura, A. (**1993**) *Makromol. Chem., Macromol. Symp.*, **67**, 187.
342. Ihara, E., Morimoto, M. and Yasuda, H. (**1995**) *Macromolecules*, **28**, 7886.
343. Yasuda, H. (**2001**) *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 1955.
344. Collins, S. and Ward, D.G. (**1992**) *J. Am. Chem. Soc.*, **114**, 5460.
345. Deng, H. and Soga, K. (**1996**) *Macromolecules*, **29**, 1847.
346. Chen, E.Y.-X. (**2004**) *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 3395.
347. Park, C., Yoon, J. and Thomas, E.L. (**2003**) *Polymer*, **44**, 6725.
348. Liu, H.Y. and Zhu, X.X. (**1999**) *Polymer*, **40**, 6985.
349. Butler, K., Thomas, P.R. and Tyler, G.J. (**1960**) *J. Polym. Sci.*, **48**, 357.
350. Huang, S.S. and McGrath, J.E. (**1981**) *J. Appl. Polym. Sci.*, **26**, 2827.
351. Xie, X. and Hogen-Esch, T.E. (**1996**) *Macromolecules*, **29**, 1746.
352. Kobayashi, M., Okuyama, S., Ishizone, T. and Nakahama, S. (**1999**) *Macromolecules*, **32**, 6466.
353. Nakhmanovich, B.I., Urman, Y.G., Krystal'nyi, E.V. and Arest-Yakubovich, A.A. (**2003**) *Vysokomol. Soedin., Ser. A i Ser. B.*, **45**, 978.
354. Eggert, M. and Freitag, R. (**1994**) *J. Polym. Sci. A*, **32**, 803.
355. Kobayashi, M., Ishizone, T. and Nakahama, S. (**2000**) *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 4677.
356. Kobayashi, M., Ishizone, T. and Nakahama, S. (**2000**) *Macromolecules*, **33**, 4411.
357. Martinez-Castro, N., Zhang, M., Pergushov, D.V. and Müller, A.H.E. (**2006**) *Des. Monom. Polym.*, **9**, 63.
358. André, X., Benmohamed, K., Litvinenko, G.I., Yakimansky, A.V.

and Müller, A.H.E. (**2006**) *Macromolecules*, **39**, 2773.
359. Yakimansky, A.V. and Müller, A.H.E. (**2006**) *Macromolecules*, **39**, 4228.
360. Kitayama, T. and Katsukawa, K.-I. (**2004**) *Polym. Bull. (Berlin)*, **52**, 117.
361. Ishizone, T. and Ito, M. (**2002**) *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 4328.
362. Hadjichristidis, N., Iatrou, H., Pitsikalis, M. and Mays, J. (**2006**) *Prog. Polym. Sci.*, **31**, 1068.
363. Pantazis, D., Chalari, I. and Hadjichristidis, N. (**2003**) *Macromolecules*, **36**, 3783.
364. Hamley, I.W. (**2003**) *Nanotechnology*, **14**, R39.
365. Alexandridis, P. and Lindmann, B. (**2000**) *Amphiphilic Block Copolymers: Self-Assembly and Applications*, Elsevier, Oxford.
366. US 1859686 (**1932**) I. G. Farbenindustrie AG, invs.: E. Tschunkur, W. Bock.
367. DE 575371 (**1933**) I. G. Farbenindustrie AG, invs.: E. Tschunkur, W. Bock.
368. Stavely, F.W. (**1956**) *Ind. Eng. Chem.*, **48**, 778.
369. BE. 627652 (**1963**) Shell Internationale Research Maatschappij NV, invs.: G. Holden, R. Milkovich.
370. DE. 3730886 (**1989**) BASF AG, invs.: H. M. Walter, H. D. Schwaben, R. Bueschl, K. Bronstert, A. Echte.
371. Knoll, K. and Niessner, N. (**1998**) *Macromol. Symp.*, **132**, 231.
372. Fredrickson, G.H. (**2008**) *Nat. Mater.*, **7**, 261.
373. Desbois, P., Warzelhan, V., Niessner, N., Deffieux, A. and Carlotti, S. (**2006**) *Macromol. Symp.*, **240**, 194.
374. Förster, S., Plantenberg, T. (**2002**) *Angew. Chem., Int. Ed.*, **41**, 688.
375. Förster, S., Abetz, V. and Müller, A.H.E. (**2004**) *Adv. Polym. Sci.*, **166**, 267.
376. Soo, P.L. and Eisenberg, A. (**2004**) *J. Polym. Sci., Part B: Polym. Phys.*, **42**, 923.
377. Discher, D.E. and Eisenberg, A. (**2002**) *Science*, **297**, 967.
378. Discher, B.M., Hammer, D.A., Bates, F.S. and Discher, D.E. (**2000**) *Curr. Opin. Colloid Interface Sci.*, **5**, 125.
379. Riess, G. and Labbe, C. (**2004**) *Macromol. Rapid Commun.*, **25**, 401.
380. Rösler, A., Vandermeulen, G.W.M. and Klok, H.A. (**2001**) *Adv. Drug Deliv. Rev.*, **53**, 95.
381. Trubetskoy, V.S. (**1999**) *Adv. Drug Deliv. Rev.*, **37**, 81.
382. Alakhov, V.Y. and Kabanov, A.V. (**1998**) *Exp. Opin. Invest. Drugs*, **7**, 1453.
383. Cölfen, H. (**2001**) *Macromol. Rapid Commun.*, **22**, 219.
384. Bockstaller, M.R., Mickiewicz, R.A. and Thomas, E.L. (**2005**) *Adv. Mater.*, **17**, 1331.
385. Yang, H. and Zhao, D. (**2005**) *J. Mater. Chem.*, **15**, 1217.
386. Segalman, R.A. (**2005**) *Mater. Sci. Eng. R: Rep*, **48**, 191.
387. Ruzette, A.V. and Leibler, L. (**2005**) *Nat. Mater.*, **4**, 19.
388. Ikkala, O. and Ten Brinke, G. (**2004**) *Chem. Commun.*, **10**, 2131.
389. Lazzari, M. and Arturo López-Quintela, M. (**2003**) *Adv. Mater.*, **15**, 1583.