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New polymeric architectures with (meth)acrylic acid segments

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Abstract

This review summarizes recent advances in the design and synthesis of novel complex polymers with (meth)acrylic acid segments using various living and controlled polymerization techniques. As polymeric architectures, we will focus on block copolymers, branched polymers, Janus micelles, and polymer brushes. Characteristic solution behavior and morphologies derived from their amphiphilic properties and three-dimensional architectures will be introduced briefly.

Keywords: Acrylic acid; Methacrylic acid; Controlled/living polymerization; Block copolymers; Branched polymers; Polymer brushes; Polyelectrolytes

Contents

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1. Introduction

Poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA) are weak polyelectrolytes, in which the degree of ionization is governed by the pH and ionic strength of aqueous solution. For example, PAA is virtually undissociated at low pH ($pH \leq 4$), whereas a fully charged chain results at $pH \geq 8$. Poly[(meth)acrylic acid]s are known to form interpolymer complexes with various non-ionic proton-accepting polymers, their derivatives, and with cationic polyelectrolytes in aqueous and organic media [1–7]. It has been shown that the nature and molecular weight (MW) of the interacting polymers as well as various environmental parameters (the nature of solvent, pH, ionic strength of solution, temperature, and polymer concentration) have significant influence on the complex formation. Numerous studies have been also devoted to the interaction of poly[(meth)acrylic acid]s with metal ions [8–11], since knowledge of association phenomena of metal ions with charged macromolecules is of importance for the understanding of their physicochemical behavior in environmental and biological systems. PAA could be successfully used as a component of characteristic 'intelligen' organic–inorganic hybrid materials [12].

Block copolymers containing (meth)acrylic acid segments belong to the class of ionic (or polyelectrolyte) block copolymers, which combine structural features of polyelectrolytes, block copolymers, and surfactants. If the ionic block is rather short compared to the non-ionic one, they are also named 'block ionomers'. Ionic block copolymers possess quite unique and attractive properties, potentially connecting materials science, pharmacy, biochemistry and polymer science, which make them a challenging subject for researchers. In particular, much interest has been received by the self-assembly of block copolymers, because of their feasibility to generate nanostructured materials and their numerous potential applications in separation technology, controlled drug delivery and release, and smart catalyst separation technology [13–19]. Recent advances of the controlled/living polymerization techniques made it possible to produce well-defined polymer structures, such as graft copolymers, star polymers, polymer brushes, etc. The interest in synthesis and characterization of such complex polymer systems containing (meth)acrylic acid segments has increased enormously. Their chemical structure and three-dimensional (3D) architectures may be tuned for a wide range of applications covering as different aspects as stabilization of colloids, crystal growth modification, induced micelle formation, components of intelligent materials, polyelectrolyte complexing towards novel drug carrier systems.

For the synthesis of well-defined polymers, living polymerization techniques have been traditionally employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination. These requirements are met in a nearly ideal way in anionic polymerization, and less ideally, in cationic polymerization. However, the application of these techniques for the synthesis of functional polymers was limited, as most of the systems are not tolerant of functional groups. Thus, typically, protected monomers have been employed, followed by

Nomenclature

AA acrylic acid
PAA poly(acrylic acid)
MAA methacrylic acid
PMAA poly(methacrylic acid)
*t*BuA *tert*-butyl acrylate
P*t*BuA poly(*tert*-butyl acrylate)
*t*BuMA *tert*-butyl methacrylate
P*t*BuMA poly(*tert*-butyl methacrylate)
TMSMA trimethylsilyl methacrylate
BzMA benzyl methacrylate
THPMA 2-tetrahydropyranyl methacrylate
PNPMA *p*-nitrophenyl methacrylate
EEMA 1-(ethoxy)ethyl methacrylate
BEMA 1-(butoxy)ethyl methacrylate
*t*BEMA 1-(*tert*-butoxy)ethyl methacrylate
MMA methyl methacrylate
PMMA poly(methyl methacrylate)
S styrene
PS poly(styrene)
*n*BuA *n*-butyl acrylate
P*n*BuA poly(*n*-butyl acrylate)
EO ethylene oxide
PEO poly(ethylene oxide)
PPO poly(propylene oxide)
PB polybutadiene
PIB polyisobutylene
PCL poly(ε-caprolactone)
DMAEMA 2-(dimethylamino)ethyl methacrylate
NIPAAm *N*-isopropylacrylamide
CRP controlled radical polymerization
ATRP atom transfer radical polymerization
GTP group transfer polymerization
RAFT reversible addition-fragmentation chain transfer
PMDETA *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine
DB degree of branching
MW molecular weight
MWD molecular weight distribution
SCVP self-condensing vinyl polymerization
SCVCP self-condensing vinyl copolymerization

a polymer-analogous deprotection, e.g. hydrolysis of protecting ester groups. A variety of protected monomers have been developed in the past few decades, and various types of tailor-made polymers with interesting architectures and functional groups have been synthesized by living anionic polymerization with the protected monomers [20,21].

Recent development in controlled radical polymerization (CRP) methods has provided another methodology to synthesize functional polymers. The systems include atom transfer radical polymerization (ATRP) [22–24], nitroxide-mediated radical polymerization [25], and reversible addition–fragmentation chain transfer (RAFT) polymerization [26]. All systems are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of dormant species, and are more tolerant of functional groups and impurities. Such controlled polymerization methods have become key tools for polymer synthesis, especially for synthesizing complex polymers with well-defined structures. However, with the exception of RAFT, no CRP method is able to polymerize acidic monomers, like acrylic acid (AA). Hence, protected monomers are still required to obtain well-defined polymers with (meth)acrylic acid segments. Protected monomers with masked acid groups involve *tert*-butyl acrylate (*t*BuA), *tert*-butyl methacrylate (*t*BuMA), trimethylsilyl methacrylate (TMSMA), benzyl methacrylate (BzMA), 2-tetrahydropyranyl methacrylate (THPMA), and *p*-nitrophenyl methacrylate (PNPMA) (Fig. 1). After acid hydrolysis, thermolysis, or catalytic hydrogenolysis, these protective groups liberate their original acid functionality. Essential prerequisites for the protected monomer are good 'livingness' under each polymerization condition and selective deprotection under mild conditions.

2. Homopolymers

2.1. Anionic polymerization

For the synthesis of PMAA and PAA homopolymers by anionic living polymerization, *t*BuMA and *t*BuA have been mainly used as protected monomers. The first report of the anionic living polymerization of *t*BuMA was published in 1981 by Müller et al. [27],

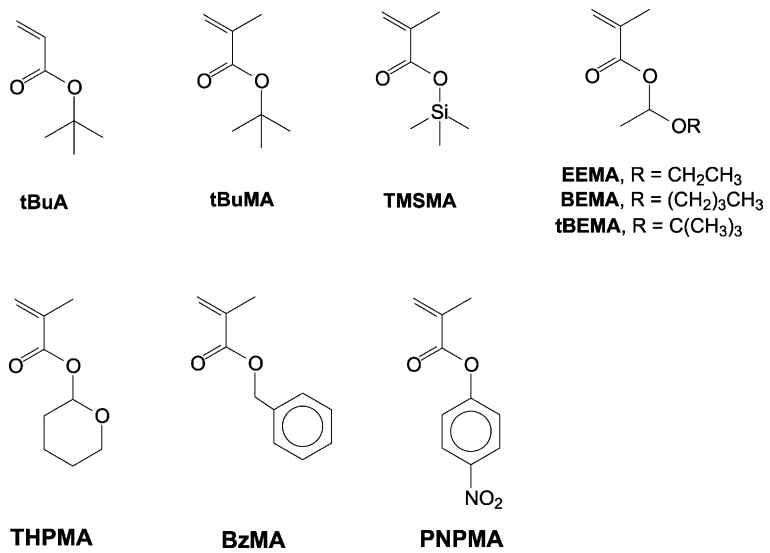


Fig. 1. Representative examples of protected (meth)acrylic acid monomers with masked acid group.

in which the polymerization with Na^+ and Cs^+ as counterions proceeds without side reactions in THF even at room temperature. The resulting molecular weight distributions (MWDs) are nearly monodisperse. The influence of solvent, additive, and polymerization temperature on the living polymerization system has been investigated later by other groups [28–30]. The synthesis of monodisperse PMAA was conducted by hydrolysis of P*t*BuMA obtained by the anionic living polymerization [31].

In 1977, the first attempts were published to obtain monodisperse PAA via living anionic polymerization of *t*BuA [32]. However, *t*BuA is much more subject to undesired termination reactions than *t*BuMA. In addition, the aggregation/dissociation equilibrium of the enolate chain ends is slow compared to propagation, leading to braod MWDs [33]. Several improvements have contributed to reach a living polymerization system. Actually, the living polymerization of *t*BuA was reported after 1986 by several groups [34–37]. Major advances during the periods include the development of new initiator systems, such as *tert*-butyl α-lithioisobutyrate [36,38], the adduct of *sec*-BuLi and 1,1-diphenylethylene [39,40] or α-methylstyrene [35], and the purification of monomer by trialkylaluminium [34], but the breakthrough was reached through the addition of μ-type ligands, in particular LiCl [35,36,41] and lithium alkoxides [36]. Recently a controlled anionic polymerization of *t*BuA was reported to be achieved with diphenylmethyl anions in the presence of triethylborane [42] and dialkylzinc [43].

TMSMA was also used as a protected monomer for the anionic living polymerization. For example, Hatada et al. reported the synthesis of highly stereoregular PMAA by anionic living polymerization of TMSMA [44]. Polymerization initiated by *tert*-BuLi in toluene at −78 °C gave isotactic polymer, while initiation with *tert*-BuLi and bis(2,6-di-*tert*-butylphenoxy)methylaluminium gave syndiotactic polymer. Another example involves anionic polymerization of alkoxyethyl methacrylate monomers, in particular 1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (*t*BEMA) [45]. These monomers could underdo anionic polymerization with 1,1-diphenylhexyllithium/LiCl at higher temperatures (−40–0 °C) than the common alkyl methacrylates to give polymers having controlled MW and narrow MWD.

For the synthesis of block copolymers and further complex polymer systems containing (meth)acrylic acid segments by living anionic polymerization, *t*BuMA and *t*BuA have been mainly used as a protected monomer. TMSMA has been also employed occasionally.

2.2. Group transfer polymerization

Group transfer polymerization (GTP) has been recognized as a useful technique for the synthesis of methacrylate (co)polymers of controlled structure and narrow MWD. As with anionic polymerization, acidic monomers, like methacrylic acid, cannot be polymerized directly, and protected monomers are required. For the synthesis of well-defined homopolymers and PMAA-based block copolymers, four protected monomers have been used; TMSMA, THPMA, BzMA, and *t*BuMA (Fig. 1).

For example, Müller et al. [46] reported the kinetic study of GTP of *t*BuMA using a silyl ketene acetal initiator and a nucleophilic catalyst and concluded that the livingness of the system appears to be influenced by the reaction temperature. GTP of BzMA was reported to proceed smoothly to give polymers of low polydispersity, with good control of MW [47]. Armes et al. reported that TMSMA polymerized only very slowly due to the reactivity of trimethylsilyl ester group with the nucleophilic GTP catalyst and the synthesis of high MW block copolymer was not possible with this monomer [48,49]. THPMA has been mainly used for the preparation of a variety of block copolymers (see Section 3.2).

2.3. Controlled radical polymerization

Conventional radical polymerization of AA or MAA is a traditional way to produce PMAA and PAA with ill-defined MWD. For the synthesis of well-defined polymers, CRPs of protected monomers have been employed. Most interest has been related with block copolymers and more complex polymer systems containing (meth)acrylic acid segments.

For the ATRP system, Matyjaszewski et al. reported controlled polymerization of *t*BuA using methyl 2-bromopropionate, as the initiator and the CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) catalyst system [50,51]. In most ATRP-based syntheses for block and further complex polymer systems, *t*BuA has been employed as a protected monomer, which may be due to the feasibility to control the polymerization and easy hydrolysis. THPMA [52] and NPMA [53] were also employed in ATRP systems.

The nitroxide-mediated radical polymerization of acrylic monomers (especially methacrylates) is complicated by the accumulation of nitroxide radicals which slow down or even prevent the polymerization. In a kinetic study of the nitroxide-mediated polymerization of *t*BuA, Fukuda et al. [54] claimed that the polymerization rate can be increased by addition of a proper amount of radical initiator, dicumyl peroxide, without causing any appreciable broadening of polydispersity. The use of di-*tert*-butyl nitroxide allowed the controlled polymerization of *t*BuA to proceed at a lower temperature (120 °C). Nitroxide-mediated radical polymerization of *t*BuA has also been used to obtain well-defined block copolymers containing acrylic acid segments [25,55,56].

2.4. Deprotection

Quantitative deprotection of the protecting groups is a key step to prepare well-defined polymers containing (meth)acrylic acid segments. The trimethylsilyl group of poly(TMSMA) can be readily removed by methanolysis or hydrolysis with or without mild acidic catalyst [44,57]. The hydrolysis of P*t*BuMA and P*t*BuA is possible by isobutylene expulsion under acidic conditions, such as *p*-toluenesulfonic acid in toluene at 100–110 °C for 8–24 h [58,59] or HCl in dioxane at 85 °C for 5 h [60]. Recently milder conditions, such as 5- to 10-fold excess of trifluoroacetic acid in dichloromethane at room temperature for 24 h, has been preferably employed for the hydrolysis of the block copolymers and other polymer complexes containing P*t*BuA segments [61–63]. Another example to hydrolyze the *tert*-butyl groups is the reaction with trimethylsilyl iodide to convert them into trimethylsilyl groups, followed by hydrolysis with water/MeOH mixtures [64]. Quantitative debenzylation can be achieved via catalytic hydrogenolysis under mild conditions (Pd/C; H_2 (1 atm); 25 °C) [47]. Removal of the 2-tetrahydropyranyl protecting group was claimed to proceed via thermolysis at 140 °C under dynamic vacuum for 48 h [65]. The protective group in poly(THPMA) could be removed quantitatively by acidic hydrolysis under mild conditions (0.1 M HCl at room temperature) [49].

In the cases of block copolymers and further complex polymer systems, conditions for the selective

deprotection are dependent upon not only the nature of the protecting groups but also the architecture and chemical structure of their neighbors. For example, Armes et al. [49,66] reported that *t*BuMA and BzMA could not be used for the synthesis of zwitterionic AB diblock copolymers of 2-(dimethylamino)ethyl methacrylate (DMAEMA) with MAA, because of the difficulty in the hydrolysis. They claimed that the conditions required to remove the *tert*-butyl group were likely to cause intermolecular cross-linking between the DMAEMA block, and benzyl groups could not be subsequently removed in the presence of the tertiary amine block, probably due to poisoning of the Pd/C catalyst. Finally, THPMA was used as a protected monomer for the synthesis of poly(DMAEMA)-*b*-PMAA.

With other alkyl esters (in particular methyl and ethyl), the hydrolysis requires hard conditions. For example, the acidic hydrolysis of PMMA was conducted by 72 h treatment with conc. H_2SO_4 [67] or 18 h reaction in acetic acid/water (80/20 vol %) in the presence of *p*-toluenesulfonic acid at 120 °C [68]. However, a relatively quantitative hydrolysis or partial formation of P(M)AA segments were reported in some systems. For example, the hydrolysis of PMMA segments in a complex polymer system was reported to be attained with KOH using 18-crown-6 as a phase transfer catalyst in 1,4-dioxane at 110 °C for 5 days (the degree of hydrolysis $>90\%$) [69]. The hydrolysis of poly(methyl acrylate) segments in a diblock copolymers was conducted in dioxane at reflux with 1N H_2SO_4 as the catalysts for 12 h [70]. Relatively mild alkaline conditions (NaOH in benzene/methanol, reflux for 3 h) were also employed for the hydrolysis of poly(methyl acrylate) in linear–dendritic diblock copolymers [71].

2.5. Direct polymerization of acrylic acid

RAFT provides a controlled polymerization of AA without protecting groups. Rizzardo et al. reported a direct synthesis of PAA with narrow MWD ($M_w/M_n = 1.23$) via RAFT polymerization of AA with 1-phenylethyl dithiobenzoate as a chain transfer agent and AIBN as the initiator at 60 °C in DMF [72]. Controlled polymerization of AA was also attained using 1-cyanoethyl 2-pyrolidone-1-carbodithioate [73] as a chain transfer agent.

Polymerization of AA was reported to be controlled in alcohol and water with phenoxyxanthates or with trithiocarbonates [74]. Controlled polymerization of AA could be also attained using dibenzyl trithiocarbonate and bis(1-phenylethyl) trithiocarbonate [75] as a chain transfer agent. Direct synthesis of well-defined PAA was achieved with a xanthate chain transfer agent (so-called MADIX process) [76,77]. The polymerization of AA was also performed under γ-irradiation in the presence of dibenzyl trithiocarbonate at room temperature, and well-defined PAA with a narrow MWD was successfully prepared [78].

Sodium methacrylate was found to be polymerized directly via ATRP in aqueous media using a Cu(I)Br catalyst and 2,2′-bipyridine with a poly(ethylene oxide) (PEO)-based macroinitiator; and the resulting PEO-*b*-poly(sodium methacrylate) copolymers were obtained in good yield and have narrow polydispersity [79]. The choice of pH and initiator is critical and the optimum pH is between 8 and 9, as there appears to be a balance between the reduced propagation rate at high pH and competing protonation of the ligand at low pH.

3. Block copolymers

Block copolymers have been extensively investigated both theoretically and practically in the past few decades. Traditional amphiphilic block copolymers containing chemically connected hydrophilic and hydrophobic segments provide a great variety of morphologies both in solid state and in selective solvents [80,81]. Zwitterionic polymers or polyampholytes [82], in which at least two of the blocks are of opposite charge, are interesting synthetic analogues for proteins and therefore are an interesting class of block copolymers. Double-hydrophilic block copolymers [83] are another new class of amphiphilic molecules of rapidly increasing importance with unique and fascinating properties. In addition to traditional AB- and ABA-type block copolymers, recently much attention has been paid to ABC triblock copolymers (or block terpolymers), as shown in Fig.2, because of their characteristic bulk morphologies. Characteristic of these block copolymers containing (meth)acrylic acid segments is their application in aqueous environments and that their self-assembled

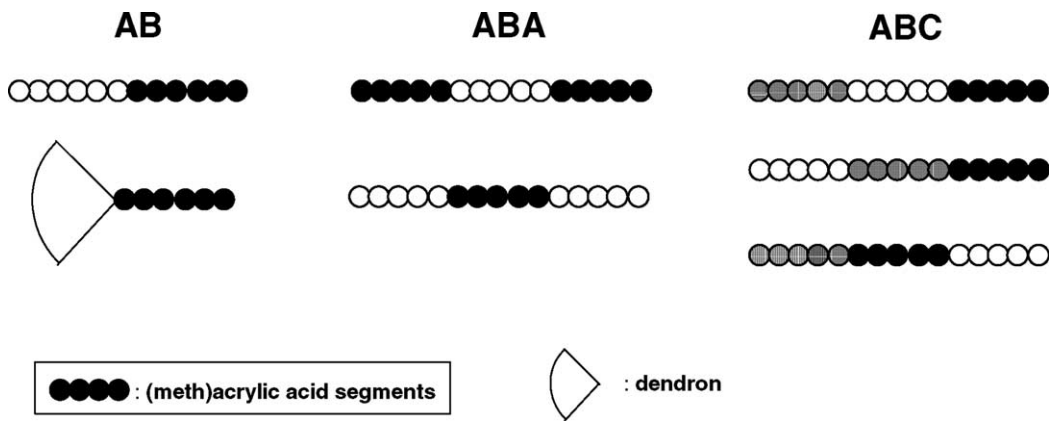


Fig. 2. Various types of block copolymers containing (meth)acrylic acid segments.

structures can be modified by salt concentration and pH changes, which is related to the properties of a weak polyelectrolyte. The chemical nature of the other segment(s) of the block copolymers and their composition can be generally manipulated by using controlled/living polymerization techniques, which provide a great opportunity to tune their chemical and physical properties as well as highly ordered structures due to the self-assembly process. A variety of controlled/living polymerization techniques could be used to achieve well-defined block copolymers.

3.1. Anionic polymerization

Anionic polymerization has been the first and the most used technique for the preparation of well-defined block copolymers. Some of the most common amphiphilic block copolymers are based on a hydrophilic segment of poly(methacrylic acid) (PMAA) or poly(acrylic acid) (PAA), which were mainly prepared by sequential living anionic polymerization of *tert*-butyl methacrylate (*t*BuMA) or *tert*-butyl acrylate (*t*BuA). In 1990, Teyssie et al. [59] reported the synthesis of AB- and ABA-type block copolymers, which were prepared by sequential anionic polymerization of styrene (S) and *t*BuA in the presence of LiCl in THF at −78 °C, followed by hydrolysis using *p*-toluenesulfonic acid as catalyst. A well-defined block copolymer, PS-*b*-P*t*BuMA, has been synthesized by sequential anionic living polymerization of S and *t*BuMA by intermediate addition of 1,1-diphenylethylene [84,85]. Subsequent elimination of *tert*-butyl groups provided well-defined PS-*b*-PMAA [85]. Such amphiphilic block copolymers can self-assemble into polymer micelles and/or vesicles with nanometer-sized dimensions when being dissolved in a selective solvent for one of the blocks, typically water. Systematic studies on micellar size and structure have been published for PS-*b*-PAA [58,86–91], PS-*b*-PMAA [92–94], and their salt forms. This type of amphiphilic block copolymers has been employed for the preparation of various advanced materials, such as semiconductor (CdS) nanoparticles [95,96], micelle-encapsulated carbon nanotubes [97], chemically patterned surfaces [98], and temperature-dependent photonic bandgap materials [99]. Mixed polymeric micelles have been investigated, which were prepared by mixing two different amphiphilic block copolymers, such as PS-*b*-PMAA and PS-*b*-PEO [100,101], or PS-*b*-PAA and PS-*b*-poly(4-vinylpyridine) [102]. A similar synthetic strategy combining sequential anionic living polymerization of a protected monomer with subsequent elimination of protective groups could provide well-defined block copolymers consisting of alkyl (meth)acrylate and (meth)acrylic acid segments [103]. The micellization of (meth)acrylate block copolymers prepared by this method has been also investigated, including PMMA-*b*-PAA [104–106], poly(2-ethylhexyl acrylate)-*b*-PAA [107], and poly(hexyl or dodecyl methacrylate)-*b*-PAA [108].

The first examples of zwitterionic block copolymers were reported by Kamachi et al. [67],

who copolymerized 2-vinylpyridine with either trimethylsilyl methacrylate (TMSMA) or *t*BuA, followed by hydrolysis. Synthesis of block copolymers of TMSMA with *p*-(*N*,*N*′-dimethylamino)styrene was reported by Morishima et al. [109]. Bekturov and co-workers have described the synthesis and aqueous solution behavior of poly(1-methyl-4-vinylpyridinium chloride)-*b*-PMAA [110,111]. Teyssie and Jerome reported the synthesis of a diblock copolymer, P*t*BuMA-*b*-poly[2-(dimethylamino)ethyl methacrylate] [112]. Adsorption of the diblock ampholytes, PMAA-*b*-poly[2-(dimethylamino)ethyl methacrylate], obtained after hydrolysis was investigated systematically [113–117]. Characteristic pH-dependent micellization has been reported for this type of copolymers [118,119]. AB-, ABA-, and BAB-type block copolymers consisting of poly[2-(dimethylamino)alkyl methacrylates], (alkyl = ethyl, propyl, and 1-ethyl methyl, respectively) as the A segment and poly(sodium methacrylate) as the B segment were synthesized and micellization was characterized in aqueous solution [120].

One interesting class of block copolymers is that containing poly(ethylene oxide) (PEO), leading to double-hydrophilic polymers. The synthesis of PEO-*b*-P*t*BuMA was first conducted by anionic polymerization from both living PEO and P*t*BuA, respectively [121], but MWD results indicate some side reactions. The synthesis of AB-, BA-, ABA-, and BAB-type block copolymers of PEO and P*t*BuMA with well-defined structure was achieved using Ph_2CHK and K naphthalene as mono and difunctional initiators, respectively [122]. The typical procedure includes polymerization of *t*BuMA at −78 °C, followed by addition of EO, and finally increasing temperature gradually to 35 °C. The block copolymer PEO-*b*-PMAA, obtained after hydrolysis has been used for the formation of interpolyelectrolyte complexes [123,124]. These block copolymers were also reported to be highly efficient dispersants for oxide ceramic powders in aqueous solution [125]. PEO-*b*-PMAA is now commercially available, and has been extensively employed as crystal growth modifier [83,126,127].

Another interesting class of block copolymers is double stimuli-responsive block copolymers, i.e. poly-mers that respond to two external stimuli, e.g. pH and temperature, with changes of their conformation. Recently Müller et al. [128] reported the synthesis of PAA-*b*-poly(*N*,*N*-diethylacrylamide) by sequential anionic polymerization of *t*BuA with diphenylhexyllithium/LiCl and *N*,*N*-diethylacrylamide (after adding triethylaluminium), followed by hydrolysis. Poly(*N*,*N*-diethylacrylamide) exhibits a lower critical solution temperature (LCST of 32 °C), whereas the degree of ionization of PAA can be controlled by pH change. Depending on pH and temperature, these polymers can form micelles, inverse micelles or hydrogels.

Diblock and ABA-type triblock copolymers with semicrystalline polyethylene and PMAA blocks were synthesized by sequential living anionic polymerization of butadiene and *t*BuMA, followed by homogeneous hydrogenation using the Wilkinson catalyst, and then hydrolysis and neutralization with NaOH [129]. Characteristic crystallization results from DSC on the phase behavior (mixing of phases and interplay between organization in the amorphous and semicrystalline phases) of these new materials were presented.

Ruckenstein and Zhang [130] demonstrated the synthesis of block copolymers by anionic polymerization of three novel alkoxyethyl methacrylate monomers, 1-(ethoxy)ethyl methacrylate (EEMA), 1-(butoxy)ethyl methacrylate (BEMA), and 1-(*tert*-butoxy)ethyl methacrylate (*t*BEMA). They pointed out that a well-controlled block copolymerization of S with EEMA or with *t*BEMA was achieved at higher temperatures (−35 °C) than usually employed (−78 °C), and even at 0 °C, a well-defined diblock copolymer consisting of PS and poly(*t*BEMA) could be obtained. An ABC triblock copolymer, PS-*b*-PMMA-*b*-poly(EEMA), was also obtained with narrow MWD. By changing the polymerization sequence, the hydrophilic segment could be located either in the center or at the end of the copolymer chain. The protecting group, 1-(alkoxy)ethyl of each of the monomers, could be easily eliminated after copolymerization, using a mild acidic environment (for instance, a small amount of a 5 M HCl solution in THF solution at room temperature for 2 min).

A variety of ABC triblock copolymers containing methacrylic acid segments has been synthesized by sequential living anionic polymerization using a protected monomer, generally *t*BuMA. For example, the synthesis of PS-*b*-PMMA-*b*-P*t*BuA was reported by Eisenberg et al. [131]. The synthesis procedure is

similar to that for the preparation of PS-*b*-P*t*BuA diblock copolymers. Morphologies formed from amphiphilic triblock copolymers, PS-*b*-PMMA-*b*-PMAA, obtained after the hydrolysis were studied in THF, dioxane, and DMF induced by addition of water. Synthesis and characterization of PS-*b*-PMAA-*b*-PMMA, in which the middle block is hydrophilic PMAA, have been reported by Macosko et al. [132]. Recently, Abetz et al. reported the synthesis of triblock copolymers, PS-*b*-polybutadiene (PB)-*b*-P*t*BuMA having different composition by sequential anionic polymerization and their hydrolyzed analogues, PS-*b*-PB-*b*-PMAA [133]. They demonstrated that the chemical modification of the third block leads to a change of the overall morphology observed in solution-cast films, which was interpreted as a consequence of the change of the incompatibility between the different components and the solvent.

ABC triblock copolyampholytes containing a neutral hydrophobic block, a polyacid, and a polybase, have been synthesized by sequential living anionic polymerization technique. Stadler et al. [134] has demonstrated the synthesis of triblock copolyampholytes, PS-*b*-poly(2- or 4-vinylpyridine)-*b*-PMAA. They investigated the polyelectrolyte complex formation of the triblock copolyampholytes in terms of pH change in solution as well as in bulk. Poly[5-(*N*,*N*-dimethylamino)isoprene]-*b*-PS-*b*-P*t*BuMA was synthesized and hydrolyzed to yield poly[5-(*N*,*N*-dimethylamino)isoprene]-*b*-PS-*b*-PMAA triblock copolyampholytes [135]. Recently, Eisenberg's group reported the synthesis of P*t*BuA-*b*-PS-*b*-poly(4-vinylpyridine) [136]. No data ware given on the hydrolyzed products.

Sequential anionic living polymerization has also been employed for the synthesis of other types of ABC triblock copolymers. For example, Ishizone et al. [137] synthesized ABC triblock copolymers containing 2-(perfluorobutyl)ethyl methacrylate, P*t*BuMA, and 2-(trimethylsilyloxy)ethyl methacrylate with various block sequences. The block copolymers then were converted into amphiphilic systems by removing the trimethylsilyl protecting group to give a poly(2-hydroxyethyl methacrylate) block. The microdomain structures of the ABC triblock copolymer film was studied in detail [138]. This triblock copolymer can be regarded as a precursor of anionic triblock copolymer containing a PMAA segment.

A novel diblock copolymer containing a polysilane, poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-PMAA, was prepared by the sequential anionic polymerization of a masked disilene, and trimethylsilyl methacrylate, followed by hydrolysis of the trimethylsilyl protecting group. The cross-linking reaction of the PMAA block with 1,10-diaza-4,7-dioxadecane and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride afforded shell cross-linked micelles of polysilane [57]. Nanometer-sized hollow particles derived from polysilane shell cross-linked micelles could be obtained since the polysilane core can undergo photochemical degradation, and it was demonstrated that the hollow particles can undergo reversible uptake of guest molecules [139]. Poly(1,1-diethylsilacyclobutane)-*b*-PMAA was synthesized by anionic living polymerization [140], and the nanostructure of their monolayer spread on water was investigated in comparison with poly(α-methylstyrene)-*b*-PMAA [141].

Recently, several groups reported a new method of construction of nanometer-sized particles by cross-linking of the core or the shell of polymer micelles. Wooley's group has reported shell cross-linked micelles of PS-*b*-PAA [142], and hollow particles by ozonolysis of shell cross-linked micelles with polyisoprene-*b*-PAA [143]. These block copolymers were prepared by anionic living polymerization.

Poly(2-cinnamoylethyl methacrylate)-*b*-PAA has been used for the preparation of water-soluble nanospheres by photo-cross-linking of the core of the spherical micelles of the block copolymers [144]. The synthetic steps include (1) synthesis of poly(2-hydroxyethyl methacrylate)-*b*-P*t*BuA by sequential living anionic polymerization of 2-(trimethylsiloxy)ethyl methacrylate and *t*BuA, followed by hydrolysis of the trimethylsiloxy group, (2) conversion of hydroxyethyl groups to cinnamoylethyl groups and selective cleavage of the *tert*-butyl esters to give poly(2-cinnamoylethyl methacrylate)-*b*-PAA, (3) formation of spherical micelles in DMF/water with poly(2-cinnamoylethyl methacrylate) as the core and PAA as the corona, (4) photo-cross-linking of the core. Such assembled structures could serve as precursors to nano or microstructures, such as palladium nanoparticle catalyst [145] and regularly packed nanochannels with CdS or Fe_2O_3 nanoparticles [146]. They also

reported the synthesis of triblock copolymers of poly(*n*-butyl methacrylate)-*b*-poly(2-cinnamoyloxyethyl methacrylate)-*b*-P*t*BuA and nanofibers by cross-linking cinnamoyloxyethyl groups photochemically and separating the cross-linked cylinders from dissolved poly(*n*-butyl methacrylate) chains [147]. Finally, nanotubes with PAA-lined channels were obtained after *tert*-butyl group removal from the P*t*BuA cores by selective hydrolysis. A triblock copolymer, PS-*b*-poly(2-cinnamoyloxyethyl methacrylate)-*b*-P*t*BuA, has been also used for the preparation of polymer/Fe_2O_3 hybrid nanofibers [148]. Another example involves the poly(isoprene)-*b*-poly(2-cinnamoylethyl methacrylate)-*b*-P*t*BuA triblock copolymer [149–151].

3.2. Group transfer polymerization

The synthesis of the amphiphilic block copolymer PMMA-*b*-PMAA has been achieved using BzMA as a protected acid monomer [48]. PMMA-*b*-PAA has also been synthesized via GTP of MMA and *t*BuA, followed by hydrolysis, and the micellar solutions were investigated [152]. GTP was also employed for the synthesis of ABA-type block copolymers, P*t*BuA to P*t*BuMA in both ends, and selective hydrolysis of *tert*-butyl groups gave amphiphilic block copolymers [153].

Patrickios et al. reported the synthesis of diblock and triblock polyampholytes of 2-(dimethylamino)ethyl methacrylate (DMAEMA), MAA, and MMA, via GTP using BzMA as a protected monomer [65,154]. Subsequently, Lowe et al. synthesized zwitterionic AB diblock copolymers of DMAEMA with MAA using THPMA [49,66]. They demonstrated that conversion from THPMA to PMAA was achieved via acid hydrolysis at room temperature. Two different types of zwitterionic shell cross-linked micelles were synthesized from PDMAEMA-*b*-PTHPMA [155]. Kriz et al. prepared an ABC triblock copolymer, poly(2-ethylhexyl acrylate)-*b*-PMMA-*b*-PAA, via GTP using *t*BuA as a protected monomer and studied its aqueous solution properties [156]. A core–shell–shell structure in water was suggested for the spherical micelle of the copolymer. Patrickios et al. synthesized ABC, ACB, and BAC triblock copolymers of DMAEMA, MMA, and THPMA [157]. The THPMA residues were converted to MAA residues by mild acid hydrolysis, yielding the triblock polyampholytes. The acid-labile tetrahydropyranyl group in block copolymers prepared by GTP has been found to be useful in chemically amplified photoresists or photolithography [158,159].

Block copolymers containing dimethyl siloxane and carboxylic acid sequences were synthesized by GTP of various methacrylates and acrylates using silyl ketene acetal terminated poly(dimethylsiloxane) as initiator, followed by hydrolysis of the ester sequences [160]. *t*BuMA, TMSMA, and the corresponding acrylates could be employed. The amphiphilic polymers poly(dimethylsiloxane)-*b*-PMAA and poly(dimethylsiloxane)-*b*-PAA were obtained after quantitative hydrolysis. The authors also claimed that most copolymers were contaminated by unincorporated homo-poly(dimethylsiloxane), which was efficiently removed by hexane or supercritical CO_2 extraction. The interesting role of these block amphiphilic block copolymers in stabilizing dispersion polymerizations in supercritical CO_2 was also reported [161,162].

As mentioned above, GTP is an effective tool for synthesizing amphiphilic block copolymers containing PMAA segments by using protected monomers. However, block copolymers with a non-polar monomer, such as styrene, cannot be obtained by this method, because GTP cannot be applied to non-polar monomers.

3.3. Atom transfer radical polymerization

Using the ATRP process, block copolymers can be generated from a macroinitiator synthesized by either ATRP or a different mechanism (cationic, anionic, etc.) [23]. Furthermore, the growth of subsequent blocks can be achieved from an isolated macroinitiator or by in situ addition of a second monomer to a reaction near completion. Generally, a protected monomer is still required during ATRP process because acid monomers can poison the catalysts by coordinating to the transition metal. In addition, nitrogen-containing ligands can be protonated, which interferes with the metal complexation ability.

The controlled synthesis of a P*t*BuA precursor could be attained using the CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) catalyst system [50,51]. The use of P*t*BuA as a macroinitiator allows for the preparation of amphiphilic block copolymers, after the hydrolysis of the ester groups

[51]. In addition, the preparation of an ABC triblock copolymer, P*t*BuA-*b*-PS-*b*-poly(methyl acrylate), was reported [50]. A series of well-defined diblock, triblock, and star-block copolymers composed of PS and PAA were synthesized by the method and used as stabilizers in emulsion polymerization [61]. Characterization of aqueous micellar solutions of the amphiphilic block copolymers was investigated toward the control of the number of particles in emulsion polymerization [163]. ATRP has been also employed for the synthesis of amphiphilic block copolymers containing methacrylic acid segments, such as PS-*b*-PMAA [164] and PMMA-*b*-PMAA [165], through hydrolysis of *tert*-butyl groups of P*t*BuMA block. The preparation of PS-*b*-PMAA block copolymer was also achieved by hydrolysis of PS-*b*-poly(PNPMA) obtained via ATRP [53]. A well-defined amphiphilic triblock copolymers containing conjugated polyfluorene and PMAA were synthesized by vacuum thermolysis of poly(THPMA)-*b*-polyfluorene-*b*-poly(THPMA) [52]. The precursor block copolymers were prepared by using ATRP with a 2-bromoisobutyrate end-capped polyfluorene as the macroinitiator. The block copolymers were found to form aggregates in water, as revealed by UV–vis and fluorescent spectroscopy and ^{1}H NMR studies.

ATRP was employed for the polymerization of *t*BuA, methyl acrylate, and S to generate well-defined diblock and triblock copolymers, which were converted to PAA-*b*-poly(methyl acrylate) and PAA-*b*-poly(methyl acrylate)-*b*-PS via hydrolysis reaction [166]. The self-assembly of the ABC-type amphiphilic triblock copolymer in aqueous solution, followed by conversion into stable complex nanostructures via cross-linking reactions between the hydrophilic PAA chains comprising the peripheral layers, produced mixtures of spherical and cylindrical topologies. Diblock copolymers consisting of 4-fluorostyrene and methyl acrylate were prepared by ATRP [70]. Hydrolysis of the poly(methyl acrylate) segment gave the amphiphilic block copolymers, which were converted into shell-cross-linked nanoparticles by covalent intermolecular cross-linking of the PAA residues in the shell using 2,2′-(ethylenedioxy)bis(ethylenediamine).

Synthesis of novel linear–dendritic diblock amphiphiles with linear PAA as the hydrophilic block and dendritic poly(benzyl ether) as the hydrophobic block was reported by Zhu et al. [71]. The synthetic process consisted of two steps: (1) ATRP of methyl acrylate initiated by dendritic poly(benzyl ether) bromides with different generations (G_i-Br, $i = 1–3$), and (2) hydrolysis of linear poly(methyl acrylate) under a mild alkaline condition (NaOH in benzene/methanol, reflux for 3 h). The dynamic properties of the micelles of the resulting amphiphiles were also studied in aqueous solution [167]. The luminescence enhancement of Tb^{3+} ions was investigated in which the ions complex with the PAA chain of the block copolymer to form a supramolecular luminophore [168].

3.4. Reversible addition–fragmentation chain transfer polymerization

Rizzardo et al. reported the synthesis of poly(*n*-butyl acrylate)-*block*-poly(acrylic acid), P*n*BuA-*b*-PAA, by the RAFT process using 1-phenylethyl dithiobenzoate in DMF [169]. PMMA-*b*-PMAA and poly(BzMA)-*b*-PMAA were also obtained from methacrylic acid (MAA). After (meth)acrylic acid groups were converted to methyl (meth)acrylate units with tetrabutylammonium hydroxide and methyl iodide, GPC analysis showed low polydispersity.

RAFT polymerization with 1-cyanoethyl 2-pyrolidone-1-carbodithioate as a chain transfer agent was successfully used to synthesize novel double stimuli-responsive block copolymers, poly(NIPAAm)-*b*-PAA [73]. For the synthesis of the block copolymer, PAA was used as a macromolecular chain transfer agent. *N*-isopropylacrylamide (NIPAAm) was polymerized to homo [170] and block copolymers with narrow MWD in most cases. Since poly(NIPAAm) exhibits a lower critical solution temperature (LCST at 32 °C) and the degree of ionization of PAA can be controlled by pH change, the block copolymers of NIPAAm and AA can be regarded as a double stimuli responsive polymers. Micelle formation of the block copolymer in aqueous solution was investigated for their response to pH and temperature, leading to micelles, inverse micelles and their aggregates. The presence of dithiocarbamate end groups in the polymer allows for the conjugation of proteins or drugs after hydrolysis of the end groups to the corresponding thiols. Thus, thermo- and pH-responsive systems can be created for the control of enzyme activity or molecular recognition processes [171].

Amphiphilic block copolymers of PAA-*b*-P*n*BuA were prepared using the trithiocarbonate or the xanthate as a chain transfer agent in a one-pot reaction [172]. These block copolymers were prepared by a straightforward approach: the polymerization of AA to completion was followed by the polymerization of *n*BuA. The authors also investigated the amphiphilic behavior of the copolymer in water, and the characteristics of this surfactant in an emulsion polymerization.

The MADIX process in aqueous media was applied for the synthesis of double-hydrophilic block copolymers comprising acrylamide and acrylic acid units starting from either a mono or difunctional xanthates [173]. The resulting AB- and ABA-type double-hydrophilic block copolymers showed molar masses predicted by the initial molar ratio of the monomers to the xanthate precursor and polydispersities of up to 1.5. The synthesis of PS-*b*-PAA was also conducted by the MADIX process, by which PS-*b*-poly(ethyl acrylate) was first synthesized in emulsion, followed by hydrolysis of the ethyl acrylate units [174].

The so-called iniferter (*ini*tiator–trans*fer* agent–*ter*minator)-based 'living' radical polymerization was also employed for the synthesis of block copolymers containing PMAA segments. PS with α- and ω-diethyldithiocarbamyl end groups was used as a macroiniferter [175]. Polymerization of *t*BuMA from the macroiniferter under UV light irradiation showed some characteristics in common with living radical polymerization, that is, the MW of the resulting polymers increased with reaction time. Subsequent hydrolysis afforded amphiphilic ABA triblock copolymers containing PMAA segments.

3.5. Other reactions

Yasuda et al. have successfully used samarocene complexes for a coordinative polymerization of (meth)acrylates [176,177]. For example, $SmMe(C_5Me_5)_2(THF)$ was used as an efficient initiator for the block copolymerizations of TMSMA with MMA [178]. Syndiotactic poly(TMSMA) (syndiotacticity >85%) could be obtained by using the catalysts system. All copolymerizations proceeded quantitatively in a short period and the resulting polymers exhibit high MW with rather narrow MWD ($M_w/M_n < 1.5$). The resulting poly(TMSMA) block in the copolymers was hydrolyzed with aqueous HCl solution to afford the corresponding PMAA block.

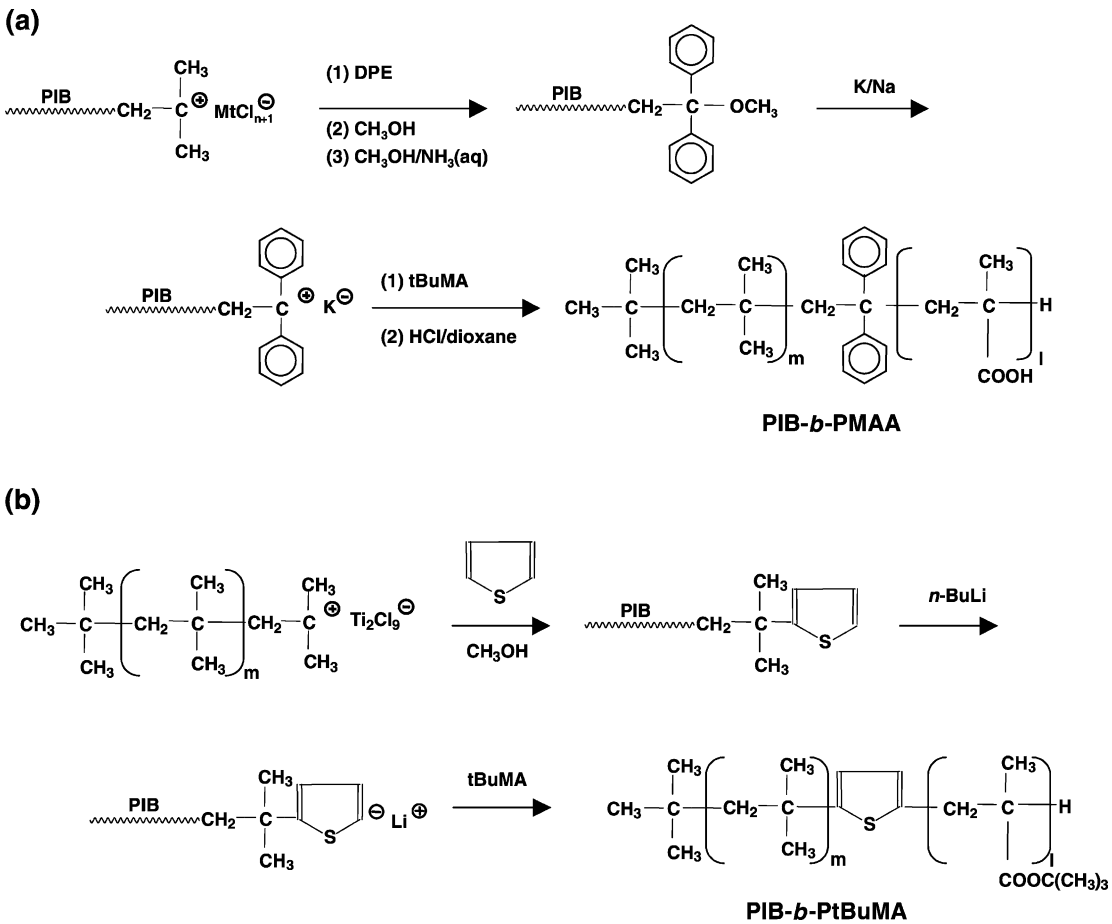
3.6. Multi-mode polymerizations

Since specific living polymerization methods (e.g. anionic and carbocationic polymerizations) are applicable only to a limited number of monomers, the combination of different living polymerization techniques is considered to lead to a new and unique approach for the design of novel polymeric architectures. Actually the combination of different 'living' polymerization techniques to produce various block copolymers represents a significant scientific challenge. Even AB block copolymers, which are simplest polymeric structures derived from such a combination of different polymerization techniques, usually require a significant synthetic effort.

3.6.1. Combination of cationic and anionic polymerizations

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

Several approaches have been reported for the synthesis of block copolymers composed of isobutylene and (meth)acrylic monomers. Many attempts led to insufficient block efficiency [179–181]. In the first fully successful report, isobutylene was polymerized with 2-chloro-2,4,4-trimethylpentane as the initiator and $TiCl_4$ as the catalyst in CH_2Cl_2/hexane at −78 °C (Scheme 1). The living PIB was end-capped with diphenylethylene (DPE) and quenched with methanol and ammonia to form PIB with a methoxydiphenyl terminus. Ether cleavage with K/Na alloy in THF at room temperature leads to an anionic macroinitiator that was used to polymerize *t*BuMA at −20 °C [182]. Subsequently the *tert*-butyl groups of the P*t*BuMA



Scheme 1. Synthesis procedures for polyisobutylene-*b*-poly(methacrylic acid) via cationic and anionic polymerizations.

block were hydrolyzed with hydrochloric acid to form a PIB-*b*-PMAA (Scheme 1a). Aggregation behavior of PIB-*b*-PMAA and the structure of their assemblies were investigated in aqueous solutions [183,184]. Since PIB has a low glass transition temperature ($T_g \sim 65$ °C), the micelles formed by these copolymers might be expected to be 'dynamic', that is, being able to exchange unimers. This behavior is significantly different from PS-*b*-PAA, in which so-called 'frozen' micelles are generated, such micelles being unable to exchange unimers, i.e. single block copolymer molecules, due to a high glass transition temperature ($T_g \sim 100$ °C) of PS. Interaction of PIB-*b*-PMAA micelles with a strong cationic polyelectrolyte, poly(*N*-ethyl-4-vinylpyridinium bromide) formed peculiar water-soluble micellar complex onion-like species (Fig. 3), containing a hydrophobic PIB core, an interpolymer complex shell, and a hydrophilic PMAA corona [185].

Recently a new effective route was presented [186] to prepare anionic macroinitiators by end capping of living PIB with one thiophene molecule and subsequent lithiation with *n*-butyllithium (Scheme 1b). The resulting stable macrocarbanion, PIB-thiophene$^-$Li$^+$, was used to initiate the living anionic polymerization of *t*BuMA, yielding PIB-*b*-P*t*BuMA block copolymers with high blocking efficiency.

3.6.2. Combination of cationic polymerization and ATRP

Synthesis of block copolymers via combination of cationic polymerization and ATRP was carried out by initiating ATRP with PIB macroinitiators, 1-chloro-1-phenylethyl-telechelic PIBs [187]. It was demonstrated

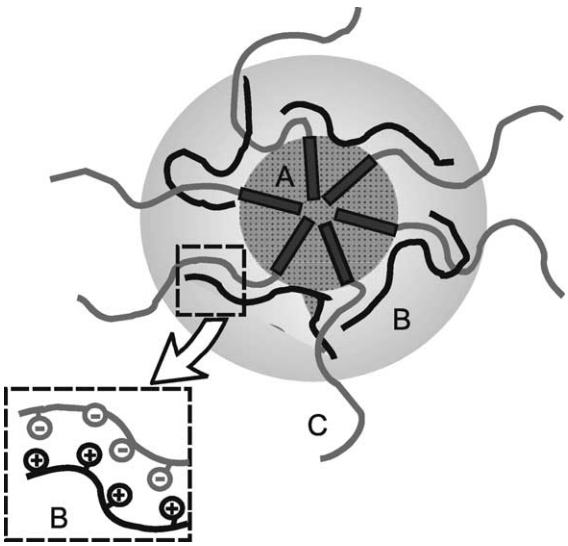


Fig. 3. Hypothetical architecture of a particle formed by micellar interpolyelectrolyte complexation. Reprinted with permission from J Phys Chem 2003;107:8093. © American Chemical Society [185].

that the PIB macroinitiators were efficient macroinitiators for ATRP of styrene and *p*-acetoxystyrene to form desired ABA-type triblock copoylmers.

Recently, Kennedy et al. [188] reported the synthesis of a series of novel block copolymers consisting of PIB and PMAA segments by the combination of cationic polymerization and ATRP. The specific targets were diblocks (PIB-*b*-PMAA), triblocks (PMAA-*b*-PIB-*b*-PMAA), and three-arm star-blocks [(PIB-*b*-PMAA)$_3$] consisting of rubbery, long PIB blocks (DP = 50–1000) connected to short blocks of PMAA (DP = 5–20). Here, the site transformation of the *tert*-chloro-terminal PIBs obtained by living cationic polymerization was conducted to termini capable of initiating ATRP proceeded by CuCl (or CuBr)/PMDETA systems. The rheological (dynamic viscoelastic) and mechanical properties of the block copolymers and their blends were investigated aiming to control these properties by intermolecular self-assembly via hydrogen bonding and ionic aggregation [189].

3.6.3. Combination of anionic polymerization and ATRP

Combination of anionic ring-opening polymerization and ATRP has been also utilized for the synthesis of block copolymers containing (meth)acrylic acid segments. For example, an amphiphilic block copolymer, poly(ε-caprolactone)-*block*-poly(acrylic acid), PCL-*b*-PAA, was prepared by selective hydrolysis of a PCL-*b*-P*t*BuA precursor, which was synthesized by anionic ring-opening polymerization of ε-caprolactone followed by ATRP of *t*BuA [190]. Self-assembly of PCL-*b*-PAA into polymer micelles followed by cross-linking of the hydrophilic shell layer via condensation reactions between the carboxylic acid functionalities of PAA and the amine functional groups of 2,2′-(ethylenedioxy)bis(ethylamine) in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide methiodide afforded shell-cross-linked nanoparticles. Another example involves block copolymer containing poly(ethylene oxide) (PEO). PEO macroinitiators were prepared by anionic ring-opening polymerization of EO and modification of the hydroxyl end groups with α-haloesters, which were used for the polymerization of *t*BuA [191].

4. Branched polymers

Branched polymers containing (meth)acrylic acid segments can be divided into two categories; homopolymers, which include dendritic (randomly branched and hyperbranched), comb-shaped, and star polymers, and segmented copolymers, which include amphiphilic graft copolymers, heteroarm/miktoarm star polymers, and starblock copolymers (Fig. 4). Branched copolymers containing (meth)acrylic acid segments typically show amphiphilic properties.

4.1. Homopolymers

Recently, branched polyelectrolytes have become of special interest because of their industrial importance and scientifically interesting properties [192]. Due to their different topologies, branched and linear polyelectrolytes should have quite different properties, especially distribution of counterions [193]. As another practical point, branched polyelectrolytes can act as predecessors or fragments of polyelectrolyte gels. Variation in the degree of branching (DB) leads to a continuous change in the properties of branched macromolecules from linear chains to soft nanoparticles with highly compact structures. A variety of theoretical approaches have been reported on

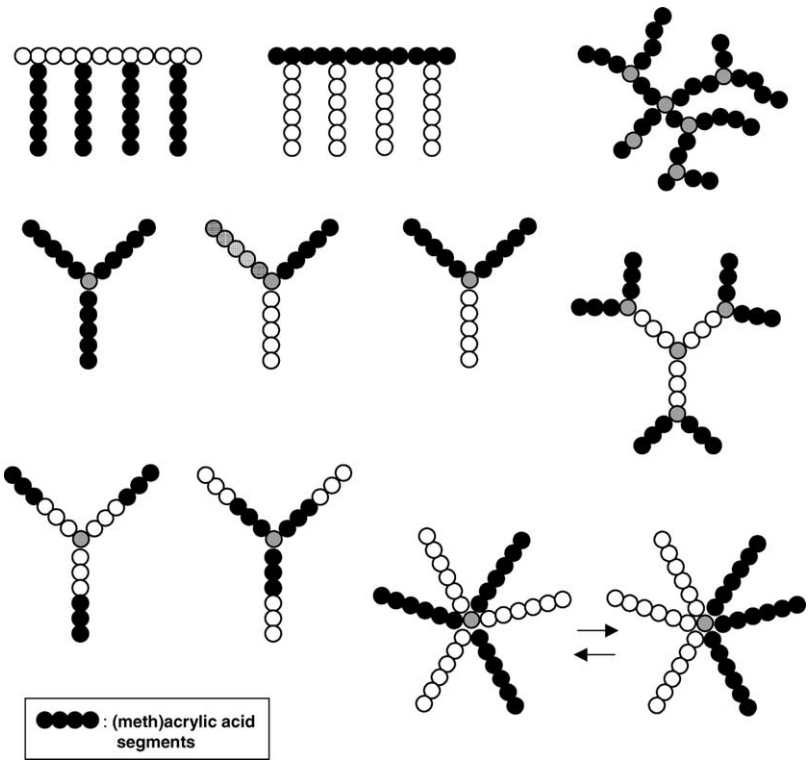


Fig. 4. Branched polymers containing (meth)acrylic acid segments.

the investigations of branched polyelectrolytes [194–198]. However, the correlation of the topology and the properties of branched polyelectrolytes have not been studied very much experimentally, because of difficulties in the synthesis of well-defined branched polymers with ionic or ionizable groups. One challenge in this field is, therefore, to produce randomly or regularly branched polyelectrolytes, which are suitable for various applications as well as for quantitative characterization. The material properties of branched polymers depend not only on the MW and DB, but also on topology of branching. It is, therefore, desirable to establish precise synthetic methods for various topologies of branched polymers (dendritic, comb, and star).

4.1.1. Dendritic (randomly branched and hyperbranched) polymers

Dendritic or arborescent polymers contain several branch points which are distributed irregularly in the polymer chains. Due to the statistical nature of branching, branches on branches can occur especially when a certain degree of branching (DB, defined as the added fractions of branchpoints and endgroups) is exceeded. Such polymers are frequently called hyperbranched polymers. It is expected that the DB has a significant effect on the solution properties of polyelectrolytes.

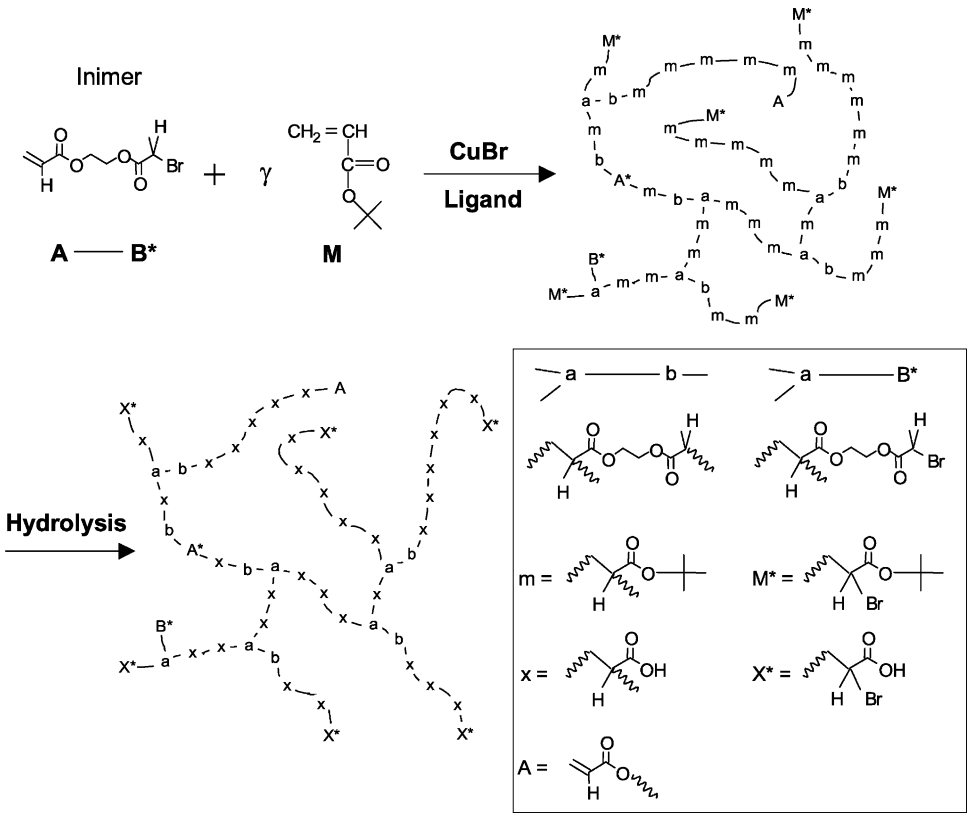
The recent discovery of self-condensing vinyl polymerization (SCVP) made it possible to use vinyl monomers for a convenient, one-pot synthesis of hyperbranched vinyl polymers with DB ≤ 0.5. Initiator-monomers ('inimers') are used of the general structure AB*, where the double bond is designated A and B* is a group capable of being activated to initiate the polymerization of vinyl groups [199]. Cationic [200], anionic [201], group transfer [202], controlled radical [203–207], and ring-opening mechanisms [208] have been used. By copolymerizing AB* inimers with conventional monomers, this technique was extended to self-condensing vinyl copolymerization (SCVCP), leading to highly branched copolymers with DB controlled by the comonomer ratio [209–212]. Depending on the chemical nature of the comonomer,

ionic or ionizable groups can be incorporated in the branched polymer, leading to highly branched polyelectrolytes. The copolymerization method is a facile approach to obtain functional branched polymers, since the DB and MW can be modified easily by a suitable choice of the comonomer ratio in the feed.

Highly branched P*t*BuMA was synthesized by SCVCP of *t*BuMA with an inimer having a methacrylate group (A) and a silylketene acetal group (B*), capable to initiate GTP [211]. Characterization using multi-detector SEC showed that the corresponding intrinsic viscosities of the resulting copolymers is lower than that of linear P*t*BuMA, suggesting a branched structure. Acid-catalyzed hydrolysis of the *tert*-butyl groups and neutralization with NaOH produced a water-soluble, highly branched PMAA sodium salt [213].

The synthesis of randomly branched PAA was conducted by SCVCP of *t*BuA with an inimer having an acrylate (A) and an α-bromopropionate group (B*), capable to initiate ATRP, followed by hydrolysis of the *tert*-butyl groups (Scheme 2) [62]. Characterization of the branched P*t*BuAs was conducted by multi-detector GPC and NMR analysis, demonstrating that DB, the composition, MW, and MWD can be adjusted by an appropriate choice of the catalyst system, the comonomer composition in the feed, and the polymerization conditions. The water solubility of the branched PAAs decreases with increasing DB and decreasing pH. Aqueous-phase GPC and dynamic light scattering confirm the compact structure of the randomly branched PAAs. Studies at different pH indicate that a marked stretching of the branched chains takes place when going from a virtually uncharged to a highly charged stage.

Another approach involved the SCVP of a 'macroinimer', which is a heterotelechelic P*t*BuA



Scheme 2. General route to randomly branched poly(acrylic acid), PAA, via self-condensing vinyl copolymerization of an acrylate-type inimer with *tert*-butyl acrylate (*t*BuA), followed by hydrolysis.

possessing both an initiating and a polymerizable moiety, via ATRP [214]. GPC/viscosity measurements indicated that the intrinsic viscosity of the branched polymer is less than 40% of that of the linear one at highest MW area. A significantly lower value for the Mark–Houwink exponent ($\alpha = 0.47$ compared to $\alpha = 0.80$ for linear P*t*BuA) was also observed, indicating the compact nature of the branched macromolecules.

4.1.2. Star polymers

There are two basic synthetic routes for star polymers [215]: the 'core first' method (polymerization from multi-functional initiators or microgels), and the 'arm first' method, where growing polymer chain ends are reacted with a multi-functional terminating agent or a divinyl compound. Whereas the use of multi-functional initiators or terminators leads to stars with a well-known (but often low) number of arms, the use of microgels or divinyl compounds leads to a rather broad arm number distribution, where the average arm number can be quite high.

Living anionic polymerization with the 'arm first' method has been applied for the synthesis of star-shaped PAA or PMAA. Linear P*t*BuA with narrow MWD and well-defined MW is achieved by anionic living polymerization, and the star-shaped structures can be formed by the reaction of carbanion chain ends with a multi-functional terminating agent or divinyl compound. However, the controlled synthesis of well-defined star polymers of (meth)acrylates is not easy, because of the reduced reactivity towards multi-functional terminating agents at the low temperatures which typically must be used in order to avoid side reactions. For example, P*t*BuMA star polymers were prepared via living anionic polymerization using two different terminating agents, 1,3,5-trisbromomethylbenzene and octa[(3-iodopropyl)]-silsesquioxane, in order to further react them to form model PMAA networks [216]. Subsequent cleavage of the *tert*-butyl ester moieties by acidic hydrolysis gave access to photo-cross-linkable, monodisperse PMAA star polymers. A series of star polymers consisting of P*t*BuA arms and an ethyleneglycol dimethacrylate microgel core were synthesized using anionic polymerization via an arm first method [217]. The effect of the various reaction parameters on the average number of arms and solution properties, such as radius of gyration and intrinsic viscosity, of the star-shaped P*t*BuAs was investigated. Star-shaped PAAs were obtained after the hydrolysis of the *tert*-butyl esters [192,218]. The PAA star showed much less contraction than the corresponding P*t*BuA stars, due to Coulomb repulsion between the arms. Osmotic measurements of the sodium salts showed a much higher fraction of counterions within the polymer than for linear polyelectrolytes.

The synthesis of P*t*BuA star polymers by the 'core first' method via anionic polymerization was conducted from living multi-functional microgel cores prepared by the reaction of divinylbenzene with lithium naphthalenide or short living polystyrene chains [219].

The formation of PAA star polymers using the 'core first' method has been demonstrated in ATRP process by the use of multi-functional initiators [220,221]. The influence of the polyelectrolyte architecture on the adsorption process at the air/water interface was studied using linear and star-shaped PAAs [221]. The difference in the PAA architecture resulted in different structures of polyelectrolyte/amphiphilic complex monolayers on the interface, and led to the change in the surface pressure during adsorption over time. Star-shaped P*t*BuAs have been synthesized by ATRP via via 'core first' [222,223] and 'arm first' [224] methods.

4.2. Copolymers

Similar to block copolymers containing (meth)acrylic acid segments (see Section 3), amphiphilic branched polymers can form a variety of superstructures as a result of self-organization, and the resulting assembled structures should be governed by the branched architecture, in addition to the chemical nature of the components, their composition, and MW. In order to achieve highly ordered assembly systems and to get better understanding, the relation between the primary branched architectures and assembled structures based on self-organization, it is necessary to first produce well-defined branched polymers containing (meth)acrylic acid segments.

4.2.1. Graft copolymers

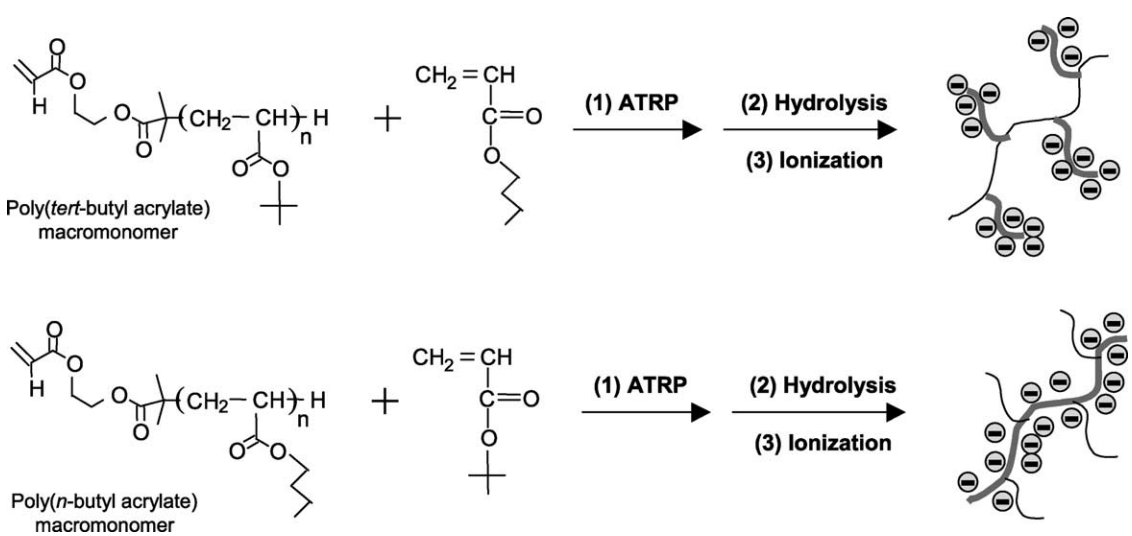
The structure of graft copolymers is determined by three parameters: (i) the length of the backbone,

(ii) the length and (iii) the *average* spacing of the side chains. There are basically three routes for preparing amphiphilic graft copolymers, i.e. 'grafting from' or 'grafting onto', and via copolymerization of macromonomers ('grafting through', see Scheme 3). Similar to amphiphilic block copolymers, the micelle formation in solution is of interest in amphiphilic graft copolymers. However, most of older work, with some exceptions, deals with rather ill-defined copolymers, characterized by chemical and compositional heterogeneity, broad MWDs, and poor control over the number and the placement of the branches along the backbone. Therefore, the influence of the molecular architecture of complex systems on the micellization process is a less studied field, even if the change of architecture imposes constraints that may affect the properties of the micelles, i.e. degree of aggregation, shape and density of micelles, etc.

Amphiphilic graft copolymers can have either a hydrophobic backbone and hydrophilic/ionic side chains or, inversely, a hydrophilic/ionic backbone and hydrophobic side chains. The latter structures can form reversible hydrogels above a critical concentration and may find use as associative thickeners. A series of graft copolymers containing (meth)acrylic acid segments in the main chain or side chain with relatively well-defined structures was synthesized using various methods.

The synthesis of polymers with P(M)AA main chain was recently reviewed [192]. For example, PAA-*g*-PS, with different degrees of grafting density were synthesized by using the 'grafting onto' technique [225]. The grafting reaction was achieved by reacting an amino-terminated PS with PAA activated by 1,3-dicyclohexylcarbodiimide to promote amide formation. An amino-terminated PS was synthesized by anionic polymerization techniques using cumyl potassium as an initiator, whereas the backbone of the graft copolymer, PAA, was synthesized by free radical polymerization. The micellar behavior of these copolymers in aqueous media was also investigated. This type of amphiphilic graft copolymer has been used to form 'nanoreactors' for the synthesis of gold clusters [226]. Graft copolymers, PAA-*g*-poly(*N*-isopropylacrylamide) [227] and PAA-*g*-poly(*N*,*N*-dimethylacrylamide) [228], were synthesized using the macromonomer method, and characteristic temperature- and pH-sensitive properties have been investigated. The synthesis of P*t*BuA-*g*-P*n*BuA via the macromonomer technique was also reported [229]. Hydrolysis led to PAA-*g*-P*n*BuA, which shows shear-thinning rheology at higher concentrations in water [230].

A variety of amphiphilic graft copolymers with hydrophobic backbone and P(M)AA side chains has been reported. A review was given recently [231].



Scheme 3. Synthesis of graft copolymers, poly(*n*-butyl acrylate)-*g*-poly(acrylic acid) and poly(acrylic acid)-*g*-poly(*n*-butyl acrylate), via the macromonomer method.

Graft copolymers consisting of PS backbones and PMAA branches were prepared using the 'grafting onto' technique, in which bromomethylated PS was added to a solution containing living P*t*BuMA chains, followed by hydrolysis of the *tert*-butyl groups with HCl [232]. Micellar properties were reported for PS-*g*-PMAA in THF, a solvent selective for the PS backbone, and in water–THF mixed solvent. Poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide)-*g*-poly(acrylic acid) (PEO-*b*-PPO-*b*-PEO-*g*-PAA, Pluronic-PAA) were synthesized by free radical grafting copolymerization of acrylic acid monomers onto PEO-*b*-PPO-*b*-PEO (Pluronic F127). The aqueous solution properties were characterized [233,234]. Novel amphiphilic graft copolymers, PS-*b*-poly(ethylene-*co*-butylene)-*b*-PS-*g*-PAA, were synthesized by ATRP of *t*BuA from chloromethylated PS-*b*-poly (ethylene-*co*-butylene)-*b*-PS, followed by hydrolysis [235]. The graft density was controlled by the degree of chloromethylation of the styrene units in the backbone. Because of the use of near-monodisperse triblock copolymers (Kraton G1652) as a backbone and of the 'grafting from' approach via ATRP, the resulting graft copolymers showed relatively narrow MWD before the hydrolysis.

P*n*BuA-*g*-P*t*BuA was synthesized using the macromonomer method via ATRP [229]. Quantitative hydrolysis of the P*t*BuA segments resulted in P*n*BuA-*g*-PAA. The micellization and micellar structure in aqueous solution was studied and compared to the corresponding block copolymers by Müller et al. [236]. The non-polar block/backbone has a low glass transition temperature, thus dynamic micelles were expected. Both block and graft copolymers form spherical micelles, where the aggregation number is increasing drastically with decreasing pH value (Fig. 5). The topology of the copolymers significantly influences the aggregation behavior: at the same molar fraction of acrylic acid, graft copolymers form smaller micelles than the corresponding block copolymers. This was attributed to the fact that graft copolymers more easily form unimolecular miecelles.

4.2.2. Starblock copolymers

Hedrick et al. [220] reported the synthesis of amphiphilic starblock copolymers with six- and 12-arms and low polydispersities by ATRP in the consecutive polymerization of *t*BuA and MMA from multi-functional initiators. Subsequent selective deprotection of the acrylate block led to a structure with PAA hydrophilic block and PMMA as the hydrophobic component. These polymers showed a unique response of the molecular geometry to

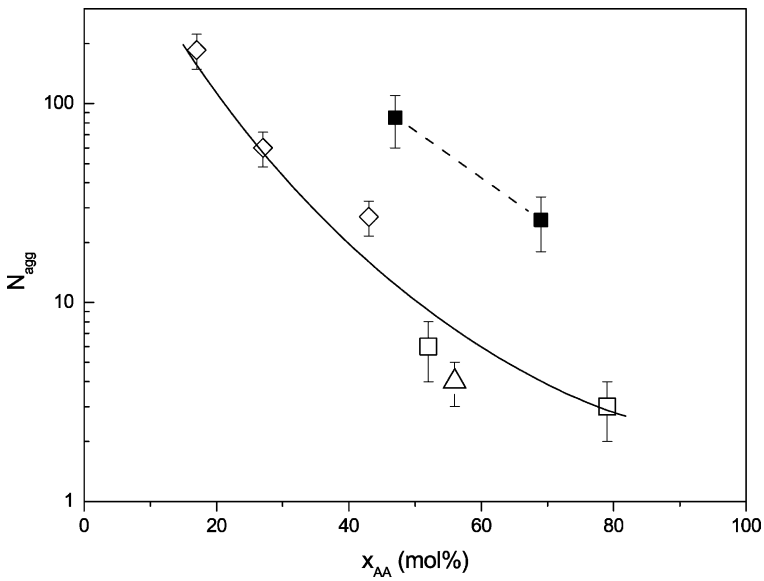


Fig. 5. Dependence of the degree of micellization on the molar fraction of acrylic acid and topology in PAA/P*n*BuA block and graft copolymers. Open symbols: graft copolymers with PAA side chains, closed symbols: block copolymers.

the polarity of the solvent as indicated by ^{1}H NMR spectroscopy. Three-arm star-block copolymers composed of PS and PAA [61] were synthesized by ATRP, and three-arm star-blocks, (PIB-*b*-PMAA)$_3$ [188], were also achieved by the combination of cationic polymerization and ATRP.

Starblock copolymers (PEO-*b*-PAA)$_3$ and dendrtic starblock copolymers (PEO-*b*-PAA$_2$)$_3$ consisting of three inner poly(ethylene oxide) (PEO) arms and either three or six peripheral PAA blocks were derived by a 'core first' approach [237]. The OH end groups of three-arm PEO stars prepared anionically were derivatized into either three or six bromo-ester functions (via the reaction with 2-bromoisobutyryl bromide or a branching agent, 4,4-bis[4-(2-bromoisobutyryloxy)-phenyl]valeric acid, respectively), that served to grow the P*t*BuA blocks by ATRP in a controlled fashion. Alternatively, an 'arm first' methodology utilizing a divinyl monomer as the linking agent was applied to access star-block copolymers incorporating an inner PAA part and a peripheral PEO layer. In this approach, preformed PEO-*b*-P*t*BuA diblock copolymers were reacted with divinylbenzene in anisole in the presence of CuBr/PMDETA. Finally, selective hydrolysis led to the expected double-hydrophilic star-block copolymers (PAA-*b*-PEO)$_f$.

4.2.3. Hetero/miktoarm copolymers

Star polymers containing chemically different arms have been designated heteroarm or miktoarm (mixed arm) star polymers when they are comprised of two ore more different kinds of arms, respectively. They reveal interesting properties in the solid state as well as in solution due to their unique architectures [238]. Recent synthetic developments using living and controlled polymerizations techniques made it possible to produce such star polymers with (meth)acrylic acid segments. Ionic heteroarm star copolymers bearing PS and PAA arms (PS$_n$PAA$_n$) were prepared by quantitative hydrolysis of the P*t*BuA arms of the corresponding PS$_n$P*t*BuA$_n$ star copolymer [239,240]. The precursors were made by a three-step anionic process. A PS star was made via the 'arm first' method, by coupling with divinylbenzene. The cores of the resulting star polymers still contained the active sites and could therefore, be used to initiate the polymerization of *t*BuA. The aggregation properties of these copolymers were studied in THF [241], 1,4-dioxane, and 1,4-dioxane/water mixture [240]. Anionic polymerization has been also utilized for the preparation of various star polymers containing PMAA [242] or P*t*BuMA [243–245]. Star polymers composed of poly(ε-caprolactone) (PCL) and PAA blocks were prepared by 'miktofunctional' initiators, combining three initiator sites each for both anionic ring-opening polymerization and ATRP arranged in an alternating fashion [246]. Consecutive anionic ring-opening polymerization of ε-caprolactone and ATRP of *t*BuA from the miktofunctional initiators, and subsequent cleavage of the *tert*-butyl ester yielded amphiphilic block copolymers containing three PCL and three PAA arms.

PS(PAA)$_2$ heteroarm stars carrying one PS and two PAA arms were prepared by combination of ATRP and chemical modification of the termini of ATRP-derived polymers [247]. The key reaction steps are modification of the bromo end groups of the PS chains by 2-amino-1,3-propanediol (serinol), followed by esterification of the hydroxyl functions of PS(OH)$_2$ with 2-bromoisobutyryl bromide. The resulting ω,ω-bis(bromo) macroinitiator was used to initiate the P*t*BuA blocks by ATRP, and PS(PAA)$_2$ stars with chemically different PS and PAA arms were obtained after hydrolysis.

4.2.4. Janus micelles

Janus micelles are non-centrosymmetric, surface-compartmentalized nanoparticles, in which a cross-linked core is surrounded by two different corona hemispheres. Their intrinsic amphiphilicity leads to the collapse of one hemisphere in a selective solvent, followed by self-assembly into higher ordered superstructures. The term 'Janus' used to describe the property of having two faces (a hydrophobic and a hydrophilic one) was first used in natural science by Veyssié et al. who created 'Janus beads' by a partial hydrophobic modification of commercial glass spheres [248]. Depending on their shape, Janus micelles can be divided into Janus spheres, cylinders, and sheets (Fig. 6). Various strategies can be designed to construct these structures.

One effective method for the synthesis of Janus micelles is based on the selective cross-linking reaction of one component in ABC triblock copolymers. Due to self-assembly process of ABC triblock

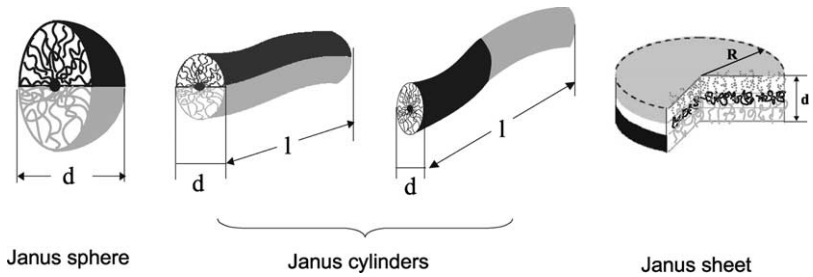


Fig. 6. Various possible Janus micelles.

copolymers in the bulk, they can form, e.g. lamellae–sphere, lamellae–cylinder, or lamellae–lamellae morphologies, depending on their composition [249–251]. Selective cross-linking of the middle block and redissolution can lead to various Janus structures, where the 3D architectures can be manipulated by the original bulk morphologies. Cross-linking of one component in AB-type diblock copolymer micelles has been used as an effective tool for construction of nanometer-sized polymeric objects (see Section 3). Different from the strategies using AB block copolymer, the inherently non-centrosymmetric nature of ABC triblock copolymers can give a great opportunity to create non-centrosymmetric Janus micelles structures. So far, a few reports have been published on the Janus micelles with (meth)acrylic acid segments or their precursors. However, the strategies shown here can basically be applied for the synthesis of such (meth)acrylic acid-containing Janus structures. Given the rich variety of morphologies known for ABC triblock copolymers, this approach may well be utilized to create a variety of complex supramolecular objects via the synthetic detour through the bulk phase.

Spherical architectures were obtained via a three-step procedure (see Fig. 7): (i) a film of an ABC triblock copolymer (block terpolymer) with lamellae of the outer blocks embedding spherical domains of the middle block (the so-called lamellae–sphere or ls-morphology) is prepared by solution casting, (ii) the spherical domains of the middle blocks are cross-linked in the bulk state, and (iii) the bulk phase is redissolved in a good solvent. The Janus micelles' precursor, a polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate), PS-*b*-PB-*b*-PMMA, triblock copolymer, was synthesized via sequential anionic polymerization in THF. This approach was used in order to synthesize spherical Janus micelles with PS and PMMA hemi-coronas [252]. It was shown that these micelles form larger aggregates in non-selective organic solvents, on a silicon surface and at the air/water interface [252,253].

Janus cylinders with the separation plane parallel to the cylinder axis were obtained in a similar way by cross-linking the PB core PS-*b*-PB-*b*-PMMA block terpolymers that formed a lamellae–cylinder morphology in the bulk [254]. The topologies of these particles visualized by scanning electron microscopy and scanning force microscopy indicated that the observed long, rod-like cylindrical nano-objects consist of only one non-aggregated Janus cylinder each. In contrast to the corresponding spherical Janus micelles, no supermicelles of these cylinders were formed.

By hydrolysis of the ester groups of the PMMA arms, truly amphiphilic spherical Janus micelles were obtained with a hydrophobic hemi-corona, made of PS, and a hydrophilic hemi-corona, made of PMAA, surrounding a cross-linked PB core [69]. These particles are soluble in water, when using several sequential dialysis steps (starting from 1,4-dioxane). However, due to the non-polar nature of both the PB core and the PS hemi-corona, they collapse to a core, which is fully or partially surrounded by the swollen PMAA arms. The vast majority of these particles self-assembles to larger, spherical entities of well-defined size confirmed using chromatography, scattering, and imaging techniques (Fig. 8). Most likely, the non-polar components form the core and the PMAA arms are stretched into the surrounding solution. This situation is comparable to classical surfactant micelles in which the building entities are replaced by polar spheres, as schematized in Fig. 7.

Another strategy to form Janus micelles is based on the self-assembly of block copolymers in solution. In

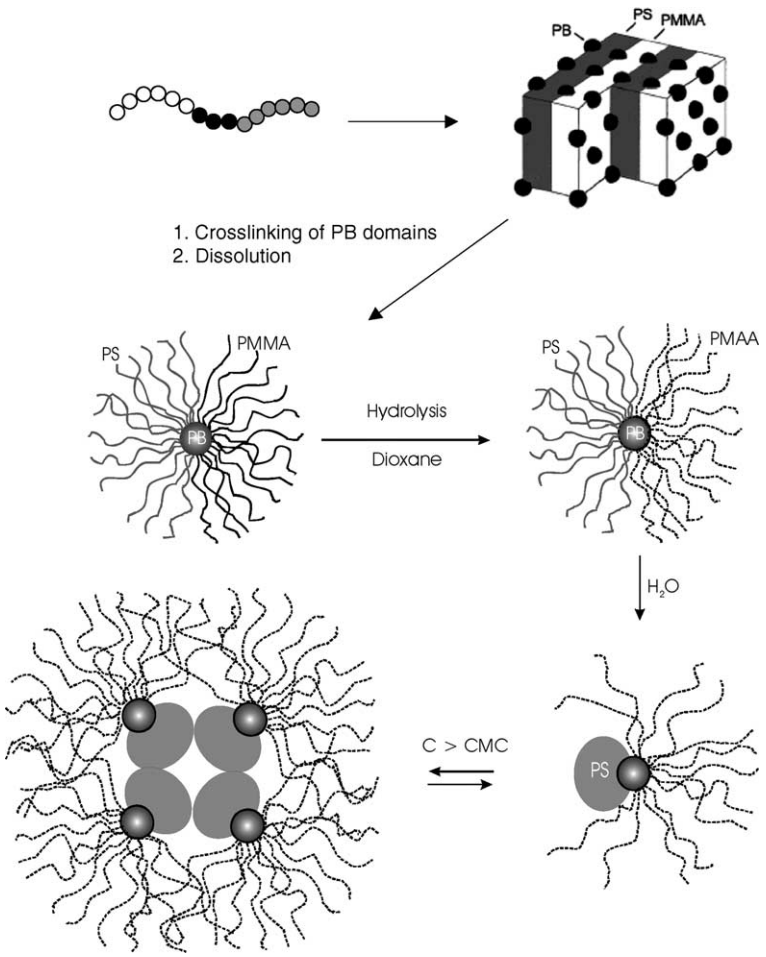


Fig. 7. Synthesis and tentative structure of amphiphilic Janus micelles and their supermicelles.

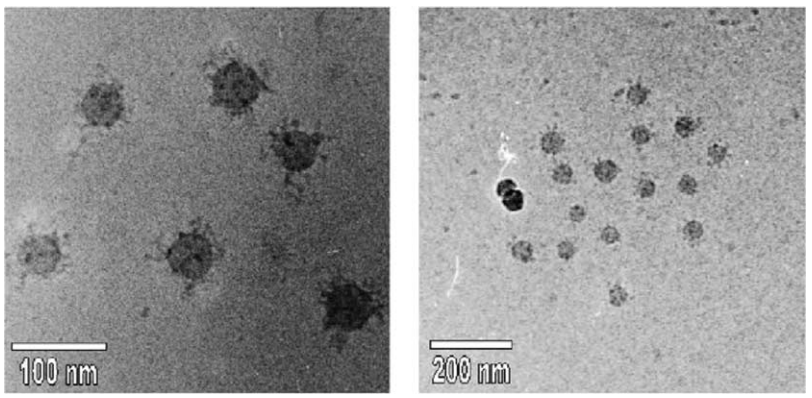


Fig. 8. Cryogenic transmission electron micrograph of Janus supermicelles in solution. Reprinted with permission from J Am Chem Soc 2003;125:3260. © American Chemical Society [69].

one approach, block terpolymers can form micellar solutions in a solvent that dissolves the outer blocks but is a non-solvent for the middle block. Cross-linking of the core again should form Janus micelles [255]. However, phase separation of the outer blocks may not be as pronounced as in the bulk approach. Another self-assembly approach is based on the electrostatic interactions of AB and CD diblock copolymers, PB-*b*-poly(cesium methacrylate) and PS-*b*-poly(1-methyl-4-vinylpyridinium iodide), where B and C form insoluble complexes, e.g. interpolyelectrolyte complexes, in a solvent for blocks A and D [256]. The first reported approach has led to non-symmetric vesicles rather than to Janus spheres. Saito et al. [257] also reported synthesis of Janus type microspheres by cross-linking of PVP spherical domains in PS-*b*-poly(2-vinyl pyridine)-*b*-P*t*BuMA ABC triblock terpolymer film with PS/P*t*BuMA lamellae-poly(2-vinyl pyridine) spherical structures. Some of miktoarm star copolymers (see Section 4.2.3) prepared through living anionic polymerization [239, 240] and combination of ATRP and ring-opening anionic polymerization [246] can be regarded as Janus micelles containing a PAA hemi-corona.

5. Polymer brushes

Polymer brushes refer to an assembly of polymer chains which are tethered by one end to a surface or an interface. Fig. 9 summarizes the possible polymers

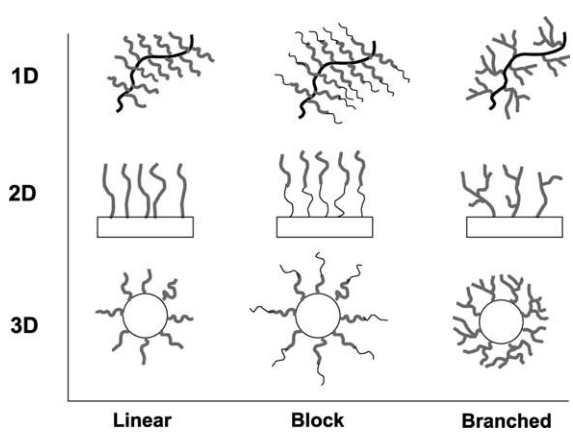


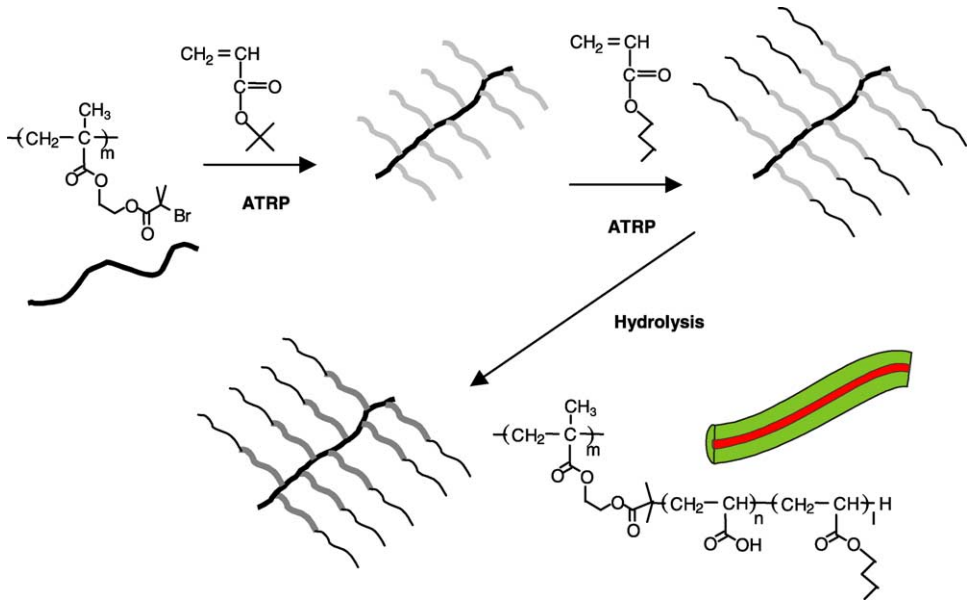
Fig. 9. Surface-grafted linear, block, and branched (co)polymers containing (meth)acrylic acid segments: from 1D to 3D.

brush architectures. Depending upon the substrates, they can be divided into 3D, 2D, and 1D brushes, which correspond to products grafted on spherical particles, planar surfaces, and linear polymers, respectively. In terms of chemical compositions and architectures, polymer brushes tethered on a substrate surface can be also divided into homopolymer brushes, mixed homopolymer brushes, block copolymer brushes, and branched polymer brushes. For the synthesis of well-defined polymer brushes containing (meth)acrylic acid segments, CRP techniques have been employed preferentially.

5.1. 1D (cylindrical) brushes ('bottle brushes')

Cylindrical polymer brushes which have the same number of side chains as the degree of polymerization of the main chain, are architecturally interesting for both experimental and theoretical chemists because of the possibility to form extended chain conformations, based on the intramolecular excluded-volume interactions between side chains densely grafted to the backbone. Similar to graft copolymers, the homopolymerization of macromonomers, 'grafting onto', and 'grafting from' can be used to synthesize cylindrical polymer brushes. The first one, which was widely used in the past decade, is the conventional radical polymerization of macromonomers. However, these polymerizations normally yield polymer brushes with a broad chain length distribution. Aiming at better-defined brushes, ring-opening metathesis [258], living anionic [259], and atom transfer radical [260,261] polymerizations of macromonomers were performed. The second method is the 'grafting onto' technique. However, grafting efficiency was often insufficient. Finally, in the 'grafting from' process, the side chains of the brush are formed via ATRP, initiated by the pendant initiating groups on the backbone [262,263]. By this method, well-defined polymer brushes with high grafting density and rather narrow distributions of both backbone and side chains can be obtained, and the purification of resulting polymer brushes is much simpler compared to the other two methods.

So far, there have been only few reports about the synthesis of polymer brushes with (meth)acrylic acid segments or their precursors. Müller et al. synthesized PAA brushes and core–shell brushes with PS-*b*-PAA, PAA-*b*-PS, P*n*BuA-*b*-PAA, or PAA-*b*-P*n*BuA,



Scheme 4. Synthetic procedure for amphiphilic core–shell cylindrical brushes.

as side chains via the 'grafting from' technique using ATRP [63,264]. The procedure includes the following steps (Scheme 4): (1) synthesis of a well-defined polyinitiator by the reaction of 2-bromoisobutyryl bromide with poly(2-hydroxyethyl methacrylate) obtained via ATRP of 2-hydroxyethyl methacrylate (HEMA) or anionic polymerization of silyl-protected HEMA, (2) ATRP of the first monomer from the polyinitiator, yielding cylindrical brushes with homopolymer side chains, (3) addition of a second monomer forming the cylindrical brushes with diblock copolymer side chains, and (4) hydrolysis of the P*t*BuA block. These polymers undergo an anisotropic change of dimension by changing the solvent quality ($CDCl_3$ and $CDCl_3/CD_3OD$), as confirmed by ^1H NMR analysis. The core–shell cylinder brushes can be visualized by scanning force microscopy (SFM). Fig. 10 shows cylinders with 1500 side chains having 31 AA and 48 *n*BuA units each which show a very uniform size distribution.

In this structure, the brushes with amphiphilic diblock copolymer side chains resemble normal or inverse block copolymer micelles in structure and therefore, can be regarded as unimolecular wormlike

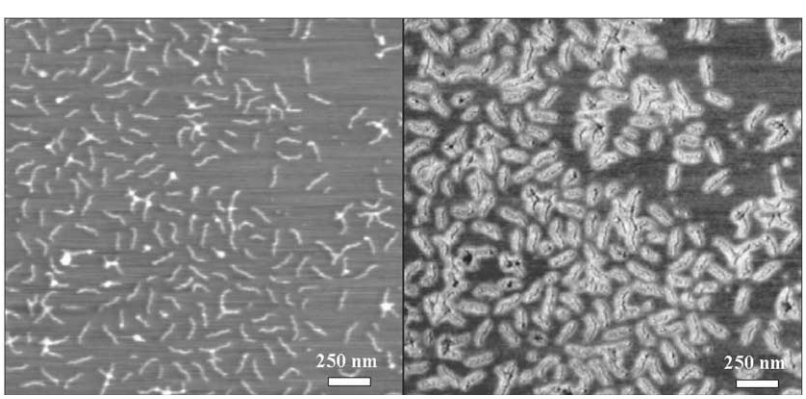


Fig. 10. SFM tapping mode images of the brush, $[(AA)_{31}\text{-}b\text{-}(n\,BuA)_{48}]_{1500}$, dip-coated from dilute $CH_3OH/CHCl_3$ (1/1) solution on mica: (left) height image (*z*-range: 6 nm) and (right) phase image (range: 40°) [63].

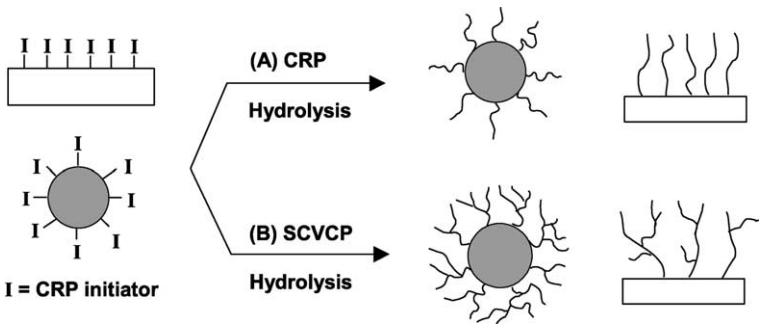
micelles. Compared to block copolymer micelles, they are very stable towards environmental changes since the side chains are covalently linked to the backbone. In addition, their length can be controlled in a much better way than for self-associating micelles. The ability of the hydrophilic PAA core of the amphiphilic core–shell brushes to coordinate with different metal cations can be used for the synthesis of novel nanosized organic/inorganic hybrids. Müller et al. reported the preparation of polychelates of polymer brushes by the reaction of Fe^{3+} and Fe^{2+} cations with amphiphilic core–shell cylindrical brushes with PAA core [265]. Using the 'grafting from' technique via ATRP, one can easily control the chain lengths of the backbone and side chains independently by changing the monomer to initiator ratio and monomer conversion during each polymerization step, which corresponds to the length and diameters of the resulting nanowires.

5.2. 2D (planar) brushes

PAA and PMAA chains attached to planar and spherical surfaces have recently attracted much interest as academic model systems and as candidates for various industrial applications. For example, PAA brushes are classified as 'annealed' brushes, in which the fraction of charged monomers may not only depend on the pH but also on the salt concentration and on the grafting density. 'Annealed' brushes have been the subject of several recent theoretical and experimental studies [266–269], and they are opposite to 'quenched' brushes in which strong polyacids are bound to surfaces [270]. The well-defined brushes can be used further to prepare smart materials to serve as functional devices on a nanometer scale, since they react collectively to environmental stimuli such as changes of the pH or ionic strength, temperature, solvent quality, or mechanical forces. For example, Ito et al. have demonstrated that PAA or PMAA chains grafted on a polycarbonate porous membrane [271,272] and porous glass filter [273] act as pH-sensitive polymer brushes. Their basic concept is to control the permeability by manipulating the pore size via pH change. Many attempts have also been reported on the synthesis and applications of PAA or PMAA grafted on surfaces, such as porous polyethylene membranes [274], poly(vinylidene fluoride) membranes [275,276], or poly(ethylene terephthalate) films [277], most of which are related with biomedical applications, such as drug delivery systems and tissue engineering. In general, uncontrolled methods, such as grow charge treatment, electron irradiation, ozone treatment, have been used to form PAA or PMAA chains on surfaces.

Many grafted polymers have been prepared by adsorption of end-functionalized polymers or block copolymers onto the surfaces ('grafting to' approach) [278,279]. These systems, however, have a limited grafting density as further grafting is hindered by the polymer chains already adsorbed on the surface. Surface-grafted PAA or PMAA have been also synthesized by 'grafting from' techniques via conventional radical polymerization [280] or photoemulsion polymerization [269,281], achieving higher grafting density. However, there is poor control over chain length and chain end functionality. CRP from surfaces [278,282] allows better control over MW and MWD of the target polymer. Only few approaches have been reported on the CRP grafting of PAA or PMAA from planar and spherical surfaces. In order to amplify initiators patterned on films of gold, ATRP was applied for grafting of P*t*BuMA from a planar gold surface [283]. ATRP was also used for grafting a PS-*b*-P*t*BuA block copolymer from silicon, followed by conversion to PS-*b*-PAA [284]. ATRP was also used for the preparation of PMAA grafted from poly(vinylidene fluoride) [285]. Hawker and workers [286] used TEMPO-mediated radical polymerization to prepare a P*t*BuA brush on a silicate substrate. Using photolithography technique, photogenerated acid converted P*t*BuA brushes to PAA brushes, yielding a patterned surface containing distinct areas of hydrophobic and hydrophilic brushes.

The surface chemistry and interfacial properties of highly branched polymer brushes become a field of growing interest [287–289]. Recently, Zhou et al. [290] reported the preparation of a highly branched PAA film attached to a self-assembled monolayer of mercaptoundecanoic acid on gold using a series of repeated 'grafting to' steps using a telechelic PAA. Surface-confined hyperbranched polymers are suitable for a number of technical applications, including corrosion inhibition, chemical sensing, cellular engineering, and micrometer-scale patterning [291–295]. The same strategy has been employed for the synthesis of hyperbranched PAAs grafted on



Scheme 5. Synthesis of surface-grafted linear and branched PAAs (or their precursors) by (A) CRP and (B) SCVCP from planar surfaces and spherical particles.

polyethylene [296,297], polypropylene [298], and porous alumina supports [299].

On the other hand, surface-initiated SCVCP via ATRP has been applied as a facile, one-pot synthesis of branched P*t*BuA grafted from a surface (Scheme 5) [300]. Because both the initiator-monomer ('inimer') and the functionalized silicon wafer with an ATRP initiator layer have groups capable of initiating the polymerization of vinyl groups, the chain growth can be started from both the initiators immobilized on the silicon wafer, and an α-bromopropionate group in the inimer. The one-step SCVCP of the inimer with a comonomer (*t*BuA) via ATRP from the surface gave a branched P*t*BuA with characteristic surface topography, which may be due to the branched architectures. The surface topography, branched structure, film thickness, and surface functionality (bromine content) could be modified easily by a suitable choice of the comonomer ratio in the feed and polymerization method. Hence, this method is a novel and convenient approach towards the preparation of smart interfaces.

5.3. 3D (spherical) brushes

PAA (or PMAA) grafted on spherical particles has been extensively investigated, owing to many scientific and industrial applications, such as biomaterial carriers [301,302], intelligent environment-responsive surface [303], thermal reinforcement [304,305], and optical chemical sensing [306]. Ballauff et al. recently reported a series of studies of PAAs grafted on PS latex particles, which were prepared by photoemulsion polymerization [269, 270,281,307]. However, ill-defined PAA or PMAA prepared by uncontrolled polymerization methods have been generally used in these works. Surface-initiated SCVCP of an acrylic AB* inimer with *t*BuA from silica nanoparticles functionalized with monolayers of ATRP initiators has been employed as a new method for the synthesis of branched P*t*BuA–silica hybrid nanoparticles [308]. Well-defined polymer chains were grown from the surface to yield nanoparticles comprised of silica cores and branched P*t*BuA shells. Hydrolysis of the ester functionality created branched PAAs grafted on silica nanoparticles. The chemical composition and the architectures of the branched PAAs grafted on the silica nanoparticles were controlled by composition in the feed during the SCVCP. Chain growth of *t*BuA from the surface via ATRP yielded linear P*t*BuA grafted on the silica nanoparticles. These methodologies can be applied to a wide range of inorganic materials for surface-initiated SCVCP to allow the preparation of new 3D branched polyelectrolyte/inorganic hybrid materials.

6. Summary and perspective

This review has summarized the synthetic approaches for a variety of tailor-made polymers containing (meth)acrylic acid segments. In addition to recent progress in controlled/living polymerization techniques, the combination of different polymerization mechanisms, cross-linking techniques combined with self-organization of block copolymers, and surface-initiated polymerization have allowed great

advances in the design and synthesis of various nano and mesoscale polymeric materials with sophisticated structures. Block copolymers containing (meth)acrylic acid segments have been extensively investigated during the last decade in terms of the synthetic methodologies for novel architectures, characteristic bulk and solution properties related with the self-organization process, and a wide range of applications, and the knowledge has well advanced. On the other hand, the well-controlled synthesis of complex macromolecules, such as branched polymers, Janus micelles, polymer brushes containing (meth)acrylic acid segments is still a challenging subject, and more information is required to establish structure–property relationships. PAA (or PMAA) segments in the complex macromolecules can be covalently modified with a broad range of functional groups, such as fluorophores, electroactive groups, perfluorinated moieties, dyes, and other bio-related materials. From the synthetic point of view, an important challenge is to develop direct synthetic method for various PAA (or PMAA)-containing polymers without using protected monomers.

Since PAA and PMAA are weak polyelectrolytes, and the degree of dissociation of the segments in the complex macromolecules depends not only on the pH value, salt concentration, but also on the architecture, e.g. chain topology, location of the PAA (or PMAA) segments, and the nature of their neighbors. The charge, the concentration of free counterion, and the degree of swelling can, therefore, be tuned via adjustment of pH value and polymer structures, and such a turning capability is of great interest as a component of intelligent materials. PAA (or PMAA) segments in the complex macromolecules can show specific interactions, such as hydrogen bonding, acid–base interactions, and oppositely charged ionic interactions, which can help to prepare novel self-organized materials. Another attractive features is the feasibility to be used as a polymeric template, by which manipulation of nanomaterials (silica, gold, magnetic, semiconductor nanoparticles, and nanocrystals) into technologically useful highly ordered forms can be achieved. Multiscale ordering of such functional nanomaterials is a powerful technique for the creation of macroscopic materials.

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