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Functional polymers by atom transfer radical polymerization

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Abstract

Atom transfer radical polymerization (ATRP) is one of the most successful methods to polymerize styrenes, (meth)acrylates and a variety of other monomers in a controlled fashion, yielding polymers with molecular weights predetermined by the ratio of the concentrations of consumed monomer to introduced initiator and with low polydispersities. Because of its radical nature, ATRP is tolerant to many functionalities in monomers leading to polymers with functionalities along the chains. Moreover, the initiator used determines the end groups of the polymers. By using a functional initiator, functionalities such as vinyl, hydroxyl, epoxide, cyano and other groups have been incorporated at one chain end, while the other chain end remains an alkyl halide. The polymer can be dehalogenated in a one-pot process or the halogen end groups can be transformed to other functionalities using nucleophilic substitution reactions or electrophilic addition reactions. Moreover, utilizing the ability of the halogen chain end to be reactivated, radical addition reactions can be used to incorporate allyl end groups, insert one less reactive monomer unit at the chain end, or to end-cap the polymer chain. With ATRP, functionality and architecture can be combined resulting in multifunctional polymers of different compositions and shapes such as block copolymers, multiarmed stars or hyperbranched polymers.

Keywords: Functional polymers; Atom transfer radical polymerization; Review

Contents

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1. Introduction

Radical polymerization is industrially the most widespread method to produce polymeric materials such as plastics, rubbers and fibers [1]. The advantages of radical polymerizations over ionic or coordination polymerizations are numerous: a large variety of vinyl monomers have been polymerized or copolymerized and the reaction conditions require only the absence of oxygen. Water, as in suspension or emulsion polymerization, or other impurities are well tolerated and the reactions occur at a convenient temperature range, typically from 0 to 100°C. The major drawbacks of conventional radical polymerizations are related to the lack of control over the polymer structure. Due to the slow initiation, fast propagation and subsequent transfer or termination, polymers with high molecular weights and high polydispersities are generally produced. These features are reflected in the physical and mechanical properties of the produced polymers and to alter and improve these properties, random copolymerizations have been traditionally used.

The development of ionic polymerization methods allowed for the preparation of well-defined polymers with controlled chain end functionalities and the synthesis of well-defined block and graft copolymers [2–5]. However, these polymerizations have to be carried out with nearly complete exclusion of moisture and often at very low temperatures. Moreover, only a limited number of monomers can be used, and the presence of functionalities in the monomers can cause undesirable side reactions.

A relatively new method to synthesize well-defined polymers and copolymers is controlled radical polymerization [6–9]. In this field, several systems have been applied to control molecular weights and end functionalities: iniferters [10,11], nitroxides [12–22], Co-based systems [23,24], degenerative transfer with alkyl iodides [25–28], most recently the RAFT-process [29], and Ru- [30] and Ni-mediated [31] polymerizations. One of the most successful methods, however, is atom transfer radical polymerization (ATRP), based on a copper halide/nitrogen based ligand catalyst [32,33]. This controlled radical polymerization allows for the polymerization of a wide range of monomers such as styrenes [34–36], acrylates [37,38] and methacrylates [39,40] including a variety of functional monomers (vide infra).

Nomenclature

AcGEA 2-(2′-3′-4′-6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-ethylacrylate
BA *n*-butyl acrylate
BIEA 2-(2-bromoisobutyryloxy)ethyl acrylate
BIEM 2-(2-bromopropionyloxy)ethyl acrylate
BPEA 2-(2-bromopropionyloxy)ethyl acrylate
BPEM 2-(2-bromopropionyloxy)ethyl methacrylate
BPN 2-bromopropionitrile
bpy 2,2′-bipyridine
BzBr benzyl bromide
BzCl benzyl chloride
DEAA *N*,*N*-diethylacrylamide
DMAA *N*,*N*-dimethylacrylamide
DMAEMA 2-(dimethylamino)ethyl methacrylate
DMF *N*,*N*-dimethylformamide
DMS dimethylsiloxane
DMSO dimethylsulfoxide
dNbpy 4,4′-di(5-nonyl)-2,2′-bipyridine
dTbpy 4,4′-di-*t*-butyl-2,2′-bipyridine
DVB *p*-divinylbenzene
HEA 2-hydroxyethyl acrylate
HEMA 2-hydroxyethyl methacrylate
HPMA *N*-(2-hydroxypropyl) methacrylamide
MA methyl acrylate
MAIpGlc 3-*O*-methacryloyl-1,1:5,6-di-*O*-isopropylidine-D-glucofuranose
MBP methyl 2-bromopropionate
MCP methyl 2-chloropropionate
Me_4Cyclam 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
Me_6TREN tris[2-(dimethylamino)ethyl]amine
MMA methyl methacrylate
1-PEBr (2-bromoethyl)benzene
1-PECl (2-chloroethyl)benzene
PMDETA *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine
St styrene
TsCl *p*-toluenesulfonyl chloride
tBAA *t*-butylacrylamide
4VP 4-vinylpyridine

Since ATRP is a controlled/'living' radical polymerization, well-defined polymers with molecular weights determined by the ratio of consumed monomer to introduced initiator are obtained, $DP_n = \Delta[M]/[I]_0$, the polydispersities are generally low ($M_w/M_n < 1.3$). Because of its mechanism, ATRP allows for the preparation of more precisely controlled polymers and many new materials have been

synthesized [41]. New materials are made by varying the topology of the polymer (linear, branched, hyperbranched, stars, etc.) and/or the composition of the polymeric chains (statistical/gradient copolymers, block copolymers, grafts, etc.). Moreover, with this process, the end groups of the polymers are well-defined as they derive from the initiator used. As a variety of initiators can be used, including initiators containing functional groups, end functionalities can easily be incorporated [42,43].

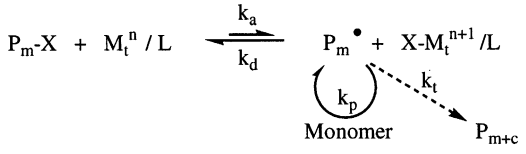
This review is focused on the ATRP process and its use to obtain functional polymers. The use of different functional monomers and initiators containing functional groups will be outlined and the transformation of the halogen end groups will be discussed as well.

2. Functional polymers by ATRP

2.1. Fundamentals of ATRP

The control over radical polymerizations is based on two principles [44–47]. First, initiation should be fast, providing a constant concentration of growing polymer chains. Secondly, because of the persistent radical effect [48–50], the majority of these growing polymer chains are dormant species that still preserve the ability to grow because a dynamic equilibrium between dormant species and growing radicals is established. By keeping the concentration of active species or propagating radicals sufficiently low throughout the polymerization, termination is suppressed.

ATRP is a radical process [51] that fulfills these requirements by using a transition metal, in combination with a suitable ligand [30,31,40,52–55]. The catalyst complex establishes a reversible equilibrium between growing radicals and dormant species (the proposed mechanism for ATRP is shown in Scheme 1). The equilibrium is attenuated by the choice of the ligand and the ligand also increases the solubility of the catalyst complex in the polymerization medium. Additionally, when the concentration of propagating radicals is sufficiently low in comparison with dormant chains, the proportion of terminated chains, P_{m+c}, can be often neglected (<5%). This may enable the preparation of highly functional polymers (>95%).



Scheme 1.

In homogeneous systems, the rate of ATRP has been shown to be first order with respect to the monomer and initiator [34,56]. The rate of the polymerization is also influenced by the ratio of concentrations of the activator to deactivator, although this may change during polymerization.

$$R_p = k_{app}[M] = k_p[P^{\cdot}][M] = k_p K_{eq}[R - X]\frac{[Cu(I)]}{[Cu(II)]}[M]$$

The opportunity to incorporate a functional end group in a linear polymer chain is available by varying

the initiator, i.e. a low molecular weight organic compound RX, containing an activated halogen X. After initiation has occurred, the initiator fragment R is present at one end of the chain while the halogen at the other end can be further transformed to various functionalities by means of standard organic procedures. Moreover, because of the radical nature of ATRP, a wide range of functional monomers can be polymerized yielding polymers with pendant functional groups. The produced polymer can further be used to obtain block copolymers because of the 'livingness' of the radical process.

2.2. Functional monomers

2.2.1. Substituted styrenes

Sts with electron withdrawing as well as with electron donating substituents were polymerized by ATRP [35]. The polymerizations were carried out either in bulk or in diphenyl ether at 110°C, with substituted St/initiator/CuBr/2,2′-bipyridine (bpy) in a ratio 100/1/1/3. Homogeneous catalytic systems with 4,4′-dialkyl substituted bpy have also been used. The molecular weights and the polydispersities of the polymers synthesized are shown in Table 1. The polymerization of monomers with electron withdrawing substituents were faster due to both increased monomer reactivity resulting in larger radical propagation rate constants and decreased stability of dormant species resulting in larger equilibrium constants for the atom transfer process. Polymerization of Sts with strong electron donating substituents such as 4-OMe was not successful under these conditions, presumably due to oxidation of radicals to carbocations [35,57]. The rate constants were correlated with the monomer structure, the order being 3-CF_3, 4-CF_3 > 4-Br, 4-Cl > 4-F, 4-H > 3-Me > 4-Me > 4-CMe_3. The apparent polymerization rate constants followed the Hammett equation, $\rho = 1.5$.

Poly(4-acetoxystyrene) was prepared by ATRP by polymerizing 4-acetoxystyrene in bulk at 90°C, α,α′-dibromo-*p*-xylene was used as the difunctional initiator and CuBr/bpy was used as the catalytic system. The molecular weight increased linearly with conversion and the molecular weight distribution remained low throughout the polymerization. ($M_w/M_n = 1.11 - 1.18$) [58].

Table 1
Molecular weights and polydispersities of R-substituted poly(styrenes) polymerized in diphenyl ether at 110°C, [M] = 4.37 M, $[M]_0/[I]_0/[CuBr]_0/[bpy]_0 = 100/1/1/3$

R	M_n	M_w/M_n
4-Me	4200	1.38
3-Me	10,800	1.17
4-*t*Bu	6600	1.52
4-Br	10,100	1.13
4-Cl	13,300	1.12
4-F	7100	1.14
4-CF_3	65,500	1.06
3-CF_3	12,400	1.17
4-OAc	5600	1.32
H	11,300	1.06
H	55,300	1.12

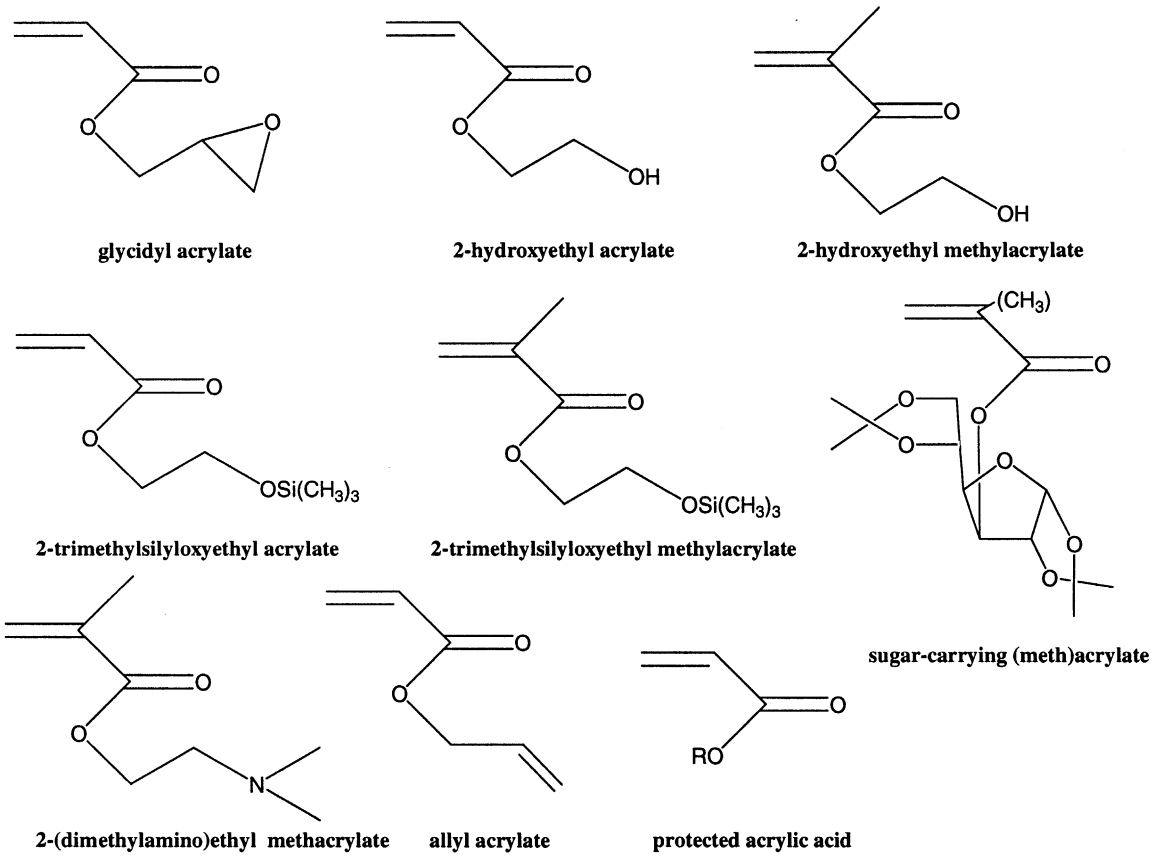


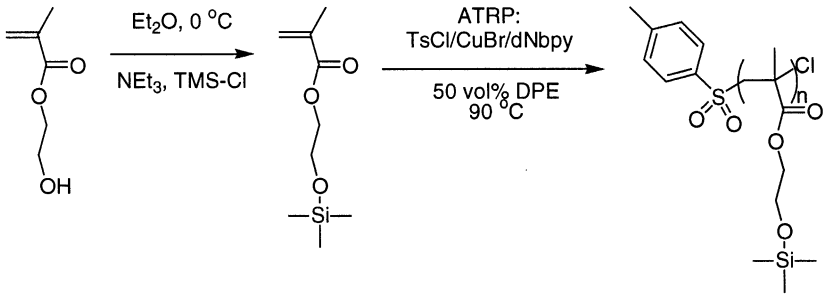
Fig. 1. Functional (meth)acrylates polymerized using ATRP.

2.2.2. (Meth)acrylates

The robustness of the ATRP technique concerning its tolerance towards functionalities may be best demonstrated with the polymerization of several functional (meth)acrylates (Fig. 1).

2.2.2.1. Glycidyl acrylate [59]. Poly(glycidyl acrylate) is an interesting functional acrylate since its pendant oxirane rings can be opened and subsequent modifications are possible. Glycidyl acrylate was polymerized to high molecular weight polymers ($M_n = 50,000$) in bulk using methyl 2-bromopropionate (MBP) as the initiator and CuBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) as catalyst. The M_n of the final polymers was controlled by the ratio $[M]_0/[I]_0$ and the polymers had narrow molecular weight distributions, $M_w/M_n < 1.25$.

2.2.2.2. 2-Hydroxyethyl acrylate [60]. Poly(2-hydroxyethyl acrylate) (poly(HEA)), is a water-soluble polymer with applications in the fields of coatings and biomaterials. HEA was polymerized at 90°C in bulk or in a 1:1 (by volume) aqueous solution. An important factor in the process was the purification of the monomer in order to remove diacrylates and residual acrylic acid as these impurities cause



Scheme 2.

cross-linking and interfere with the ATRP catalyst complex, respectively. Poly(HEA) was obtained with molecular weights as high as $M_n = 78,000$ and relatively low polydispersity, $M_w/M_n = 1.3$.

To aid the synthesis of block copolymers, the hydroxyl group of HEA was protected by trimethylsilyl (TMS) group. This monomer was then used to prepare amphiphilic block copolymers with *n*-butyl acrylate (BA) [61]. Diblock and triblock copolymers were synthesized, after which the alcohol groups were deprotected by acidic hydrolysis. Amphiphilic copolymers were also prepared using HEA directly, but such synthesis required the polymerization of BA first, because poly(BA) is soluble in HEA but poly(HEA) is insoluble in BA [62].

2.2.2.3. 2-Hydroxyethyl methacrylate [63,64]. Bulk ATRP of 2-hydroxyethyl methacrylate (HEMA) is very fast and difficult to control using CuBr/bpy catalyst. For example, when a ratio of monomer/initiator = 100 was used, the polymerization was completed within 20 min, even at room temperature, and the resulting polymer had a molecular weight significantly higher than the theoretical molecular weight and a broad molecular weight distribution. The reaction was slowed down by using a 50% (by volume) mixed solvent system, *n*-propanol/2-butanone (30/70). Polymers with molecular weight up to $M_n \approx 40,000$ were prepared, with $M_w/M_n < 1.5$.

Even more well-defined poly(HEMA) was obtained by protecting the hydroxyl group of the monomer with a TMS group (Scheme 2).

Polymerization of TMS-protected HEMA resulted in polymers with molecular weights up to $M_n \approx 1,00,000$ and polydispersities $M_w/M_n < 1.2$. Transesterification of poly(HEMA–TMS) with 2-bromoisobutyryl bromide yielded a macroinitiator for the synthesis of densely grafted copolymers [65].

2.2.2.4. 2-(Dimethylamino)ethyl methacrylate [66]. Poly(2-(dimethylamino)ethyl methacrylate) (poly (DMAEMA), and quaternized poly(DMAEMA) are water-soluble polymers that find applications in the fields of environmental protection, drug delivery and sensors [67,68]. Amphiphilic block copolymers of DMAEMA form micelles and can be used as stabilizers in dispersion polymerizations. DMAEMA was polymerized by ATRP with CuBr/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as catalyst complex and MBP as initiator. The reactions were carried out at 50°C in a relatively polar solvent such as dichlorobenzene. Polymers with molecular weights up to $M_n = 20,000$ and with $M_w/M_n = 1.25$ were prepared. It is worth noting that successful polymerization of DMAEMA requires polydentate ligands, preferably tetradentate, to avoid the displacement of the ligand on the copper complex by the polymer chain.

Block copolymers of DMAEMA with methyl methacrylate (MMA), methyl acrylate (MA) or St were successfully synthesized by ATRP, yielding well-defined AB block copolymers with polydispersities $M_w/M_n \cong 1.2$ [69]. Starting from difunctional polyacrylates, ABA triblock copolymers were prepared using well-defined poly(MMA) or poly(MA) as macroinitiators. To maximize chain extension, poly(MMA) with chlorine end groups was used as the macroinitiator. The block copolymerization with DMAEMA was carried out with CuCl/HMTETA as the catalyst, in 50% (by volume) dichlorobenzene at 90°C. For the poly(MA) macroinitiator, bromine end groups were preferred, in combination with CuCl/HMTETA as the catalyst complex. The halogen exchange process increased the blocking efficiency [70,71]. Poly(St) was a less efficient macroinitiator.

2.2.2.5. Vinyl and allyl acrylate [72]. Vinyl acrylate was polymerized in bulk at 60°C, using monomer/MBP/CuBr/dNbpy = 30/1/1/2. Poly(vinyl acrylate) ($M_n = 3000$, $M_w/M_n = 1.2$), which was soluble in common organic solvents was obtained. The presence of the vinyl protons was observed in ^{1}H NMR. From this result, it was concluded that the vinyl groups do not interfere in ATRP when low molecular weight polymers were desired.

By contrast, the allyl acrylate polymerization was accompanied by cross-linking reactions. Even at 0°C, with low amounts of catalyst, an insoluble product was obtained within a few minutes.

2.2.2.6. (Meth)acrylic acid. Polymers based on acrylic acid have become increasingly important in applications for coatings and biomaterials. However, acrylic acid or methacrylic acid are difficult to be directly polymerized by ATRP because of interactions of the carboxylic acid functionalities with the catalyst. Presumably, carboxylic acids react with Cu^{II} species by displacing the halogen atom, resulting in the formation of metal carboxylates which inhibit deactivation. Additionally, since many of the ligand systems utilized in ATRP are nitrogen based, protonation of the nitrogen may occur, disrupting its coordination to the Cu center. Therefore, precursors of poly(acrylic acid), e.g. poly(*t*BA), were synthesized by ATRP, after which the carboxylic acids were deprotected yielding well-defined poly(acrylic acid) [37,73–75].

*t*BA was polymerized in bulk at 90°C, using [MBP]/[CuBr]/[dNbpy] = 1/1/2, and well-defined polymers with molecular weights up to $M_n = 50,000$ and polydispersities as low as $M_w/M_n < 1.2$ were obtained [37]. Low molecular weight poly(*t*BA) ($M_n = 6000$, $M_w/M_n < 1.1$) was also synthesized using $Cu^{I}Br$/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) catalytic system at 60°C [74,75]. Polymerization control was optimized by the addition of a small amount of $Cu^{II}Br_2$/PMDETA (5% relative to Cu^{I}) and 25 vol% acetone or *N*,*N*-dimethylformamide (DMF) to homogenize the catalyst. After the polymerization reactions, the *t*-butyl groups were hydrolyzed by refluxing the polymer in 1,4-dioxane in the presence of hydrochloric acid. Characterization using ^{1}H NMR and FT-IR confirmed complete hydrolysis of the ester groups. Amphiphilic block copolymers containing the hydrophobic portion in the middle of the chain were also successfully prepared by the hydrolysis of poly(*t*BA)–poly(St)–poly(*t*BA) ($M_n = 23,900$, $M_w/M_n = 1.13$) [76].

Other acid protecting groups have been used as long as they remain stable under the applied polymerization conditions used (Fig. 2) [77]. This was demonstrated in the synthesis of well-defined poly(benzyl methacrylate). The benzyl group was removed under mild conditions by hydrogenolysis.

Recently, acidic monomer, sodium methacrylate has been polymerized under ATRP conditions in water using CuBr/bpy as catalyst at 90°C. When 2-hydroxyethyl 2-bromoisobutyrate was used as the initiator the molecular weight was close to the theoretical $M_n = 1300$ and the polydispersity was

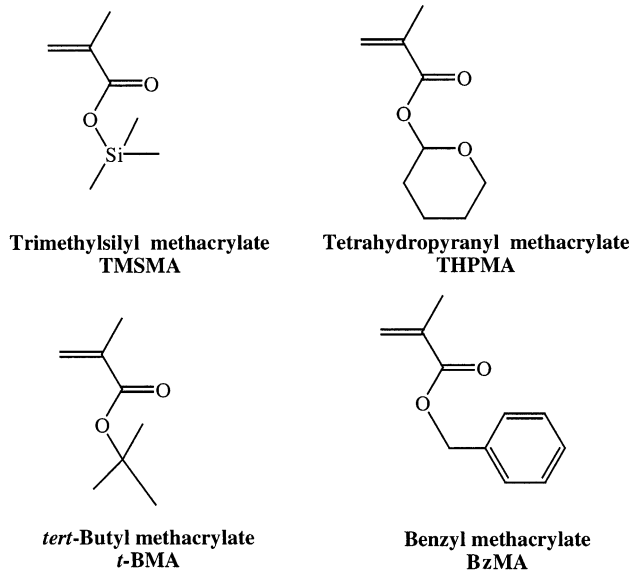
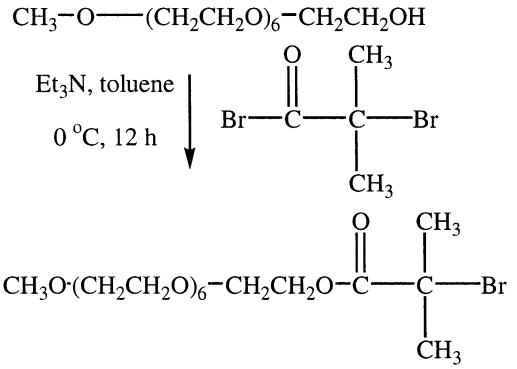


Fig. 2. Structures of the protected methacrylic acids successfully polymerized by ATRP.

$M_w/M_n = 1.23$. A water-soluble block copolymer was also synthesized by using (**1**) in Scheme 3 below as the initiator. (**1**) was formed by reacting poly(ethylene glycol) monomethyl ether with 2-bromoisobutyryl bromide. The resulting block copolymers had molecular weights close to the theoretical and the polydispersity index was $M_w/M_n < 1.3$ [78,79].

2.2.2.7. Sugar and nucleoside-containing acrylates. Sugar-carrying methacrylate, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidine-D-glucofuranose (MAIpGlc) was polymerized with ATRP resulting in polymers with controlled molecular weights, up to $M_n = 200,000$ and low polydispersity, $M_w/M_n < 1.5$ [80]. Also, diblock copolymers with St, poly(St)–*b*–poly(MAIpGlc), were prepared. The acidolysis of the homo- or block copolymers provided well-defined glucose-carrying water-soluble polymers poly(MAGlc) and poly(St)–*b*–poly(MAGlc), respectively.



Scheme 3.

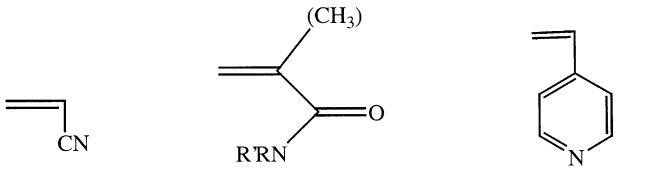


Fig. 3. Functional monomers.

Polymerization of 2-(2′-3′-4′-6′-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-ethyl acrylate (AcGEA) at 80°C, using 1-PEBr initiator and $Cu^{I}Br$/bpy system, yielded well-defined poly(AcGEA) with molecular weight $M_n = 24,600$ and polydispersity $M_w/M_n < 1.4$ [81]. O-protecting acetyl groups of poly(AcGEA) were quantitatively removed by reaction with dilute CH_3ONa solution in $CHCl_3/CH_3OH$ to afford glycopolymer, poly[(2-β-D-glucopyranosyloxy)ethyl acrylate].

Nucleoside-containing methacrylate, 5′-methacrylouridine, was also polymerized by ATRP in a TMS protected form [82]. The reaction was carried out at 90°C using $Cu^{I}Br$/N-(*n*-pentyl)-2-pyridylmethanimine catalyst and ethyl-2-bromoisobutyrate as initiator to yield well-defined polymer with molecular weight $M_n = 6500$ and polydispersity $M_w/M_n = 1.12$.

2.2.3. Other functional monomers

Other functional monomers such as acrylonitrile, 4-vinylpyridine (4VP) and (meth)acrylamides (Fig. 3) were also polymerized with ATRP.

2.2.3.1. Acrylonitrile. Polyacrylonitrile is commercially important because of its attractive properties such as hardness and rigidity, its compatibility with certain polar substances and its low gas permeability. Well-defined polyacrylonitrile was prepared at 50°C using 2-bromopropionitrile (2-BPN) as the initiator (0.1 mol%) and CuBr (0.01–0.05 mol%)/bpy as the catalyst [83,84]. The use of a solvent, e.g. ethylene carbonate, was required because poly(acrylonitrile) is not soluble in its own monomer. Polymers with molecular weights up to $M_n = 10,000$ and polydispersities $M_w/M_n < 1.1$ were obtained. At molecular weights higher than 10,000, loss of the polymerization control resulted in the curvature of the first-order kinetic plots and increase in the polydispersities ($M_w/M_n > 1.3$) [85]. Possible side reactions included loss of halide groups from the chain end by fast radical–radical termination, outer sphere electron transfer process and interaction of the cyano group with the copper catalyst.

Acrylonitrile was successfully copolymerized with St using ATRP [86,87]. Also, ABA block copolymers of acrylonitrile with BA or 2-ethylhexyl acrylate were prepared by ATRP [88].

2.2.3.2. 4-Vinylpyridine [89,90]. Pyridine-containing polymers find applications as water-soluble polymers and coordination reagents for transition metals, but their synthesis via ATRP was quite challenging. 4VP and its polymer are both strong coordinating ligands that can compete for the binding site on the copper catalyst. Since the monomer is typically present in large excess over the employed ligand, there is a possibility for ligand displacement and the formation of pyridine-coordinated copper complexes which are not effective catalysts for ATRP [34]. This was observed using $Cu^{I}Br$/2bpy and

Table 2
Results of the polymerization of (meth)acrylamides using the initiating system MCP/$Cu^{I}Cl$/Me_6TREN (experimental conditions: monomer:solvent = 1:3 (wt/vol.); target $M_n = 10,000$; MCP:$Cu^{I}Cl$:Me_6TREN = 1:1:1; room temperature)

Monomer	Solvent	Time (h)	Conv. (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
DMAA	Toluene	22.25	56	5600	6860	1.11
*t*BAA	DMF	19.25	38	3800	4100	1.15
HPMA[a]	Ethanol	22.25	18.5	1850	4480	1.29

[a] MCP:$Cu^{I}Cl$:Me_6TREN = 1:0.5:0.5.

$Cu^{I}Br$/PMDETA catalytic systems. Therefore, a strong coordinating ligand that could not be easily displaced by 4VP or poly(4VP) was employed. Polymerization was successfully carried out using a tetradentate ligand, tris[2-(dimethylamino)ethyl]amine (Me_6TREN), in combination with $Cu^{I}Cl$. 1-Phenylethyl chloride (1-PECl) was used as the initiator. The use of the chlorine end groups reduced the susceptibility of the end groups towards nucleophilic substitution reactions with pyridine. With 1-phenylethyl bromide (1-PEBr) as the initiator, only limited conversions could be obtained. The polymerization was carried out at 40°C in a polar solvent such as 2-propanol. Polymers with molecular weights up to $M_n = 20,000$ and $M_w/M_n < 1.2$ were prepared.

The synthesis of block copolymers containing 4VP was successfully carried out using ATRP conditions. Starting from a poly(MMA)–macroinitiator ($M_n = 7660$, $M_w/M_n = 1.07$), an amphiphilic poly(MMA)–*b*–poly(4VP) ($M_n = 89,500$, $M_w/M_n = 1.35$) was synthesized [89].

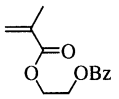
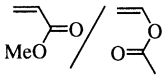
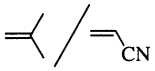
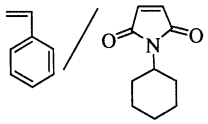
2.2.3.3. (Meth)acrylamides. Various (meth)acrylamides such as *N*-(2-hydroxypropyl)methacrylamide (HPMA), *N*,*N*-dimethylacrylamide (DMAA), *N*,*N*-diethylacrylamide (DEAA) and *t*-butylacrylamide (*t*BAA) were polymerized under ATRP conditions. Catalytic systems based on CuBr and substituted and unsubstituted bipyridines, PMDETA and Me_4Cyclam afforded poorly controlled polymerization [91,92]. However, good control was achieved when Me_6TREN was used as the ligand in conjunction with $Cu^{I}Cl$ and methyl 2-chloropropionate (MCP) at ambient temperatures (Table 2) [174].

Sawamoto and coworkers [93] also reported controlled polymerization of DMAA and DEAA using $RuCl_2(PPh_3)_3$ complex and $CH_3CH(CONMe_2)Br$ initiator in the presence of $Al(O\textit{i}\text{-}Pr)_3$ in toluene at 60–80°C. Poly(DMAA) and poly(DEAA) were synthesized with controlled molecular weights and relatively narrow molecular weight distributions ($M_w/M_n < 1.6$).

Diblock copolymers of DMAA and HPMA were prepared using macroinitiators prepared by ATRP, such as poly(MA–Br) ($M_n = 30,400$, $M_w/M_n = 1.08$) or poly(BA–Br) ($M_n = 10,700$, $M_w/M_n = 1.17$). As a result, diblock copolymers poly(MA)–*b*–poly(DMAA) ($M_n = 48,600$, $M_w/M_n = 1.33$) and poly(BA)–*b*–poly(HPMA) ($M_n = 34,000$, $M_w/M_n = 1.69$) were obtained [91].

2.2.3.4. Others. Monomers that do not form radicals stabilized by resonance and inductive effects have not yet been polymerized successfully by ATRP. This may be due to very low values of the equilibrium constant. Also, they may participate in some side reactions. However, they have been copolymerized under the appropriate conditions. Thus, vinyl acetate, isobutene and *N*-(cyclohexyl)maleimide were successfully copolymerized with other monomers such as MA, acrylonitrile and St (Table 3) [94]. Additionally, vinyl acetate has been block copolymerized with St and BA by combination of conventional polymerization and ATRP [95,96].

Table 3
Functional monomers successfully homo- or copolymerized by ATRP

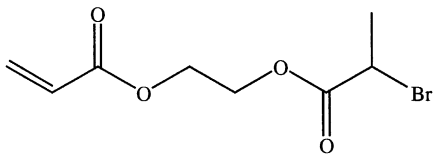
Monomer					
M_n	2000	5780	11,140	2880	4730
M_w/M_n	1.15	1.28	1.16	1.46	1.19

Monomers such as *N*-vinylpyrrolidinone were successfully homopolymerized using Me_4Cyclam as a ligand [97]. Another approach to incorporate this monomer into a well-defined structure was made by synthesizing graft copolymer poly(*N*-vinylpyrrolidinone–*g*–styrene) which formed a hydrogel with high swelling ability in water [98].

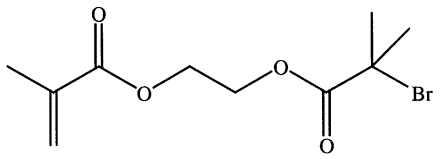
Graft copolymers of poly(vinyl chloride) with St and (meth)acrylates were prepared by ATRP using poly(vinyl chloride)–*co*–(vinyl chloroacetate) as a macroinitiator [99]. The GPC traces of the resulting graft copolymers were monomodal and the molecular weights increased significantly when compared with that of the initial polymer.

2.2.4. AB*-monomers

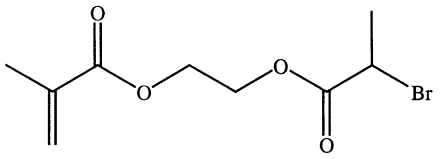
Several AB*-monomers, e.g. 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) (Fig. 4), were polymerized by ATRP resulting in hyperbranched polymers [100]. Low molecular weight polymers with high polydispersities, e.g. poly(BPEA) ($M_n = 6500$, $M_w/M_n = 3.3$), were obtained (calibration against linear polySt standards). The hyperbranched polymers bear multiple halogen end groups, which were modified by radical addition reactions (vide infra) or nucleophilic displacement reactions. The hyperbranched poly(BPEA) was treated with TMS azide yielding the hyperbranched polymer with azido functional groups [101]. Moreover, the hyperbranched polymers were used as macroinitiators for the preparation of multi-armed stars. Conventional radical polymerization or TEMPO-mediated polymerization of the AB*-monomers followed by ATRP of a second monomer resulted in graft copolymers or star burst like polymers [102,103]. For example, conventional radical polymerization of 2-(2-bromoisobutyryloxy)ethyl acrylate (BIEA) resulted in a linear polymer with pendant initiating sites for ATRP. Using this polymer as a macroinitiator for ATRP of BA resulted in the creation of a bottle-brush like polymer [65,104]. In the other approach, acrylates and BIEA (10%) were copolymerized in a conventional radical polymerization and the resulting polymer was used to graft BA from the backbone [105]. Homopolymerization of BIEA using ATRP resulted in the formation of a hyperbranched polymer where the number of bromine atoms per macromolecule was equal to the number of repeat units. Each of the bromine atoms can be abstracted by copper(I) bromide to yield a radical. Thus, a hyperbranched polymer of BIEA can be used as a macroinitiator for the formation of stars. This has been illustrated by applying hyperbranched poly(BIEA) as an initiator for BA under ATRP conditions [105]. The conditions for the polymerization of some of the AB*-monomers shown in Fig. 4 have to be carefully adjusted, including the addition of small amounts of Cu^0 [106].



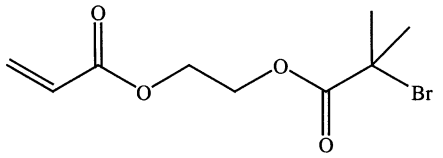
2-(2-Brompropionyloxy)ethyl Acrylate
BPEA



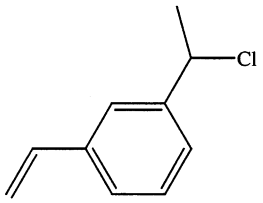
2-(2-Bromoisobutyryloxy)ethyl Methacrylate
BIEM



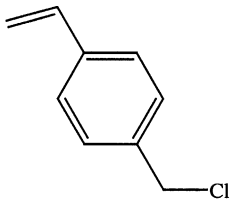
2-(2-Bromopropionyloxy)ethyl Methacrylate
BPEM



2-(2-Bromoisobutyryloxy)ethyl Acrylate
BIEA



m-(1-Chloroethyl)styrene



p-Chloromethylstyrene

Fig. 4. AB*-monomers.

2.3. Functional initiators

2.3.1. Introduction

Initiator efficiency is of prime importance for successful ATRP because it determines the number of initiated chains. In the initiation step, the transition metal complex abstracts the halogen from the organic halide RX, creating a radical $R^{\cdot}$ that adds to the vinyl monomer and the resulting radical species further propagate. Suitable initiators require an apparent initiation rate constant greater than (or at least equal to) the apparent propagation rate constant. Moreover, they should not induce side reactions. Structural adjustment of the alkyl part R and the leaving group X in order to make the R–X bond more labile than the P_n–X bond, provides a handle to fine-tune the rate of initiation in the ATRP system. Generally, alkyl halides RX with either inductive or resonance stabilizing substituents are efficient initiators for ATRP. Often, the structure of the initiator is analogous to the structure of the polymer end group. However, this guideline does not always hold for tertiary radicals as demonstrated in the polymerization of MMA; e.g. ethyl 2-bromoisobutyrate was not, but *p*-toluenesulfonyl chloride (TsCl) was an efficient initiator for the polymerization [107]. Inherent in the ATRP mechanism is the incorporation of the alkyl

group R at one polymer chain end and the halogen at the other chain end. An obvious route to prepare end functional polymers is using initiators that contain functional group(s).

2.3.2. Various initiators containing functional groups for the polymerization of styrene and (meth)acrylates

To synthesize polySt, the most commonly used initiator is 1-phenylethyl halide. However, various initiators that contain functional groups have been successfully used. In Table 4, a list of initiators used for the polymerization of St is presented [42,43,101]. The polymerizations were carried out in bulk at 110°C with $[M]_0/[I]_0/[CuBr]_0/[dNbpy]_0 = 100/1/1/2$. The list contains benzyl halides, allylic halides and initiators containing cyano, epoxy and hydroxyl groups. All initiators except allyl 2-chloroacetate and 2-chloroacetamide allowed for the preparation of well-defined polymers with polydispersities $M_w/M_n < 1.2$, which indicated that efficient initiation, and no interference with the functionalities occurred.

For the polymerization of MA, a list of useful initiators is presented in Table 5. Polymerizations were carried out in bulk at 90°C, with $[M]_0/[I]_0/[CuBr]_0/[dNbpy]_0 = 100/2.5/1/2$. Again, it was shown that functionalities such as cyano, hydroxyl and epoxy groups do not interfere with the polymerization. Also allyl esters, lactone or vinyl ester groups were tolerated. The ATRP of MA proceeded faster than that of St due to higher initiator concentration.

ATRP of MMA and St with uridine and adenosine derivatized initiators in conjunction with Cu^IBr/*N*-(*n*-pentyl)-2-pyridyl-methanimine as a catalyst proceeded effectively at 90 and 120°C, respectively, to give polymers with controlled molecular weights and low polydispersities (Table 6) [82].

A hydroxy functional alkyl bromide, 2-hydroxyethyl 2-bromoisobutyrate was successfully used as the initiator for poly(MMA) [108]. The polymerization of MMA was also initiated by cholesteryl 2-bromoisobutyrate, an initiator bearing a cholesteryl functionality. The resulting poly(MMA) had $M_n = 3290$ and $M_w/M_n = 1.13$ [109].

Arenesulfonyl halides were used for the initiation of Sts, acrylates and methacrylates [110]. Sulfonyl radicals add fast to activated olefins and have a low tendency to dimerize, therefore the initiation efficiency is high. Substituted arenesulfonyl halides with a number of different functional groups as summarized in Table 7 were successfully used to polymerize St and MMA. Generally, the polymers produced with these initiators had polydispersities $M_w/M_n < 1.3$ for poly(St) and $M_w/M_n < 1.2$ for poly(MMA). The theoretical and experimental molecular weights were similar indicating good control of the polymerization [110].

A range of phenolic esters derived from the esterification of substituted phenols with 2-bromoisobutyryl bromide and 2-chloroisobutyryl chloride (Fig. 5) have been demonstrated to be effective ATRP initiators for the polymerization of MMA and St (Table 8) [111].

Thiol-functional poly(MMA) was also successfully synthesized by ATRP using the novel 2-(2,4-dinitrophenylthio)ethyl 2-bromo-2-methylpropionate initiator which contained a thiol group protected with Sangers reagent [112]. Polymerization was carried at 85°C using nickel catalyst and protecting groups were removed through an exchange reaction with a large excess of mercaptoethanol in the presence of triethylamine. Resulting thiol-functional poly(MMA) had $M_n = 6000$ and relatively low polydispersity, $M_w/M_n = 1.28$.

2.3.3. Acid containing initiators

Well-defined polymers with terminal acid groups can be prepared via ATRP using protected

Table 4
Results of the ATRP of styrene, carried out in bulk at 110°C with $[M]_0/[I]_0/[CuBr]_0/[dNbpy]_0 = 100/1/1/2$

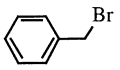
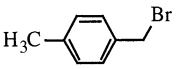
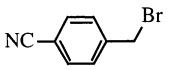
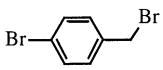
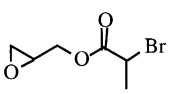
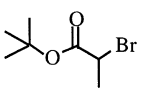
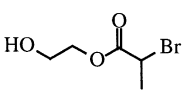
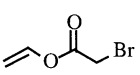
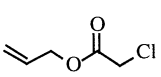
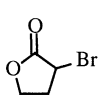
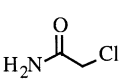
Initiator	Conv. (%)	$M_{n,Cal}$	$M_{n,SEC}$	M_w/M_n
	53.7	5370	6460	1.10
	51.1	5110	4400	1.17
	47.6	4760	5530	1.10
	47.5	4750	4520	1.16
	48.0	4800	5130	1.09
	61.9	6190	6790	1.12
	41.1	4110	4030	1.17
	48.1	4810	7520	1.10
	94.0	5000	5800	1.12
	14.3	1430	2600	1.77
	40.5	4050	4030	1.17
	12.0	1200	4010	1.51

Table 5
Results of the ATRP of methyl acrylate, carried out in bulk at 110°C with $[M]_0/[I]_0/[CuBr]_0/[dNbpy]_0 = 100/2.5/1/2$

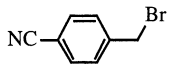
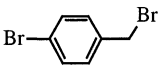
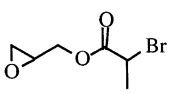
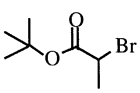
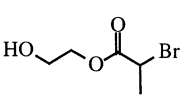
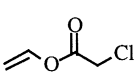
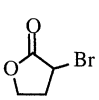
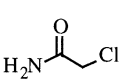
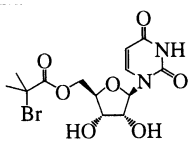
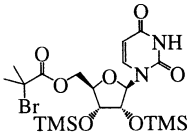
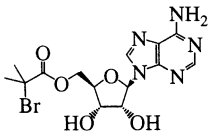
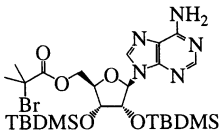
Initiator	Conv. (%)	$M_{n,Cal}$	$M_{n,SEC}$	M_w/M_n
	93.1	3720	4110	1.13
	64.6	3780	4010	1.22
	88.6	3540	6220	1.34
	2.0	3280	3550	1.10
	92.9	3720	4020	1.18
	94.3	3770	3980	1.17
	97.0	3880	4560	1.18
	70.2	2800	3260	1.34
	83.3	3330	4120	1.13
	32.2	1290	7220	1.22

Table 6
Uridine and adenosine based initiators for the polymerization of methyl methacrylate and styrene (reactions carried out in toluene (33 vol%) with [*N*-(*n*-pentyl)-2-pyridylmethanimine]/[$Cu^{I}Br$] = 2)

Initiator	Monomer	[M]/[I]	Temperature (°C)	Time (h)	$M_{n,SEC}$	PDI	I_{eff}
	MMA	100	90	19	22,500	1.19	0.46
	MMA	100	90	17	13,100	1.06	0.81
	MMA	20	90	17	3150	1.13	0.81
	St	100	120	15.5	17,000	1.15	0.64
	MMA	100	90	16	17,100	1.24	0.62
	MMA	100	90	16	12,600	1.06	0.83

α-halocarboxylic acid and carboxylic acid initiators with remote halogens. This was demonstrated in the polymerization of St at 110°C using the $Cu^{I}Br$/PMDETA catalytic system (Table 9) [73,113]. In both cases, the initiator efficiency was considerably higher (0.6–0.7) than for α-halocarboxylic acids (0.1–0.2). The reason is that the protection of carboxylic group or presence of remote halogens supresses an intramolecular cyclization reaction between α-halocarboxylic acid and St to form γ-butyrolactones. Such a reaction is known to occur under ATRA conditions [114,115].

The successful use of α-halocarboxylic acids as initiators for the ATRP of MMA was also reported [116].

4-(1-Bromoethyl)benzoic acid was used as the initiator in the $Cu^{I}Br$/bpy-mediated ATRP of St to yield carboxylic acid functionalized polySt with molecular weight as high as 15,000 and low polydispersity, $M_w/M_n < 1.30$ [117].

2.3.4. Allyl bromide, allyl chloride

In order to produce polymers with an allyl end group, allyl halides were used as initiators for ATRP [118]. The allyl group is a versatile functional group as it can be transformed to other functionalities such as epoxy and hydroxyl groups. Also, allyl end functional polymers can be used for the synthesis of block

Table 7
Arenesulfonyl halides as initiators for styrene and methyl methacrylate polymerizations. $[S]_0/[I]_0/[Cu^ICl]_0/[dnNbpy]_0 = 200/1/0.3/0.4$; $[MMA]_0/[I]_0/[Cu^ICl]_0/[dnNbpy]_0 = 100/1/0.3/0.42$

Initiator	Solvent	Time (h)	Conv. (%)	M_n^{theo}	M_n	M_w/M_n
Styrene						
4-Methoxybenzenesulfonyl chloride	Diphenyl ethyl	25	77	16,016	15,070	1.27
	Bulk	17	67	15,330	14,800	1.29
4-Methylbenzenesulfonyl chloride	Diphenyl ethyl	25	61	14,591	15,000	1.25
	Bulk	17	67	15,330	14,500	1.39
4-Fluorobenzenesulfonyl chloride	Diphenyl ethyl	25	78	16,224	16,000	1.21
	Bulk	17	66	13,728	11,300	1.24
4-Chlorobenzenesulfonyl chloride	Diphenyl ethyl	25	71	14,768	12,600	1.20
	Bulk	17	67	13,936	14,250	1.28
Benzenesulfonyl chloride	Diphenyl ethyl	25	71	16,245	15,320	1.27
	Bulk	17	68	14,144	13,550	1.33
Methyl methacrylate						
4-Methoxybenzenesulfonyl chloride	*p*-Xylene	74	63	6500	6200	1.16
4-Flourobenzenesulfonyl chloride	*p*-Xylene	74	54	5600	5800	1.15
4-Methylbenzenesulfonyl chloride	*p*-Xylene	74	73	7500	7760	1.12
Benzenesulfonyl chloride	*p*-Xylene	74	50	5200	5600	1.13

or graft copolymers via hydrosilylation [119]. α-Allyl-ω-halopolystyrene was prepared with a heterogeneous catalyst system, CuBr/bpy, in diphenyl ether at 100 or 130°C when CuCl was used. A polymer with $M_n \approx 5000$ and $M_w/M_n < 1.3$ was obtained. ^{1}H NMR (Fig. 6) demonstrated the quantitative presence of the allyl end groups.

2.3.5. Multifunctional initiators

Multifunctional initiators can be synthesized from molecules with multiple reactive sites that are efficiently converted to initiating sites. For example, hydroxyl containing molecules such as ethylene glycol were reacted with methyl 2-bromopropionyl bromide and thus converted to a difunctional initiator [120]. Pentaerythritol was converted to a four-armed star initiator, pentaerythritol tetrabromopropionate [121]. The commericial hexakis(bromomethyl)benzene has been earlier used directly to generate a six-armed star poly(St) using the CuBr/bpy system [122].

Three-armed star poly(MA) has been prepared by ATRP using 1,1,1-tris(bromoisobutyryloxy)-phenylethane as a trifunctional initiator, in combination with Cu^IBr/4,4′-di-*t*-butyl-2,2′-bipyridine (dTbpy) as a catalyst. The star polymer was subsequently functionalized by reaction with 1,2-epoxy-5-hexene at 70°C for 24 h (cf. Section 2.4.4.3) [123]. Similarly, a hyperbranched polymer, poly(BPEA)

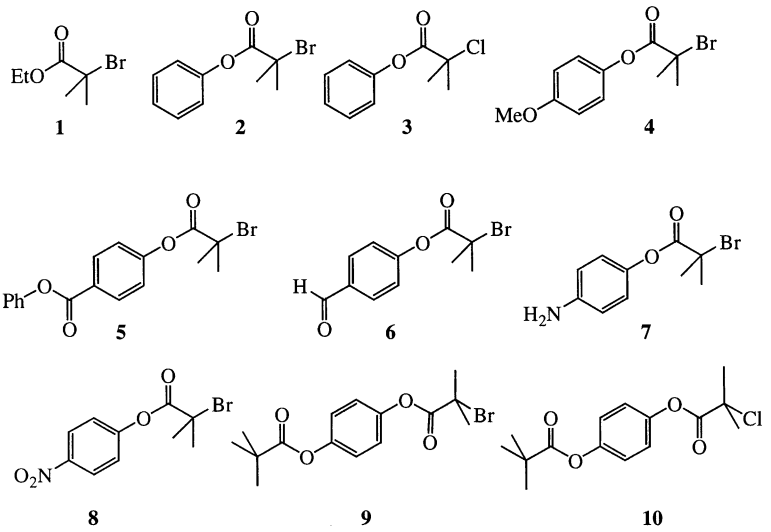


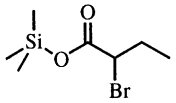
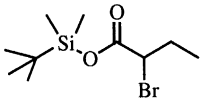
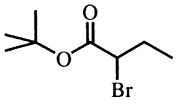
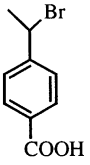
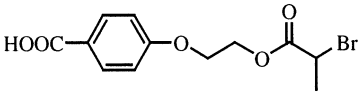
Fig. 5. Phenolic ester based monofunctional initiators.

Table 8
Atom transfer radical polymerization with phenolic ester based monofunctional initiators in xylene solution (33% v/v) at 90°C, $[MMA]_0/[Cu^IBr]_0/[L]_0/[init.]_0 = 100/1/2/1$, sampled at $t = 4$ h (L is *N*-(*n*-octyl)-2-pyridylmethanimine)

Initiator[a]	Monomer	Conv. (%)	$M_{n,SEC}$	PDI	I_{eff}
1	MMA	76.9	6350	1.19	0.82
2	MMA	84.2	6620	1.11	0.79
3[b]	MMA	72.8	7780	1.35	1.07
4	MMA	66.9	5430	1.14	0.81
5	MMA	82.2	6710	1.10	0.82
6	MMA	86.6	9340	1.19	1.08
7	MMA	76.7	6440	1.10	0.84
8	MMA	85.2	6350	1.09	0.77
9	MMA	80.6	7220	1.09	0.89
10[b]	MMA	64.6	7410	1.23	1.15
2[c]	St	29.5	1950	1.10	0.66
2[d]	St	52.8	5000	1.11	0.91
2[e]	St	56.2	5240	1.10	0.90

[a] cf. Fig. 5 for initiator structures.
[b] Cu^ICl used as catalyst.
[c] Styrene in xylene (50% v/v) at 110°C, 44% conversion after 8 h.
[d] Styrene in xylene (50% v/v) at 110°C, $[St]_0/[Cu^IBr]_0[L]_0 = 100/2/4/1$, 80% conversion after 8 h.
[e] Styrene in xylene (50% v/v) at 110°C.

Table 9
Results of the ATRP of styrene initiated by α-halocarboxylic acids and carboxylic acids with remote halogens

Initiator	Time (h)	Conv. (%)	$M_{n,th}$	$M_{n,SEC}$	PDI
Alkyl protected α-halocarboxylic acids[a]					
	3.5	60	6000	11,000	1.20
	3.4	70	7000	8500	1.15
	3.6	78	7800	7500	1.10
Carboxylic acids with remote halogens[a]					
	3.6	79	12,000	11,500	1.10
	3.6	80	12,000	12,200	1.10

[a] $[Cu^{I}Br]_0 = [initiator]_0 = [PMDETA]_0 = 0.078$ M, $[Styrene]_0 = 7.5$ M, $T = 110$°C.

was synthesized by ATRP and functionalized by dissolving it in 1,2-epoxy-5-hexene together with CuBr/dTbpy, and copper turnings. The functionalization was verified by ^{1}H NMR [123].

2,4,6,8-Tetramethylcyclotetrasiloxane has been modified by a hydrosilylation reaction with *p*-vinylbenzylchloride yielding an initiator with four initiating sites. Similarly, a six-armed initiator, 1,1,3,3,5,5-hexakis(4-(2-bromopropionyloxymethyl) phenoxy)cyclotriphosphazene, was synthesized starting from 2,2,4,4,6,6-hexachlorocyclotriphosphazene [124]. Using these initiators, well-defined star-shaped poly(Sts), poly(acrylates), poly(methacrylates) and corresponding multiarmed block copolymers with inorganic cores were synthesized [121].

Tetra-, hexa- and octafunctional initiators based on calix[*n*]arene cores ($n = 4, 6, 8$) were used for the polymerization of MMA using $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}\text{-}Pr)_3$ [125]. The resulting polymers had controlled molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.2$). The obtained octaarmed star poly(MMA) was further used to make block copolymers with BA. A similar approach, using an octafunctional calixarene derivative, was used to initiate ATRP of St in the presence of

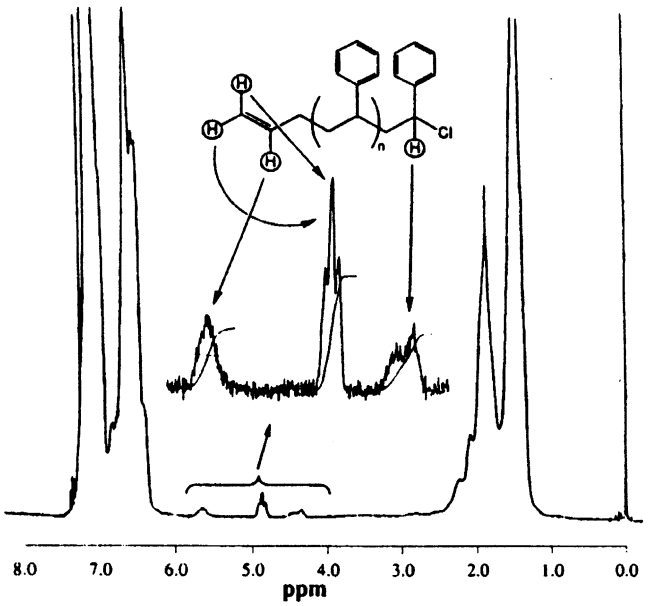


Fig. 6. ^{1}H NMR of α-allyl-ω-chloro-polystyrene. Reprinted with permission from Ref. [118]. © Copyright, 1998 by The Society of Polymer Science, Japan.

CuBr/bpy, in order to obtain well-defined octaarmed star polymers [126]. This methodology has been extended further to a dendritic twelve-armed initiator which was successfully used to polymerize MMA using $NiBr_2(PPh_3)_3$ catalyst [127].

D-glucose was used to synthesize a pentafunctional initiator by reacting 2-bromoisobutyrate with D-glucose to form the ester derivative. This multifunctional initiator was used to prepare stars of poly(MMA) with $M_n = 31,700$, which was close to the theoretical molecular weight, and $M_w/M_n = 1.18$. For stars of poly(St), the molecular weights were controlled, but the polydispersity of the polymers were as high as 1.70. This was probably due to termination by coupling of stars [128].

Incorporation of ruthenium into star shaped poly(MMA) has been achieved using a hexafunctional ruthenium-tris(bipyridine) initiator in conjunction with $NiBr_2(PPh_3)_2$ catalyst [129]. The resulting ruthenium centered star polymers had polydispersities ranging from 1.05 to 1.2.

In addition, difunctional and trifunctional phenolic ester based initiators were successfully used in the ATRP of MMA. The resulting polymers had controlled molecular weights and low polydispersities ($M_w/M_n = 1.08$–1.21) [111].

Methyl and *n*-butyl methacrylate were also polymerized using multisulfonyl chloride initiators to yield well-defined polymers and stars ($M_w/M_n = 1.08$–1.27) [130].

Recently, a well-defined anthracene-labelled poly(St) was synthesized by ATRP using bifunctional bromine containing anthracene derivative, 9,10-bis(1-bromoethylcarbalkoxymethyl)anthracene [131].

The self-condensing vinyl polymerization of 4-(chloromethyl)styrene using ATRP catalyzed by $Cu^{I}Cl$/bpy complex resulted in the formation of hyperbranched polymers with a high degree of functionality [132]. Chlorine end groups were successfully transformed to cyano, acetate and thioether end groups.

Table 10
Examples of well-defined block copolymers starting from different macroinitiators (THF, tetrahydrofuran; NB, norbornene; DCPD, dicyclopentadiene; EG, ethylene glycol; E-*co*-B, ethylene-*co*-butylene; NPMA, *p*-nitrophenyl methacrylate; ϵ-CL, ϵ-caprolactone; OE, oxyethylene; IB, isobutene; BA, butyl acrylate; FNEMA, 2-[(perfluorononenyl)oxyl]ethyl methacrylate; VDF, vinylidene fluoride)

Macroinitiator	Before			After			Reference
	M_n	M_w/M_n	$\bar{F}$	Second monomer	M_n	M_w/M_n	
Poly(THF)	15,418	1.38	1	Styrene	31,000	1.46	[136–138]
				MMA	56,700	1.21	[136–138]
				MA	28,500	1.32	[136–138]
Poly(NB)	15,000	1.09	1	Styrene	95,000	1.06	[136–138]
				MA	60,000	1.07	[136–138]
Poly(DCPD)	7000	1.24	1	Styrene	17,000	1.37	[136–138]
				MA	21,000	1.47	[136–138]
Poly(EG)	2000	1.05	1	Styrene	12,000	1.25	[140]
Poly(E–*co*–B)	4350	1.05	1	Styrene	19,500	1.29	[139]
Poly(styrene)	14,730	1.18	1	NPMA	25,200	1.26	[141]
Poly(ϵ-CL)	2500	1.15	1	Styrene	13,000	1.17	[142]
Poly(OE)	2370	1.10	1	*t*BA	4970	1.24	[143]
Poly(IB)	28,800	1.31	2	Styrene	48,820	1.14	[136–138]
				MMA	33,500	1.47	[136–138]
				MA	31,810	1.42	[136–138]
				IBA	49,500	1.21	[136–138]
Poly(BA)	96,700	1.30	2	Styrene	1,09,500	1.47	[136–138]
Poly(sulfone)	4100	1.50	2	Styrene	10,700	1.10	[136–138]
				BA	15,300	1.20	[136–138]
Poly(ester)	1750	2.50	2	Styrene	21,000	1.40	[136–138]
Poly(ether)	3700	1.08	2	Styrene	12,800	1.34	[144]
Poly(BA)	9740	1.48	2	FNEMA	25,500	1.27	[145]
Poly(EG)	2150	1.11	2	Styrene	13,300	1.36	[120]
Poly(VDF)	3870	1.10	2	Styrene	37,400	1.65	[146]
Poly(styrene)	4250	1.33	2	THF	11,900	1.38	[147]

2.3.6. Macroinitiators

Polymeric chains with halogen end groups that can be reactivated by an ATRP-catalyst system can be used as macroinitiators. In this respect, block and graft copolymers have been synthesized using ATRP (vide supra).

Not only polymers prepared by ATRP, but also commercially available polymers or polymers obtained by other polymerization techniques have been used as macroinitiators. For example, poly(St) with chlorine chain end, polymerized cationically, was further used to prepare an AB-type block copolymer with a B-segment poly(MA) [133,134]. Also, α,ω-difunctional poly(isobutene) capped with a few units of St, was shown to be an effective initiator for St, MA and MMA yielding well-defined triblock copolymers [42,120,135]. Several other examples are summarized in Table 10 [136–147]. Multifunctional macroinitiators have also been used in the synthesis of various graft copolymers [148–152] (cf. Section 2.2.4).

Other examples involve the combination of either inorganic or organic polymers. Commercially available difunctional poly(dimethylsiloxane) (poly(DMS)) was modified by attaching benzyl chloride to the chain ends. This polymer was subsequently used to make triblock copolymers consisting of a poly(DMS) center block and polySt terminal blocks yielding a thermoplastic elastomer [153–155]. Similarly, poly(DMS) with pendant benzyl chloride groups was used to prepare graft copolymers [124].

Derivatized cyclodextrin was used to initiate the polymerization of MMA. The result was 21-armed stars with $M_n = 61,200$, which was about half the theoretical value, $M_w/M_n = 1.89$ [128].

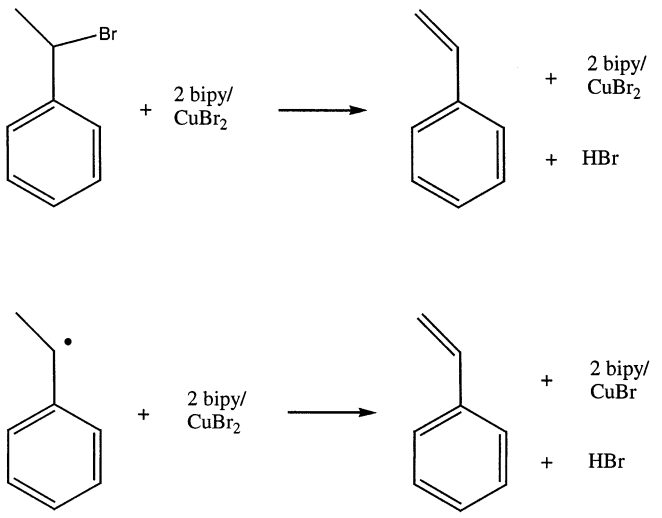
2.4. End group transformations

2.4.1. Stability of the halogen end group

Inherent in the mechanism of ATRP is the incorporation of the halogen at the chain ends. These alkyl halide end groups can be transformed into other functionalities by means of standard organic procedures. A prerequisite to reach a high degree of functionality by end group transformation is that the halogenated chain end is stable throughout the polymerization, i.e. termination must be avoided.

The stability of the bromine end group during St polymerization has been studied by investigating a model reaction of 1-PEBr and a copper complex, namely cuprous bromide with 2 eq. of dNbpy as the ligand. The reaction occurred in benzene in a sealed NMR tube at 110°C. Initially 2,3-diphenylbutane was formed due to radical coupling; with each termination event the concentration of cupric bromide increases and the probability of biradical termination decreases, this is also known as the 'persistent radical effect' [34,50]. Upon further heating, the formation of St was observed and the concentration of St increased as a function of time. The elimination reaction was found to be catalyzed by cupric bromide, which is able to react with 1-PEBr or with the styryl radical, yielding St and hydrogen bromide as shown in Scheme 4 below [156].

It was shown that the rate of the elimination reactions were three to five orders of magnitude slower than the rate of deactivation in an atom transfer process, i.e. the reaction of cupric bromide and



Scheme 4.

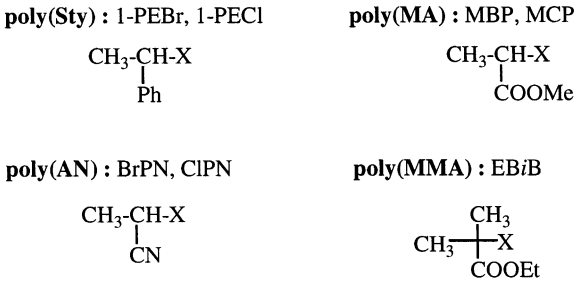


Fig. 7. Models mimicking polymer end groups.

propagating radicals to yield cuprous bromide and bromine terminated radicals. It was concluded that the bromine end group functionality could be maintained if the conversion was kept below 95%.

2.4.2. Nucleophilic substitutions

2.4.2.1. Azide and amino end groups. The halogen end group can be transformed into other functionalities by means of standard organic procedures such as nucleophilic displacement reactions. In order to investigate the feasibility and the selectivity of the nucleophilic displacement reactions, model reactions were performed. To mimic the end groups of poly(St), poly(acrylates), or poly(MMA), the model compounds 1-phenylethyl halide, methyl 2-halopropionate and ethyl 2-bromoisobutyrate, respectively, were chosen (Fig. 7). The selected nucleophiles were sodium azide, *n*-butylamine and tri-*n*-butylphosphine.

The reactions of the model compounds with sodium azide were performed at room temperature, at 1 M substrate concentration in DMF with 1.1 eq. of sodium azide. Using similar reaction conditions, the models, at 1 M concentration in DMSO, were reacted with *n*-butylamine. The course of the reactions were followed by GC and the rate constants of the reactions were calculated (Table 11). The initial

Table 11
Rate constants for the reactions of RX (1 M in solvent) with 1.1 eq. of nucleophile at 25°C (MBrP,methyl 2-bromopropionate; 1-PEBr, (2-bromoethyl)benzene; BzCl, benzyl chloride; EBr*i*B, ethyl 2-bromoisobutyrate; MClP, methyl 2-chloropropionate; 2-ClPN, 2-chloropropionitrile; 1-PECl, (2-chloroethyl)benzene)

	RX (X = Cl, Br)	k ($M^{-1}\,s^{-1}$) (RX in DMF + NaN_3)	k ($M^{-1}\,s^{-1}$) (RX in DMSO + $BuNH_2$ + 1.1 eq. Et_3N)
1	MBrP	–	4.6×10^{-3}
2	1-PEBr[a]	6.8×10^{-3}[a]	7.5×10^{-4}
3	BzCl	1.5×10^{-3}	–
4	EBr*i*B	7.2×10^{-4}	7.3×10^{-5}
5	MClP	4.3×10^{-4}	3.3×10^{-5}
6	2-ClPN	7.6×10^{-5}	–
7	1-PECl	6.7×10^{-5}	6.2×10^{-6}

[a] Determined by competition experiments.

Table 12
Results of the displacements of bromine from bromo-terminated polymers by sodium azide

Substrate	GPC	Experimental conditions	Result
Poly(St–Br)	$M_n = 1370$ $M_w/M_n = 1.2$	0.05 M in DMF 1.1 eq. NaN_3, 25°C, 1 h	Poly(St–N_3) >90%
Poly(MA–Br)	$M_n = 1830$ $M_w/M_n = 1.1$	0.05 M in DMF 1.1 eq. NaN_3, 25°C, 1 h	Poly(MA–N_3) >90%
Poly(MMA–Br)	$M_n = 1770$ $M_w/M_n = 1.3$	0.05 M in DMF 1.1 eq. NaN_3, 25°C, 12 h 0.05 M in DMF 10 eq. NaN_3, 25°C, 12 h	40% poly(MMA–N_3) 60% poly(MMA–Br) Poly(MMA–N_3) >90%

slopes of the second order plots were used to calculate the rate constants as deviation was observed at conversions above 40%.

The reactions of the brominated substrates with sodium azide occurred almost instantaneously. The rate constant of the reaction of sodium azide with 1-PEBr was therefore determined by competition experiments. Bromo-derivatives reacted about 100 times faster than chloro-derivatives. The rate of the substitution reactions were dependent on the substrates, following the order BzCl > MCP > 1-PECl. Nucleophilic substitution reactions occur faster at primary than secondary carbon centers (BzCl > 1-PECl). The reactivity of the secondary carbon center of MCP is increased by the electron withdrawing effect of the ester substituent more than by a phenyl group (MCP > 1-PECl).

In general, the substitution reactions of the different substrates with *n*-butylamine showed the same trends, however, the reactions were about 10 times slower than with sodium azide. Primary amines are good nucleophiles, but the basicity of the amine is higher than that of azide, which increases the chance of side reactions. Some elimination was indeed observed when *n*-butylamine was reacted with MCP.

Extrapolating the data obtained for the model studies to the polymeric compounds, the bromine terminated polymers are expected to be good substrates for nucleophilic displacement reactions. Chlorine end groups can also be substituted by azides but with *n*-butylamine, side reactions such as elimination are possible. The reactions on polymeric substrates were performed with low molecular weight polymers to facilitate the end group analysis. The analysis of end groups was performed with ^{1}H NMR, ESI-MS or MALDI-TOFMS.

Poly(St), poly(MA) and poly(MMA) with bromine end groups were reacted with sodium azide in DMF (Table 12). Complete substitution of the bromine by azide was observed by ^{1}H NMR and MALDI-TOFMS. As an example, the MALDI-TOFMS spectrum of pMA–N_3 is shown in Fig. 8. The obtained mass values in the spectrum were comparable in an error range of ±3 a.m.u. with the theoretical mass of pMA–N_3, $m/z = [87(CH_3CH(COOMe)–) + n \times 86(–CH_2CH(COOMe)–) + 42(–N_3) + 23(Na)]^+$. Small peaks due to the loss of N_2, N_3 and presumably $N_3 + CH_3$ during mass spectrometry were also observed.

If the use of DMF as a solvent was not desired, the halogen end groups were successfully replaced by azides in THF using TMS azide in the presence of potassium fluoride and a catalytic amount of tetrabutylammonium fluoride [157,158].

Azide end groups are interesting because they can be further converted into amino end groups. The

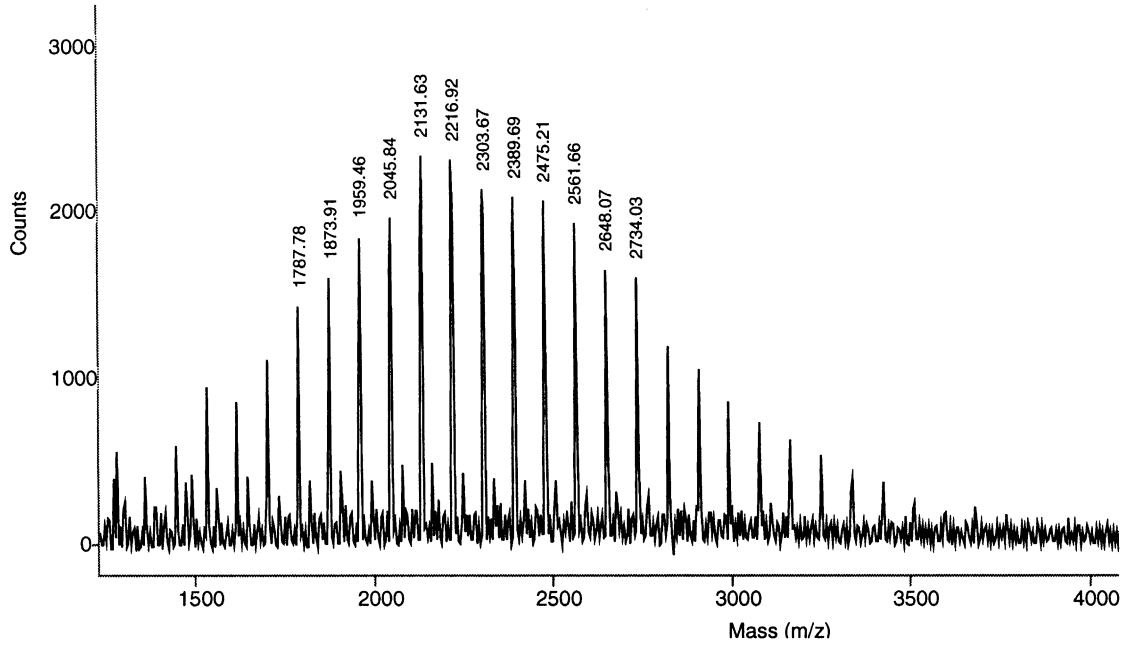
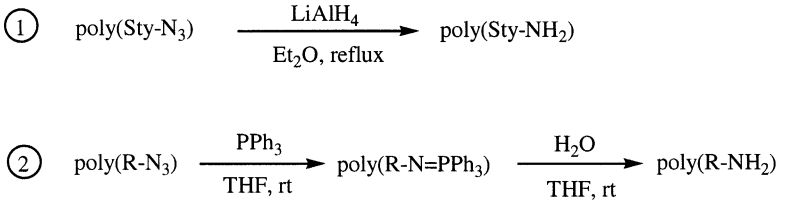


Fig. 8. MALDI-TOFMS spectrum of poly(MA–N_3) (the matrix was trans-3-indole acrylic acid doped with Na^+). Reprinted with permission from J.M.S.-Pure Appl Chem 1999;A36:667–79. © Copyright, 1999 by Marcel Dekker, Inc.

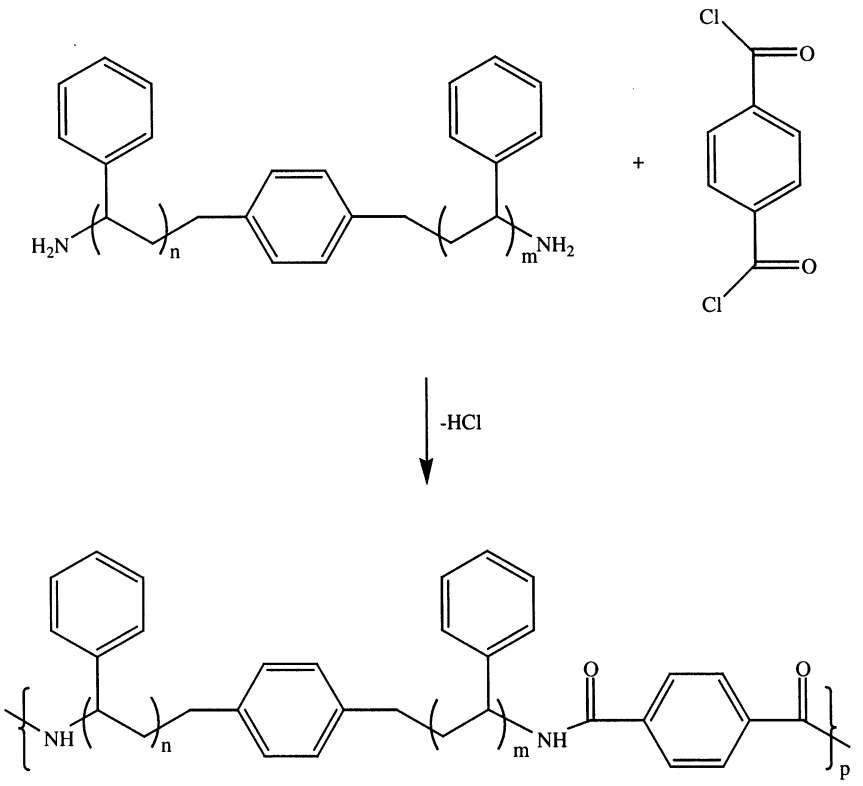
azide groups in poly(St) were reduced with lithium aluminum hydride [157], however, this procedure could not be used for poly(acrylates) because of reduction of the ester functionalities. A more general procedure is the conversion of the azide into the phosphoranimine end groups and subsequent hydrolysis to the amino end groups (Scheme 5) [159].

This reaction route was used to synthesize telechelic diamines. St polymerization was initiated by α,α′-dibromo-*p*-xylene yielding α,ω-dibromo poly(St). The polymer was isolated and the end groups were converted to the amino end groups by the mechanism shown in Scheme 5 ($M_n = 5100$, $M_w/M_n = 1.2$). The polymer was extended with terephthaloyl chloride to yield polySt with internal amide functionalities as shown in Scheme 6 ($M_n = 23,000$, $M_w/M_n = 2.3$) [43].

Poly(MA) with bromine end groups ($M_n = 2076$, $M_w/M_n = 1.12$) was reacted for 35 h with a 10-fold excess of *n*-butylamine in DMSO at room temperature. Complete substitution was observed by ^1H NMR and ESI-MS (Fig. 9). The major series in the ESI-MS spectrum corresponds to the protonated polymer



Scheme 5.



Scheme 6.

$m/z = [87(CH_3CH(COOMe)–) + n \times 86(–CH_2CH(COOMe)–) + 72(–NH–Bu) + 1(H)]^+$, the minor series at lower m/z corresponds with doubly charged species, $m/z = [87 + n \times 86 + 72 + 1(H) + 23(Na)]^+/2$.

2.4.2.2. Hydroxyl end groups [160]. The direct displacement of bromine from poly(St), poly(acrylates) and poly(methacrylates) by hydroxide anion was not successful and was accompanied by significant elimination. However, substitution of the bromine end groups with primary amines can be used as a method to insert other functionalities, including hydroxyl groups. For example, poly(St–Br) ($M_n = 980$, $M_w/M_n = 1.15$) was reacted for 48 h at room temperature with an excess of ethanolamine, in the presence of triethylamine. Complete substitution resulting in a poly(St) chain with hydroxyl end groups was obtained (Fig. 10). With polyacrylates however, multiple substitution reactions occurred (Scheme 7). These were presumably due to the formation of a six-membered ring intermediate after the substitution of the bromine end group. The proportion of side reactions was reduced by using *n*-butanolamine.

2.4.2.3. Acetate end groups. The bromine end groups in polymers have been replaced by acetate end groups by dissolving the polymer in DMSO and adding a 25-fold excess of sodium acetate (Scheme 8).

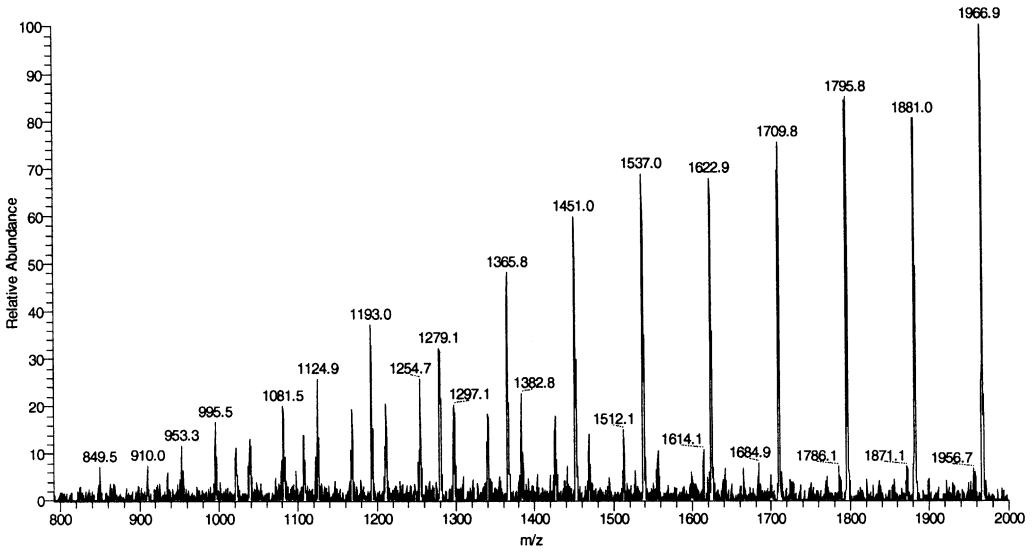
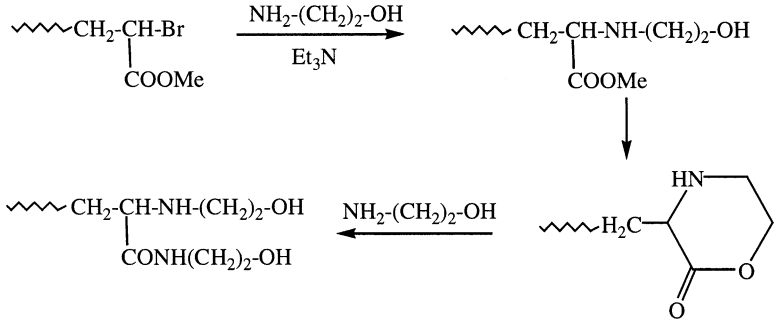


Fig. 9. ESI-MS spectrum of poly(MA–NH–Bu)(doped with Na^+). Reprinted with permission from Ref. [158]. © Copyright, 1999 by Marcel Dekker, Inc.

After stirring for 24 h at room temperature, the complete displacement of the bromine end groups by acetate end groups was verified by ^1H NMR and ESI-MS.

2.4.2.4. Phosphonium end groups [161]. To obtain cations at the polymeric chain ends, phosphines were reacted with the halide end groups. Tri-*n*-butylphosphine and triphenylphosphine were selected as nucleophiles and the feasibility and the selectivity of their reactions with the model alkyl halides was investigated. Triphenylphosphine reacted very slowly with the model compounds MBP and 1-PECl(Br), while tributylphosphine reacted about 20 times faster. The rate constants, shown in Table 13, were determined by reacting the model compounds at a 0.3 M concentration in acetonitrile with 1.1 eq. of



Scheme 7.

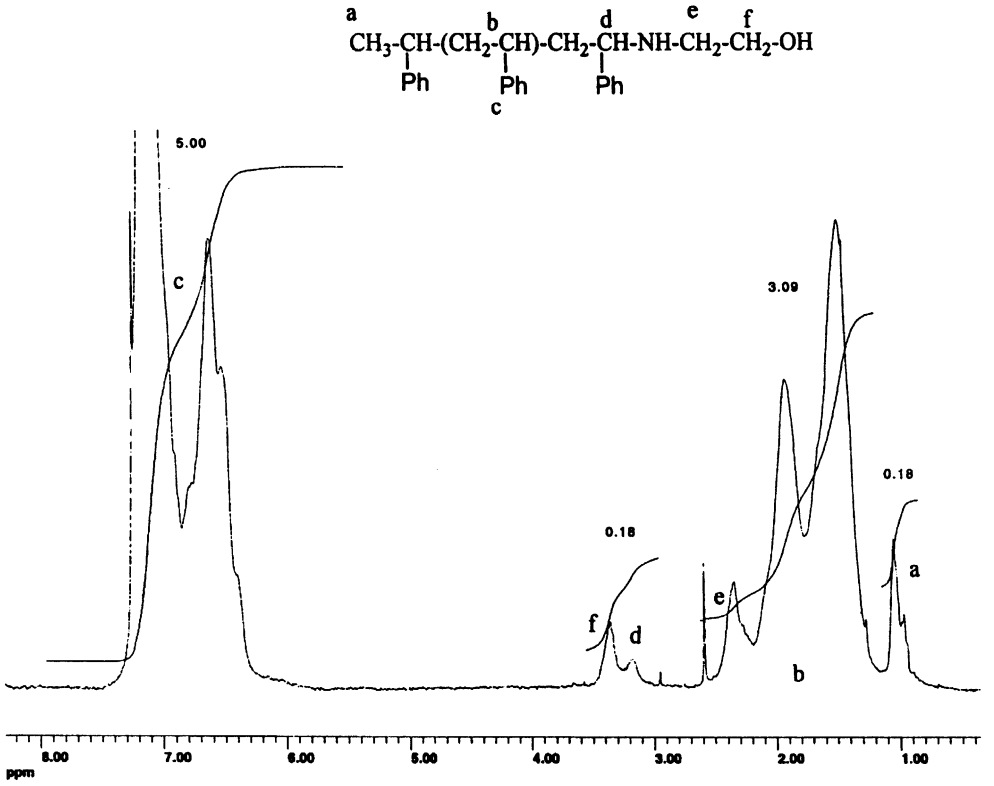


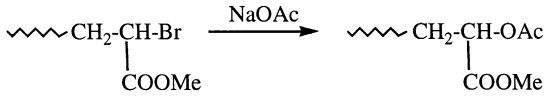
Fig. 10. NMR spectrum of poly(St–NH–CH_2–CH_2–OH). Reprinted with permission from Ref. [158]. © Copyright, 1999 by Marcel Dekker, Inc.

phosphine. In an attempt to increase the reaction rates, the temperature was increased. However, under these conditions the ester group was attacked by phosphine and degradation occurred.

Poly(MA) was prepared by the reaction with tri-*n*-butylphosphine. The presence of the phosphonium end groups was demonstrated by ^{1}H NMR and by MALDI-TOFMS, shown in Fig. 11. The peaks in the MALDI-TOFMS spectrum correspond within an error range of ±3 a.m.u. to poly(MA)-bound tri-*n*-butylphosphonium, $m/z = [87(CH_3–CH(COOMe)–) + n \times 86(–CH_2–CH(COOMe)–) + 202(–PBu_3)]^+$.

2.4.3. Electrophilic additions

Halogen end groups in polymers were successfully transformed by an electrophilic addition reaction using allyltrimethylsilane. The reaction was carried out in dichloromethane and was catalyzed by titanium tetrachloride (Scheme 9) [162]. Alternative methods to insert allyl end groups are using either



Scheme 8.

Table 13
Rate constants for the reaction of 1-phenylethyl bromide (1-PEBr) and methyl 2-bromopropionate (MBP) with phosphines in acetonitrile

	1-PEBr	MBP
PBu_3, 25°C	2.5	4.7
PBu_3, 80°C	17	≥ 40[a]
PPh_3, 25°C	0.1	0.3
PPh_3, 80°C	3.7	≥ 3.5[a]

[a] Decomposition of the phosphonium salt was observed.

allyl chloride or allyl bromide as the initiator (see above) or a radical addition reaction with allyl tri-*n*-butyltin (vide infra).

2.4.4. Radical addition reactions [163]

2.4.4.1. Allyl end groups. A one-pot procedure to displace the halogen end groups by allyl end groups was developed using allyl tri-*n*-butylstannane. The reaction of an alkyl halide with allyl tri-*n*-butylstannane is a radical reaction that tolerates the presence of other functional groups such as acetals, ethers, epoxides, hydroxyl groups and esters. Therefore, this method can be used for various functional monomers.

MA was polymerized in bulk by ATRP and at 85% conversion, allyl tributyltin was added along with an inert solvent, benzene, and Cu^0. After further reaction for 3 h, the polymer was purified by precipitation in *n*-hexanes. Nearly quantitative incorporation of the allyl groups was demonstrated by ^1H NMR (Fig. 12). Allyl end-groups were also incorporated to the poly(MMA) using allyl bromide [170].

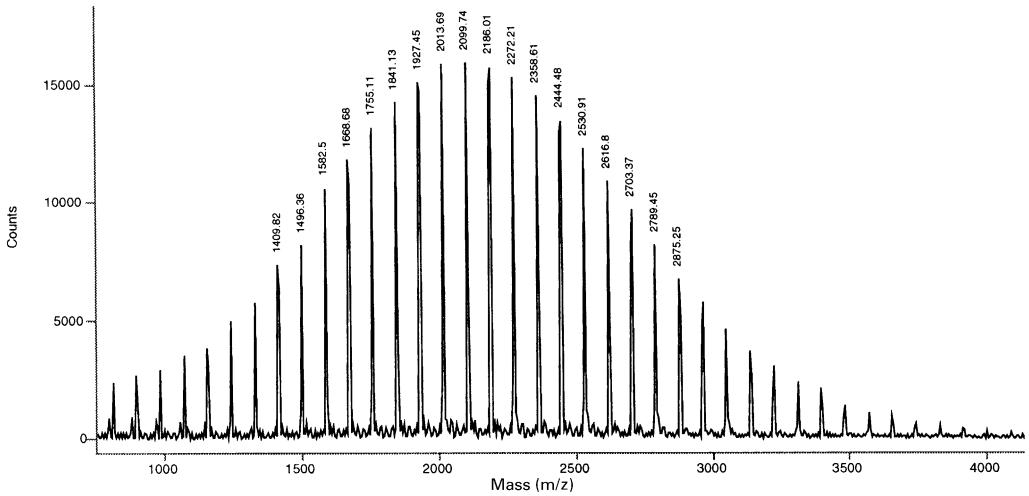
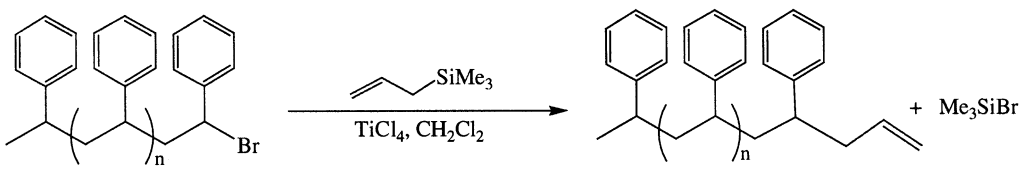


Fig. 11. MALDI-TOFMS spectrum of poly(MA–P^+Bu_3) (the matrix was trans-3-indole acrylic acid doped with Na^+). Reprinted with permission from Ref. [161]. © Copyright, 1999 by Marcel Dekker, Inc.



Scheme 9.

2.4.4.2. Dehalogenation of the polymer chains [163]. The presence of halogen end groups in polymer chains may not be desired, for example during the processing of the polymer. Therefore, a one-pot procedure for the removal of the halogen, directly after the polymerization reaction, was developed. As shown in Table 14, bromine as well as chlorine end groups in different polymers were reduced using tri-*n*-butyltin hydride, with the ATRP catalyst being the radical generator. The addition of solvent was necessary when the polymerization was performed in bulk to homogenize tri-*n*-butyltin hydride and the polymer. The nearly complete (>95%) dehalogenation of the polymeric chains was observed with ^{1}H NMR (disappearance of –CH–X) and with mass spectrometry techniques such as ESI-MS or MALDI-TOFMS. Terminal bromide was also removed from poly(MMA) in the presence of excess TEMPO [170].

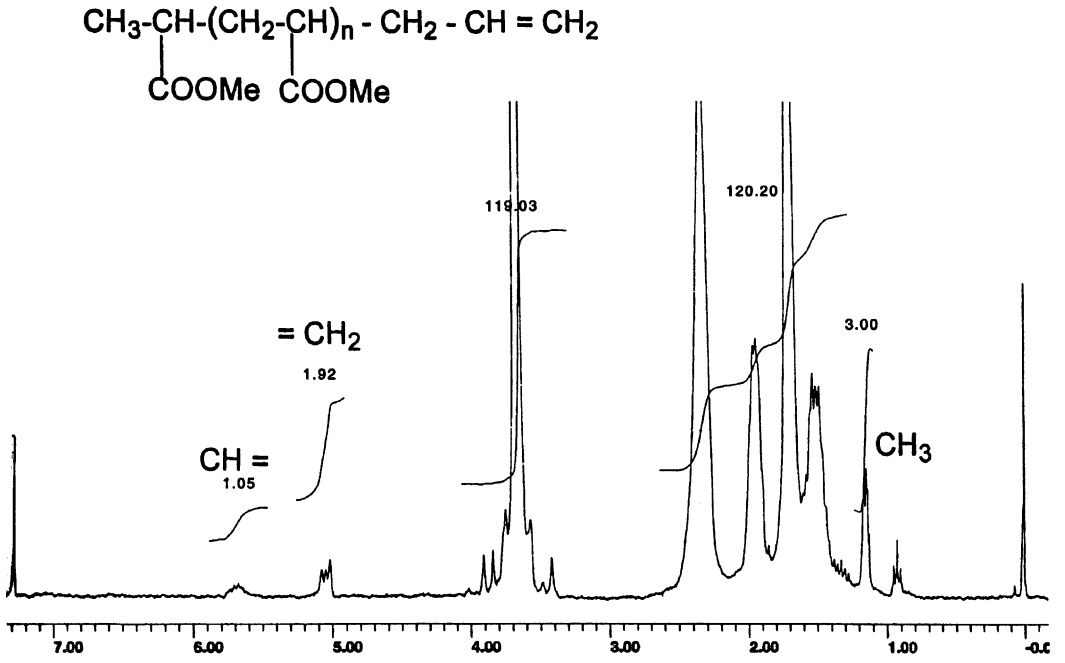


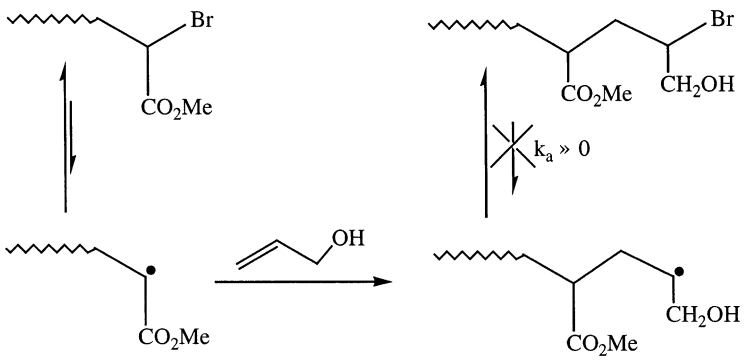
Fig. 12. ^{1}H NMR of allyl terminated poly(methyl acrylate). Reprinted with permission from Ref. [165]. © Copyright, 2000 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

Table 14
Results of the dehalogenation of various polymers prepared by ATRP with Bu_3SnH (TA, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; EC, ethylene carbonate; MB, methoxybenzene)

P–X	ATRP conditions (CuX/L, solvent, *T* (°C))	M_n	M_w/M_n	Dehalogenation procedure (eq. Bu_3SnH, solvent, 3 h)
pMA–Br	CuBr/bpy: 1/3; EC, 90	1750	1.2	1.5 eq. or 3 eq., –
pMA–Br	CuBr/TA: 1/1, –, 60	1530	1.1	3 eq., benzene
pMA–Cl	CuCl/TA: 1/1, –, 60	1220	1.2	3 eq., benzene
pSt–Br	CuBr/TA: 1/1, –, 85	2690	1.1	3 eq., benzene
pMMA–Br	CuBr/bpy: 1/3, MB, 85	7670	1.2	3 eq., –

2.4.4.3. Incorporation of less reactive monomers [164,165]. Monomers such as allyl alcohol and 1,2-epoxy-5-hexene are examples of monomers that are not polymerizable with the currently available ATRP catalyst systems. The main reason for this failure is the extremely slow activation step as the resulting radicals are not stabilized by resonance or by electronic effects. However, when these monomers were added at the end of the polymerization of acrylates, the radicals at the poly(acrylate) chain ends were able to add to these monomers. Subsequent deactivation of the polymer radical provided halogen terminated polymers (the addition of allyl alcohol to the poly(acrylate) chain is shown in Scheme 10). In this way, either a hydroxyl or epoxide functional group was incorporated at the chain end. The presence of the hydroxyl and epoxide functionalities were confirmed by ^1H NMR (Fig. 13) and ESI-MS (Fig. 14). Other less reactive, and by ATRP non-polymerizable, monomers which were incorporated to chain ends include divinyl benzene and ethylene for MMA [170] and maleic anhydride for styrene [171]. These end-functional polymers find applications as components of coatings [172, 173].

2.4.4.4. End capping agents. Silyl enol ethers such as α-(trimethylsilyloxy)styrene and *p*-methoxy-α-(trimethylsilyloxy)styrene, were efficient quenchers in the living radical polymerization of MMA using the $RuCl_2(PPh_3)_3$ complex, resulting in ketone-capped polymers (Scheme 11) [166]. Similar functionalization was accomplished in Cu-mediated ATRP of MMA [170].



Scheme 10.

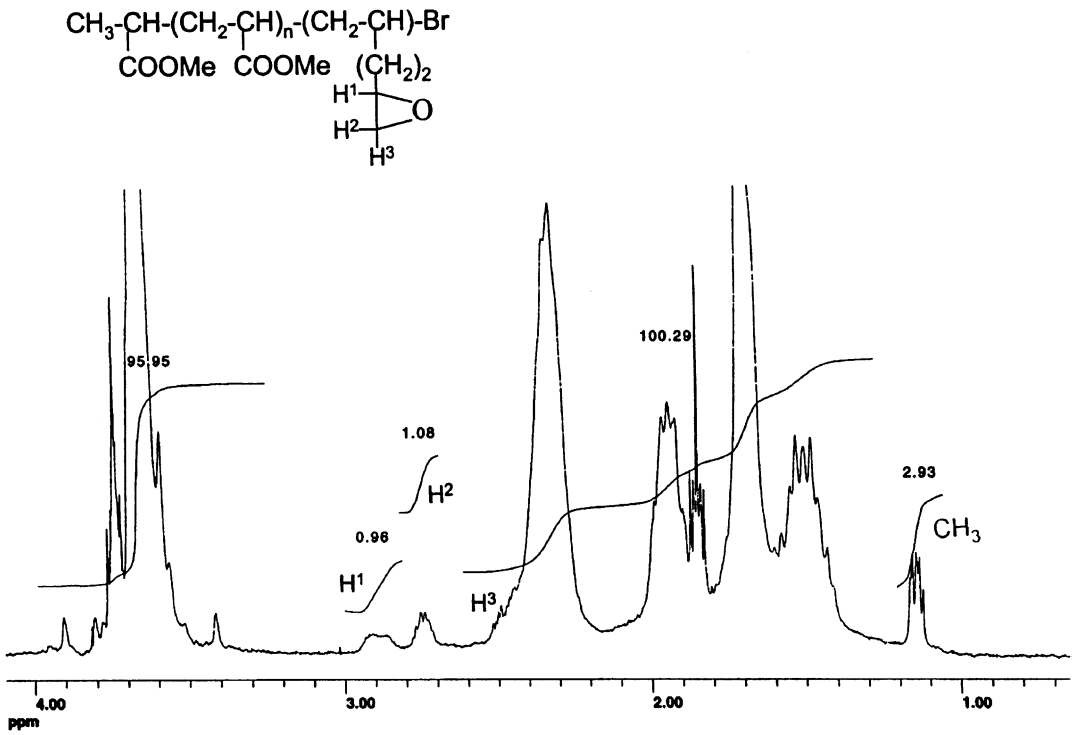


Fig. 13. [1]H NMR of poly(methyl acrylate), reacted with 1,2-epoxy-5-hexene. Reprinted with permission from Ref. [165]. © Copyright, 2000 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).

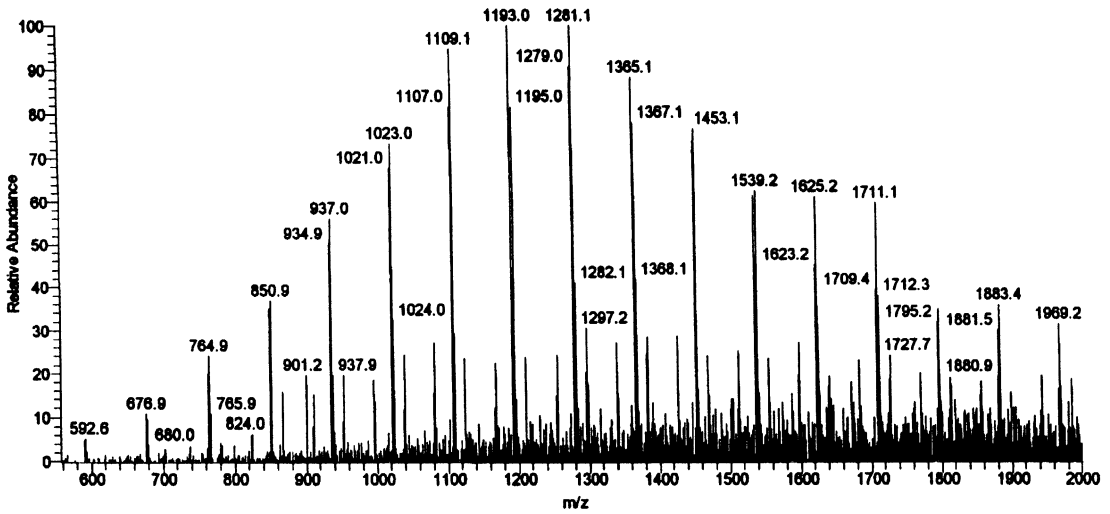
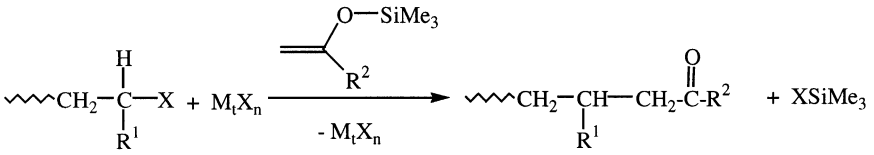


Fig. 14. ESI-MS spectrum of poly(methyl acrylate) with allyl alcohol incorporated. Reprinted with permission from Ref. [165]. © Copyright, 2000 by Wiley-VCH Verlag GmbH, D-69451 Weinheim (FRG).



Scheme 11.

2.4.5. Chain coupling

Stars have been synthesized by an arm first approach, these arms were then coupled by a commercially available coupling reagent such as divinylbenzene. Poly(*t*BA) was prepared by ATRP using MBP as an initiator ($M_n = 6900$, $M_w/M_n = 1.18$). The polymer was isolated and dissolved in anisole, it was allowed to react with the coupling agent, *p*-divinylbenzene (DVB), for 5 h at 110°C. The catalytic system was CuBr/PMDETA. The optimal ratio of DVB to polymer chains was 15 in which case the yield of stars was 95%. The molecular weight of the star polymer was $M_n = 53,600$ as measured by GPC and the polydispersity index was $M_w/M_n = 1.71$. Functionalized star polymers were synthesized by using a functional initiator to prepare the arms. 1,2-Epoxypropyl 2-bromopropionate was used to prepare poly(*t*BA) with epoxy α-functionality and bromine ω-functionality ($M_n = 5600$, $M_w/M_n = 1.22$). After the coupling of the arms with DVB the GPC trace of the star polymer had clearly shifted to higher molecular weight than the trace of the arm (Fig. 15) [167].

Another example of coupling of polymer chains has been published in the patent literature, this example involves the formation of polyols by ATRP followed by cross-linking with a trifunctional isocyanate. Polyols have also been prepared and used as precursors for poly(urethane). In this case the polyols were prepared by ATRP of BA using α-α′-dibromo-*p*-xylene as the initiator and CuBr/bpy as the catalyst, the reaction was allowed to occur at 130°C for 3 h. After the reaction mixture was cooled to

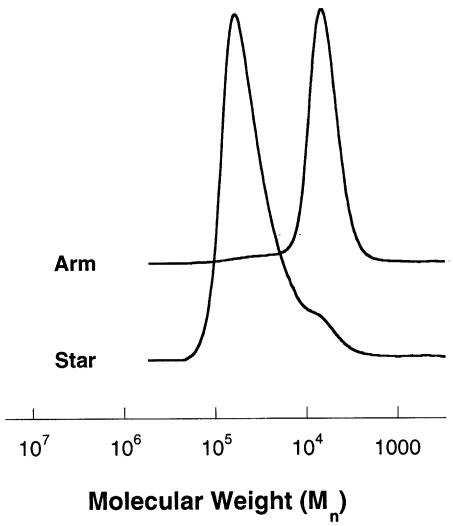
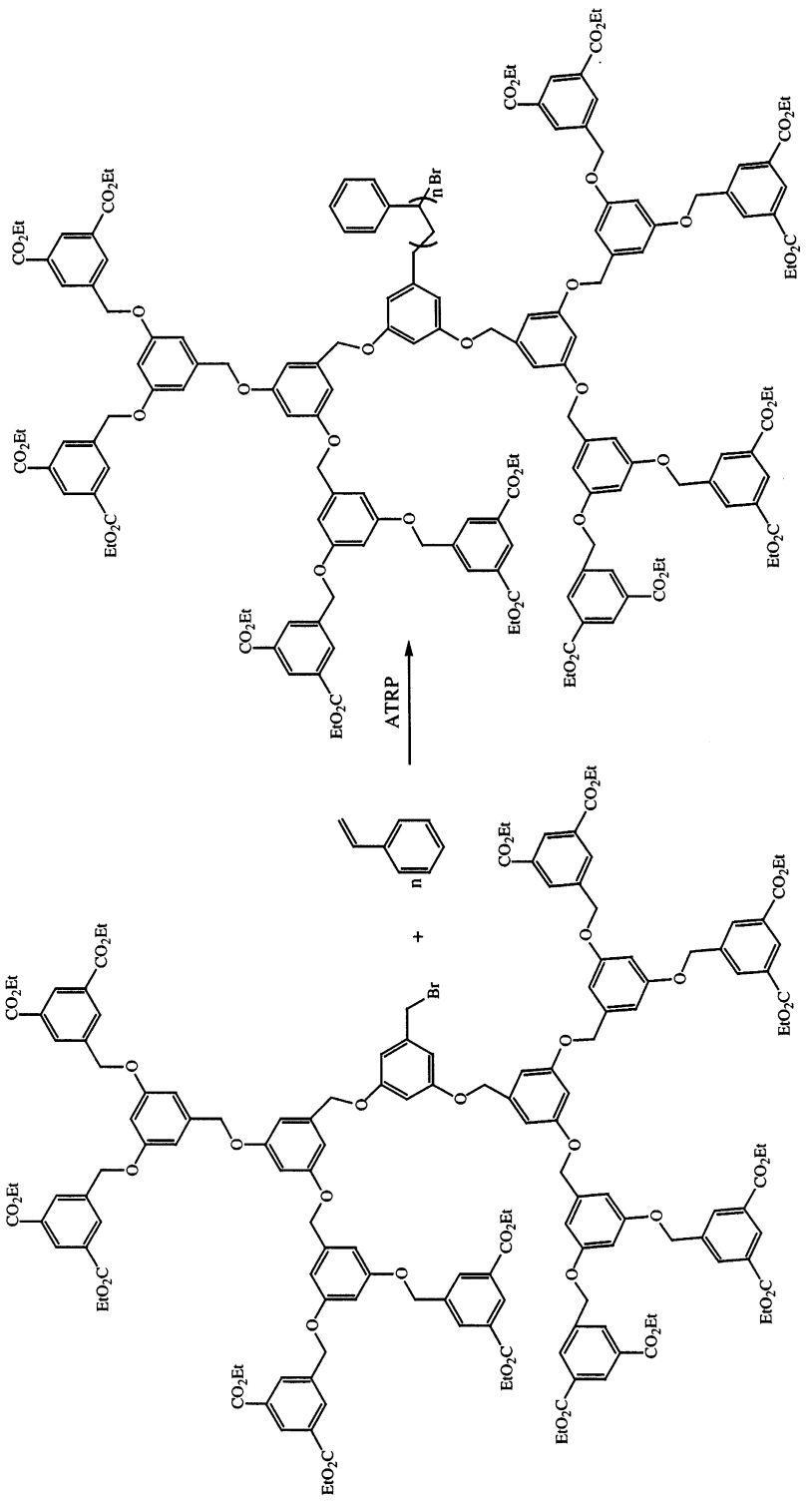
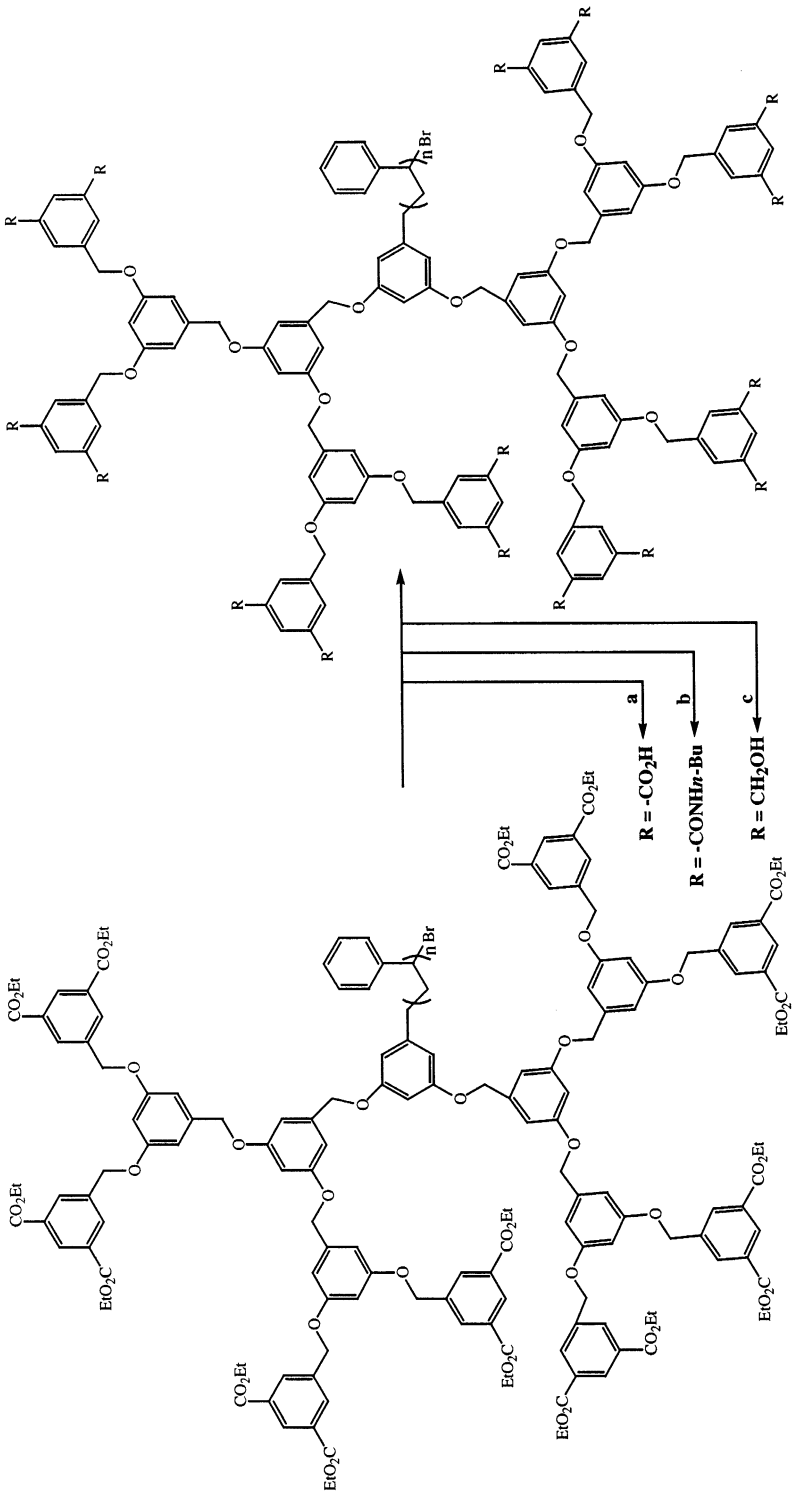


Fig. 15. GPC traces of poly(*t*-butyl acrylate) arm and the corresponding star polymer after coupling with DVB.



Scheme 12.



Scheme 13.

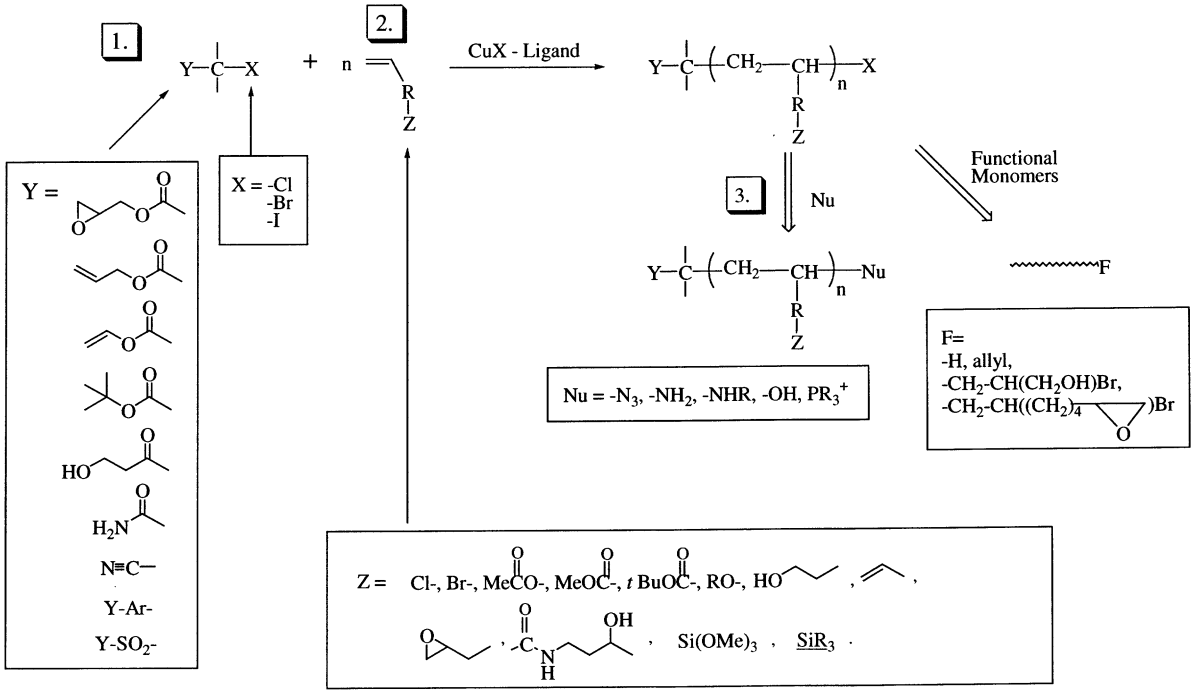


Fig. 16. General scheme representing functional polymers prepared by ATRP.

room temperature, HEMA was added, the ratio of HEMA to initiator was 4, and the reaction was allowed to occur at 80°C for 2 h. The final polymer was isolated and analyzed by ^{1}H NMR, which indicated that the polymer contained 3.2 hydroxyl groups per polymer chain. This polyol was allowed to react with a trifunctional isocyanate yielding cross-linked polyurethane [168].

2.4.6. Initiator end group transformation

Frechet and coworkers [169] have used a third generation ester functionalized dendritic bromide as the initiator for the ATRP of St. CuBr/4,4′-(di-*n*-heptyl)-2,2′-bipyridine was used as the catalyst and the polymerization was carried out at 110°C for 24 h (Scheme 12). The molecular weight of the crude polymer was $M_n = 12,800$ and the molecular weight distribution was $M_w/M_n = 1.08$.

The peripheral surface ester groups of the dendritic initiator fragment were functionalized as shown in Scheme 13 (modification reactions performed on dendritic poly(styrene) hybrid: (a) KOH, H_2O, THF, 66°C, 99%; (b) $LiAlH_4$, $CH_3(CH_2)_2CH_2NH_2$, THF, 25°C, 99%; (c) $LiAlH_4$, THF, 66°C, 98%). The ester groups were transformed to acid, alcohol, and amide groups in almost quantitative yield.

3. Conclusions

ATRP is a convenient way to prepare functional polymers (Fig. 16). Various functional monomers including Sts, (meth)acrylates and others were (co)polymerized in a controlled fashion, resulting in well-defined polymers with a good control over molecular weight and low polydispersities. To insert

functional end groups, alkyl halides containing functional groups were used to initiate ATRP. The resulting polymer contains the functionality at one end and a halogen at the other end. The halogen end groups were converted to other functional groups using either nucleophilic substitution reactions, electrophilic or radical addition reactions. This process has also been used for di- and multifunctional initiators as well as for hyperbranched polymers. Alternatively, polymers with two and several end functionalities could be prepared by a chain coupling process.

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