Synthesis of polymers with hydroxyl end groups by atom transfer radical polymerization

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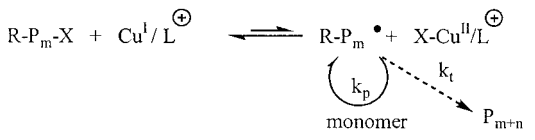
SUMMARY: Polymers prepared by atom transfer radical polymerization (ATRP) contain end groups defined by the initiator used. Alkyl halides, used as initiators, lead to polymers with an alkyl group at one end and a halide as the other chain end. Using functionalized initiators such as 2-hydroxyethyl 2-bromopropionate, hydroxyl groups can be directly incorporated at one polymer chain end while the other end functionality remains a halogen. The direct displacement of the halogen end groups with hydroxyl groups was unsuccessful due to side reactions such as elimination (for polystyrene) or hydrolysis of ester functions (for polyacrylate). Another approach to generate hydroxyl end groups was based on the substitution of the halogen end groups by ethanolamine. This was successful for polystyrene but additional substitution at the backbone esters was observed in polyacrylates. Multiple substitution reactions could be avoided by using 4-aminobutanol instead of 2-aminoethanol. Hydroxyl terminated polyacrylates were also obtained by extending the polyacrylate chain end with one allyl alcohol unit in a one-pot process by adding an excess of allyl alcohol at the end of e polymerization of acrylate.

Introduction

Atom Transfer Radical Polymerization (ATRP) combines the advantages of a radical polymerization with the features of a controlled polymerization process[1–2]. A large range of vinyl monomers can be (co)polymerized, even in the presence of different functionalities and impurities such as water. The control over the radical polymerization allows to produce polymers with molecular weights predetermined by DP = $\Delta[M]_0/\Delta[I]_0$, where $\Delta[M]_0$ and $\Delta[I]_0$ are concentrations of reacted monomer and initiator, with low polydispersities and control over functionalities[3–4]. To obtain functionalized polymers, different approaches are feasible with ATRP[5]. The controlled polymerization of functionalized monomers such as poly(2-hydroxyethyl methacrylate)[6], poly(2-hydroxyethyl acrylate)[7], poly(-glycidyl acrylate)[8] and poly(dimethylaminoethyl methacrylate)[9] to yield polymers with functional side groups has already been reported. The use of functionalized initiators leads to macromolecules with end functionalities in the polymer chains because the incorporation of the initiator is inherent in the mechanism of ATRP (Scheme 1). The most commonly used initiator in ATRP is an alkyl halide, RX. The alkyl group, R, becomes one end group and the halide, X, the other end group of the polymer chain. End-functional polymers are prepared when the alkyl part contains functionalities such as epoxides, esters or hydroxyl groups[5, 10–11].

Scheme 1: Mechanism of ATRP



The third method to incorporate functionalities in the polymer chains is the chemical modification of the halogen end groups[12]. As mentioned before, the use of an alkyl halide as initiator generates a halogen at one chain end. When di-, tri- or multifunctional initiators are used, halogen terminated telechelic or star-like polymers are produced. These halogen end groups can be transformed by means of standard organic procedures. The resulting telechelics, for example with hydroxyl end groups, may be further used in the synthesis of polyurethanes.

In this report, the introduction of hydroxyl end groups in polymers prepared by ATRP is described. Since the use of functional monomers has already been reported by our group[6–9, 13], this report will focus on the introduction of hydroxyl groups via functional initiators and especially via end group transformation reactions. The transformation reactions include solvolysis, nucleophilic substitution and radical reactions. The latter modification method is based on the extension of the polymer chain with one less reactive functional monomer unit such as allyl alcohol. This extension procedure can be applied in a one-pot process by adding the less reactive monomer to the polymerization mixture at high conversion. A similar 'end-capping' procedure for living radical polymerization of methyl methacrylate has been reported by Sawamoto[14].

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Experimental part

Materials

Tetrahydrofuran (THF) was distilled from Na/benzophenone. CuBr was purified by stirring in acetic acid, washing with methanol and then drying. Styrene has been passed through alumina, methyl acrylate was distilled. All other reagents, purchased from Aldrich or Acros, were used as received.

Analysis

Gel permeation chromatography (GPC) measurements were carried out using a Waters 510 liquid chromatography pump equipped with either four Phenogel columns (100 Å, 1000 Å, linear and guard) or PSS GPC columns (guard, 10^5 Å, 10^3 Å and 10^2 Å), with a Waters 410 differential refractometer. Calibration was performed with linear polystyrene standards. Similar results were obtained with both systems. A 300 MHz Bruker NMR spectrometer was used for ^{1}H NMR. Electrospray Ionization (ESI) MS was conducted using a Finnegan LCQ, equipped with an octupole and an ion trap mass analyzer. Polymer solutions (10^{-4} M in methanol, doped with H^+ or Na^+) were injected at 7 μl/min.

Synthesis

2-Hydroxyethyl 2-bromopropionate was obtained through a coupling reaction of 2-bromopropionyl bromide with ethylene glycol and purified by destillation (b.p. 32 °C–37 °C/ 0.2 mm Hg)[15].

2-Hydroxyethyl 2-bromopropionate as initiator of poly(methyl acrylate): CuBr, 4,4′-di(nonan-5-yl)-2,2′-bipyridine, methyl acrylate and 2-hydroxyethyl 2-bromopropionatein a ratio (0.4/0.8/46/1) were, after degassing, reacted at 100 °C for 1.25 h (90% conversion). The resulting polyacrylate ($\overline{M}_n$ = 3200, $\overline{M}_w/\overline{M}_n$ = 1.24) was precipitated in hexane.

^{1}H NMR ($CDCl_3$): δ = 4.38 (—C*H*$_2$—OCO—), 4.27 (—C*H*(CO$_2$Me)—Br), 3.60 (—CO$_2$*Me*), 3.50 (—C*H*$_2$—OH), 2.53–1.40 (—C*H*$_2$—C*H*—), 1.17 (—C*H*$_3$) ppm.

ESIMS: *m/z* = [117 (initiator) + *n* 86 (pMA backbone) + 79 (or 81) (—Br) + 1 (H)]$^+$.

2-Hydroxyethyl 2-bromopropionate as initiator of polystyrene: Styrene was polymerized using CuBr, 2,2′-dipyridyl and initiator (1/3/1) at 110 °C. The resulting polymer (GPC: $\overline{M}_n$ = 2850, $\overline{M}_w/\overline{M}_n$ = 1.29; ^{1}H NMR: $\overline{M}_n$ = 2080) was precipitated in methanol.

^{1}H NMR ($CDCl_3$): δ = 7.20–6.27 (—*Ph*), 4.40 (—C*H*(Ph)—Br), 4.28 (—C*H*$_2$—OCO—), 3.35 (—C*H*$_2$—OH), 2.25–1.20 (—C*H*$_2$—C*H*—), 0.93 (—C*H*$_3$) ppm.

Solvolysis of halogen end groups: Water (15 ml) and $CaCO_3$ (3.66 g, 35 mmol) were added to a solution of 1-phenylethyl bromide (7 mmol) in 1,4-dioxane (15 ml) and the reaction mixture was refluxed overnight. The solution was cooled to room temperature and dioxane evaporated. Methylene dichloride (30 ml) was added, followed by treatment with dilute HCl until all solids had dissolved. The organic phase was separated, washed with a $NaHCO_3$ solution, dried over $MgSO_4$, and filtered. Yield: 40%. ^{1}H NMR ($CDCl_3$): δ = 7.25–7.40 (m, —*Ph*), 4.92 (q, —C*H*—), 1.83 (b, —O*H*), 1.51 (d, —C*H*$_3$) ppm.

The same procedure was applied to methyl 2-bromopropionate. A mixture of products was obtained, partial hydrolysis of the methyl ester was observed.

Also polystyrene with bromine end groups was reacted using the same experimental conditions. From the ^{1}H NMR spectrum, it was estimated that 70% solvolysis (hydroxyl end groups) and 30% elimination (alkene end groups) had occurred.

Nucleophilic substitution of the bromine end groups: Polystyrene ($\overline{M}_n$ = 980, $\overline{M}_w/\overline{M}_n$ = 1.15) with bromine end groups was dissolved in dimethyl sulfoxide (DMSO) and triethylamine (30 eq.) and a 10-fold excess of ethanolamine was added. After stirring for 48 h at room temperature, the polymer, pSty—NH—CH$_2$—CH$_2$—OH, was precipitated in methanol.

^{1}H NMR ($CDCl_3$): δ = 7.30–6.30 (—*Ph*), 3.35 (—C*H*$_2$—OH), 3.15 (—C*H*(Ph)—NH—), 2.35 (NH—C*H*$_2$—), 2.2–1.15 (—C*H*$_2$—C*H*—), 1.0 (—C*H*$_3$, initiator) ppm.

ESIMS: *m/z* = [105 (initiator) + *n* 104 (pSty backbone) + 60 (—NH—CH$_2$—CH$_2$—OH) + 1 (H)]$^+$.

Poly(methyl acrylate) was reacted with 4-aminobutanol using the same reaction conditions. pMA—NH—(CH$_2$)$_4$—OH was obtained.

ESIMS: *m/z* = [87 (initiator) + *n* 86 (pMA backbone) + 88 (—NH(CH$_2$)$_4$OH) + 1 (H)]$^+$.

Radical addition to allyl alcohol: Methyl acrylate (1.3 ml, 14 mmol) was polymerized using CuBr, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine and methyl 2-bromopropionate (0.1/0.1/1 mmol). After 3 h at 40 °C, allyl alcohol (2 ml) and Cu(0) (20 mg) were added. After stirring overnight at 40 °C, the mixture was filtered over alumina and the polymer ($\overline{M}_n$ = 780, $\overline{M}_w/\overline{M}_n$ = 1.19) was precipitated in hexane.

To prove the incorporation of one allyl alcohol molecule at the chain end, ^{1}H NMR ($CDCl_3$) was used. Trichloroacetyl isocyanate was added to the NMR-tube to convert the —*CH*$_2$OH group, the peak of which was overlapping with the ester peaks of the polymer backbone in the ^{1}H NMR spectrum, into —*CH*$_2$OCO—NHCO—CCl$_3$, visible at 4.50 ppm.

ESIMS: *m/z* = [87 (initiator) + *n* 86 (pMA backbone) + 58 (—CH$_2$—CH(CH$_2$OH)—) + 81 (or 79) (—Br) + 23 (Na)]$^+$.

Results and discussion

In the following sections, the introduction of hydroxyl groups in polymer chains prepared by ATRP will be discussed. First, the use of functionalized initiators is described. Then, the transformation of the end groups via solvolysis, nucleophilic substitution or radical addition is discussed.

ATRP with a functionalized initiator

2-Hydroxyethyl 2-bromopropionate was used as initiator for the polymerization of methyl acrylate and styrene. For methyl acrylate, the polymerization was performed in bulk with CuBr/4,4′-di(nonan-5-yl)-2,2′-bipyridine (1/2)

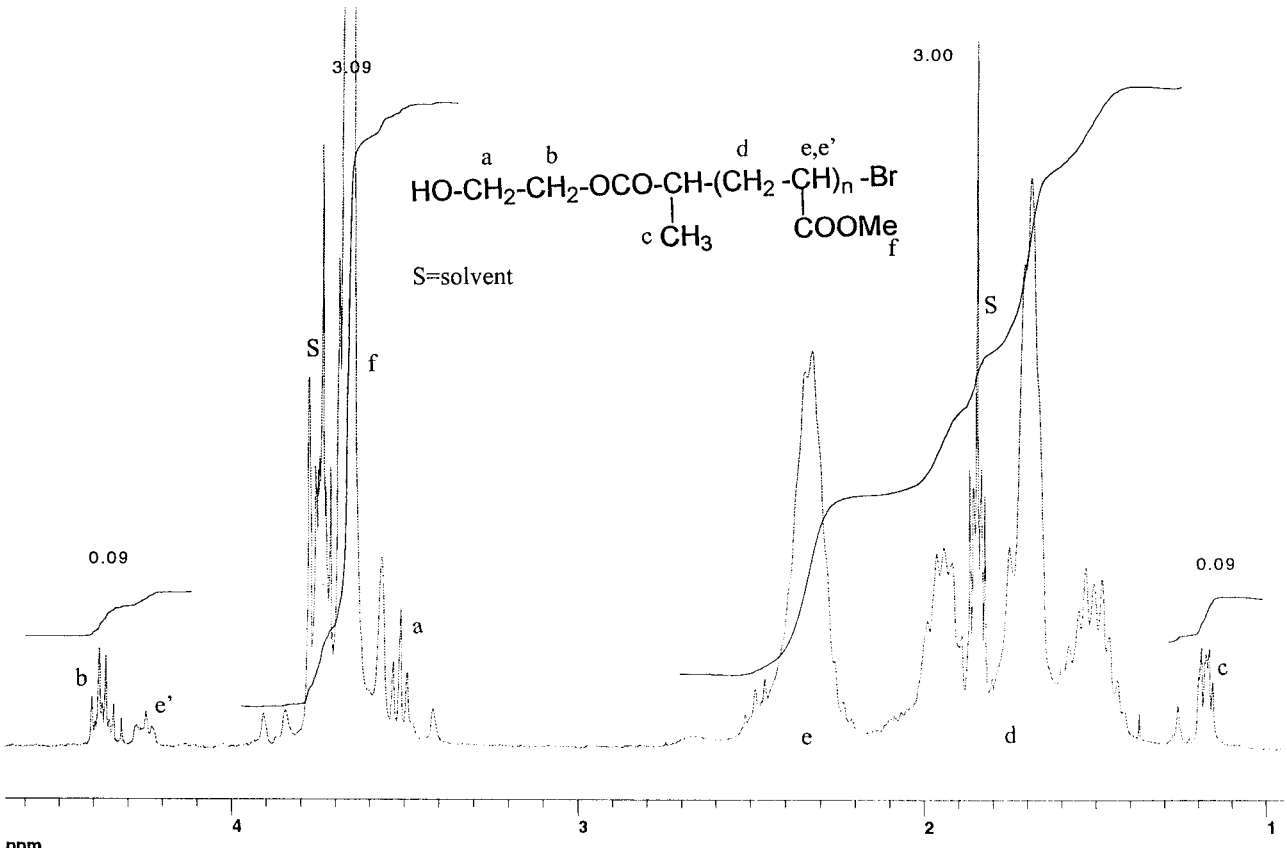


Fig. 1. ^{1}H NMR spectrum of poly(methyl acrylate), initiated by 2-hydroxyethyl 2-bromopropionate

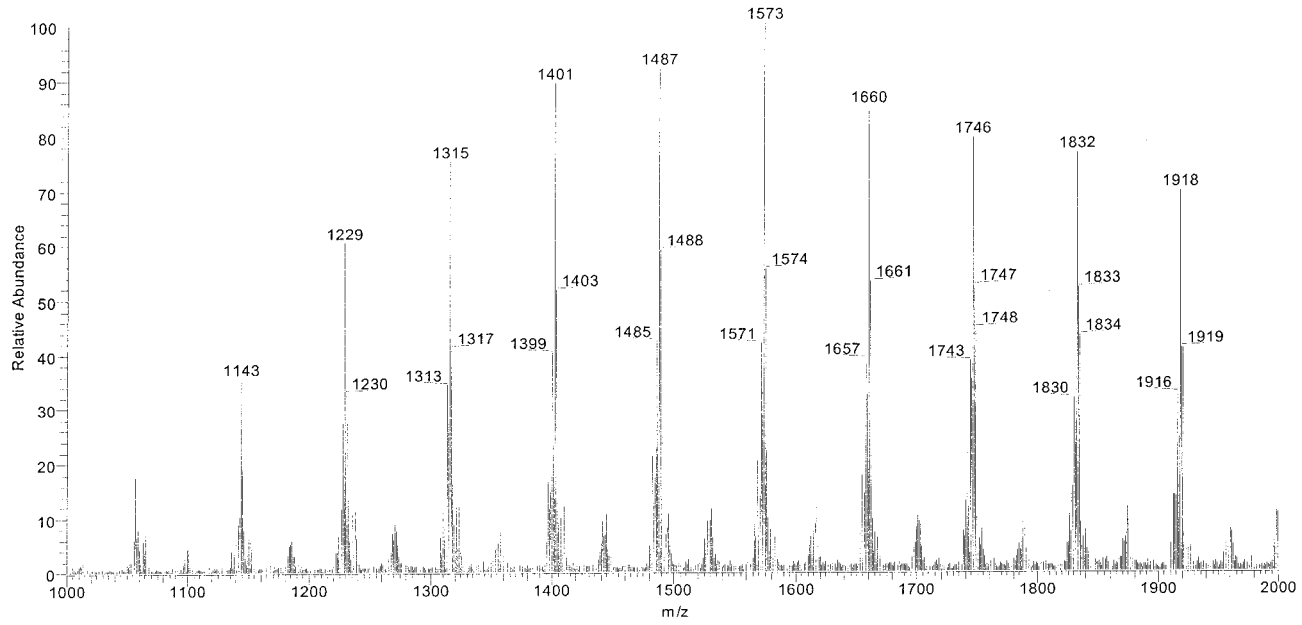


Fig. 2. ESIMS spectrum of poly(methyl acrylate), initiated by 2-hydroxyethyl 2-bromopropionate

as a metal/ligand complex. The theoretical ($\overline{M}_n$ = 3200) and obtained molecular weight ($\overline{M}_n$ = 3700) were in good agreement and poly(methyl acrylate) with a low polydispersity ($\overline{M}_w/\overline{M}_n$ = 1.24) was obtained. The presence of the initiating moiety and the bromine end group were verified by ^{1}H NMR and ESIMS; the spectra are shown in Fig. 1 and Fig. 2, respectively. In the ESIMS spectrum, singly charged (H^+) species, $m/z = [117 + n \times 86 + 79\ (81) + 1]^+$,

and doubly charged (H^+, Na^+) species, m/z = 1/2 [117 + $n \times 86$ + 79 (81) + 1 + 23]$^{++}$, were observed. The doubly charged species happened to overlap partially with the singly charged molecules, therefore the typical pattern of the isotopes for bromo-terminated chains ($^{79}Br/^{81}Br$: 50.5/49.5) was less resolved.

For polystyrene, similar reaction conditions were used. However, the molecular weight obtained was 35% higher than the calculated molecular weight (based on the molecular weight obtained by NMR). The difference in theoretical and obtained molecular weight is possibly due to an intramolecular cyclization reaction at the early stage of the styrene polymerization or to bimolecular termination during the initiation step. The polydispersity was fairly low, $\overline{M}_w/\overline{M}_n$ = 1.29. The presence of the hydroxyl and bromine end groups were confirmed by ^{1}H NMR.

In conclusion, hydroxyl end groups were successfully incorporated using a hydroxyl containing initiator for the ATRP of styrene and acrylates.

Conversion of an alkyl halide into an alcohol, solvolysis

The direct displacement of a halogen by an alcohol is often accompanied by side reactions such as elimination. The success of the existing methods which include alkaline and metal-mediated hydrolysis is largely dependent on the halocompound used[16–18]. Nevertheless, 1-phenylethyl bromide and methyl 2-bromopropionate were refluxed with calcium carbonate in a mixture of water and 1,4-dioxane, and the products were extracted with methylene chloride. 1-Phenylethyl bromide was converted to *sec*-phenylethyl alcohol but the yield was low (40%). The reaction with methyl 2-bromopropionate resulted in a mixture of products, and partial hydrolysis of the methyl ester was observed. When polystyrene with bromine end groups ($\overline{M}_n$ = 1230, $\overline{M}_w/\overline{M}_n$ = 1.14) was treated under the same reaction conditions, ^{1}H NMR indicated that the resulting product was hydroxyl-terminated polystyrene (70%) mixed with alkene-terminated polystyrene (30%) because of elimination.

To conclude, the solvolysis of the bromine end groups was unsuccessful because of the occurrence of side reactions, therefore other methods to transform the halide into hydroxyl end groups were studied.

Nucleophilic substitution of the halogen end group

As shown in previous publications, the halogen end groups of polymers prepared by ATRP can be substituted by good nucleophiles such as azides or primary amines[12, 19, 20]. The reactions were carried out under mild conditions and no significant side reactions occurred. To achieve quantitative yields, the end groups were transformed under homogeneous conditions, in solvents such as dimethylformamide (DMF) or DMSO, which promoted nucleophilic substitution reactions.

From the model studies with 1-phenylethyl bromide and methyl 2-bromopropionate, models for respectively polystyrene and poly(methyl acrylate), the rate constants of the reactions of the models with butylamine (1.1 eq.) in the presence of triethylamine (1.1 eq.) at 25 °C were determined (Tab. 1). As these results indicated that primary amines were good and selective nucleophiles to substitute the bromine end groups, 2-aminoethanol was

Tab. 1. Rate constants for the reactions of model compounds (1 M in DMSO) with butylamine (1.1 eq.), in the presence of triethylamine (1.1 eq.), at 25 °C

	1-Phenylethyl bromide	Methyl 2-bromopropionate
$k/(l \cdot mol^{-1} \cdot s^{-1})$	$7.5 \cdot 10^{-4}$	$4.6 \cdot 10^{-3}$

Tab. 2. Reaction conditions and outcome of model studies of 1-PEBr (1-phenylethyl bromide) or MBP (methyl 2-bromopropionate) (1 M in DMSO; mole ratios given) with alkanolamines

1-PEBr	NH_2—$(CH_2)_2$—OH	Et_3N	Result[a]	Yield[b]
1	1	1	Me—CH(Ph)—$NH(CH_2)_2OH$	≥ 95%
1	2	–	Me—CH(Ph)—$NH(CH_2)_2OH$	≥ 95%
MBP	NH_2—$(CH_2)_2$—OH	Et_3N		
1	1	1	Me—CH(COOMe)—$NH(CH_2)_2OH$	≥ 95%
1	2	–	Me—CH(CO_2Me)—$NH(CH_2)_2OH$	77%
			side products	23%
MBP	NH_2—$(CH_2)_4$—OH	Et_3N		
1	2	–	CH_3—CH(CO_2Me)—$NH(CH_2)_4OH$	≥ 95%

[a] Results were determined after 24 h stirring at room temperature.
[b] Yields were determined by ^{1}H NMR of the reaction mixtures.

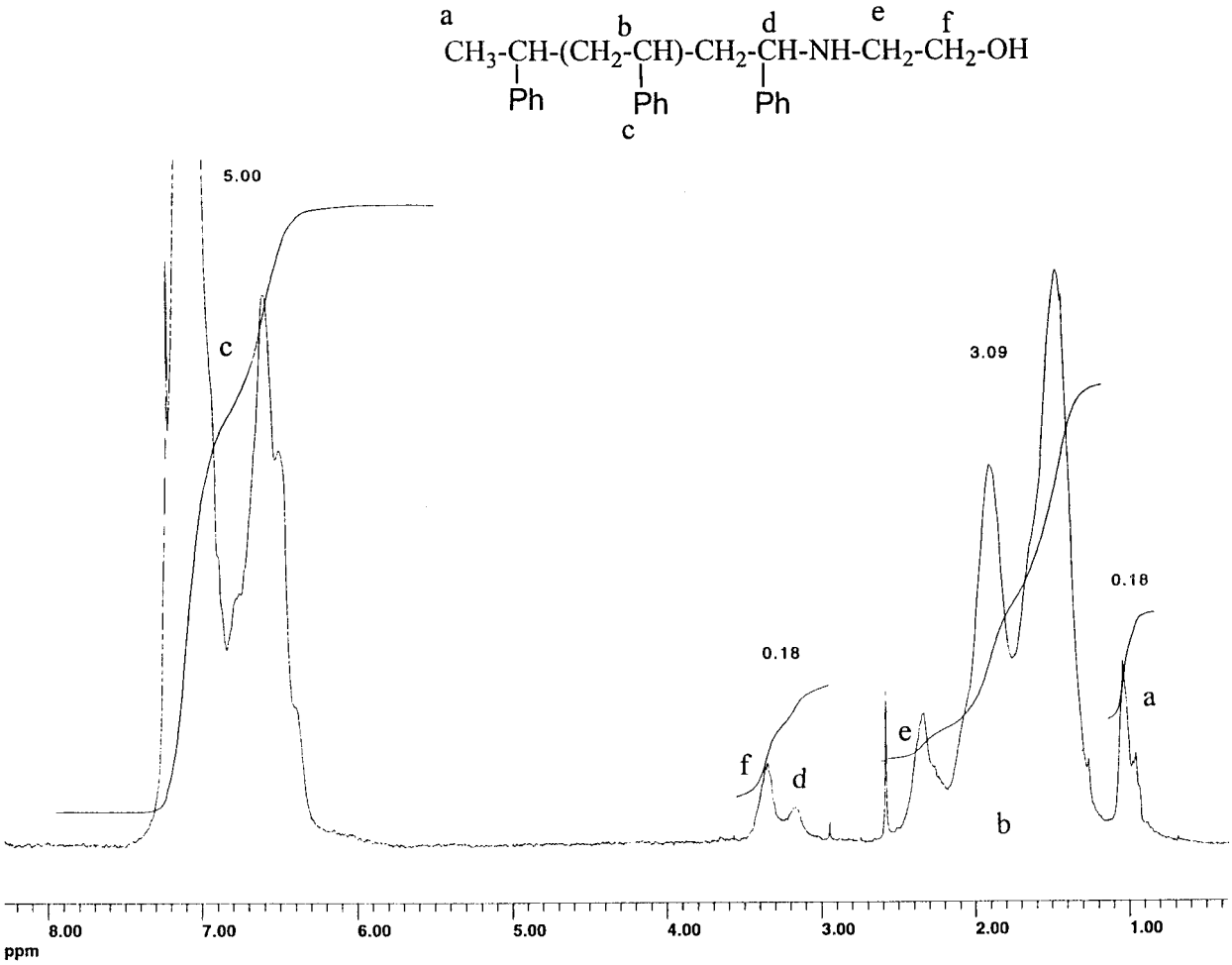
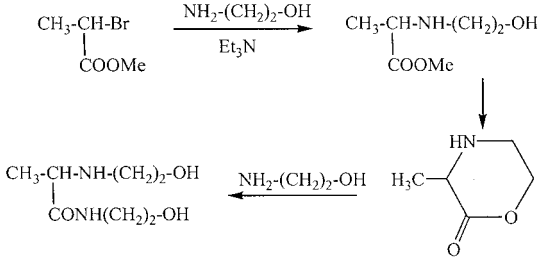


Fig. 3. ^{1}H NMR spectrum of polystyrene-NH—CH_2CH_2—OH

studied as a nucleophile in order to introduce alcohol end groups. The reactions between 1-phenylethyl bromide and 2-aminoethanol (Tab. 2) in DMSO at room temperature occurred without detectable side reactions. With methyl 2-bromopropionate however, the reaction conditions had to be altered. Methyl 2-bromopropionate mixed with one equivalent of respectively 2-aminoethanol and triethylamine gave the expected product in quantitative yields (Tab. 2). When an excess of 2-aminoethanol was used, disappearance of the methyl ester peak was observed in the ^{1}H NMR spectrum. This result was ascribed to the fact that after the substitution of the bromine by 2-aminoethanol, formation of a 6-membered ring could occur (Scheme 2). Afterwards, ring opening by attack of a second 2-aminoethanol molecule could lead to the double substituted product. With an excess of 2-aminoethanol and at higher temperatures, complete substitution of the bromine as well as of the methyl ester was observed. The structure of the double substitution product was confirmed by mass spectrometry, *m/z* = 177.

Based on the results of this model study, a selective substitution of the bromine end groups of polystyrene by

Scheme 2: Substitution of the bromine by 2-aminoethanol, followed by the formation of a 6-ring intermediate and subsequent ring opening by 2-aminoethanol



2-aminoethanol was expected. Reaction of poly(methyl acrylate)-Br with 2-aminoethanol was expected to result in multiple substituted product. As the concentration of functional end groups attached to polymer chains is lower, the use of an excess of 2-aminoethanol is necessary to enhance the reaction rate[21].

Polystyrene ($\overline{M}_n$ = 980, $\overline{M}_w/\overline{M}_n$ = 1.15) with bromine end groups was reacted with 10 equivalents of 2-aminoethanol in the presence of triethylamine at room temperature and after 48 h, complete substitution was

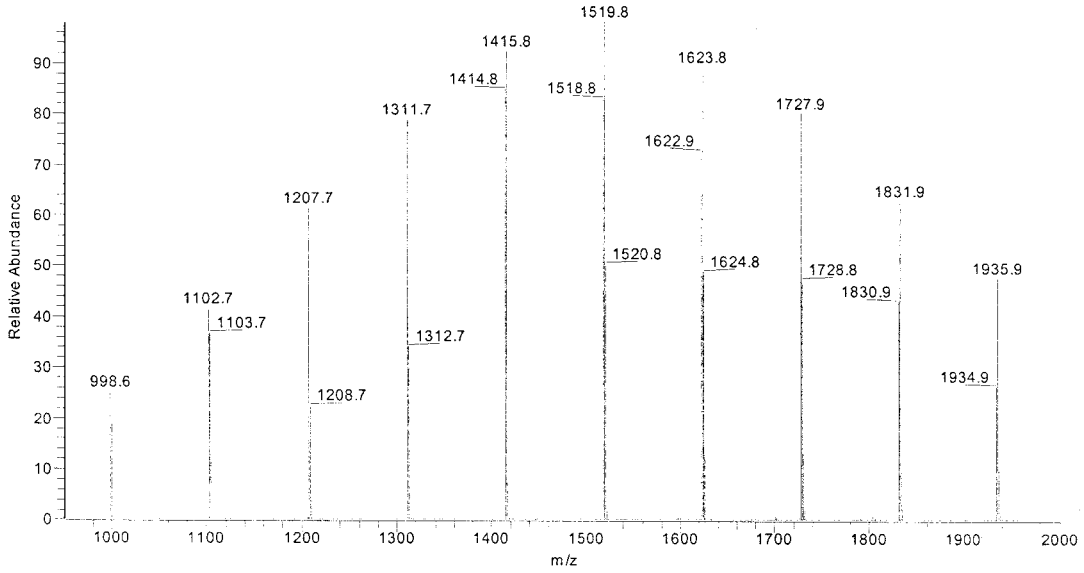


Fig. 4. ESIMS spectrum of polystyrene-NH—CH_2—CH_2—OH

observed in ^{1}H NMR. No noticeable side reactions occurred and the substitution was also confirmed by ESIMS. The spectra are shown in Fig. 3 and Fig. 4.

As expected for poly(methyl acrylate), partial substitution of the methyl ester groups from the backbone could not be avoided. Multiple substitution reactions however could be suppressed by using 4-aminobutanol instead of 2-aminoethanol as nucleophile. Model studies (Tab. 2) indicated that when methyl 2-bromopropionate was reacted with an excess of 4-aminobutanol, substitution of only the bromine was obtained. Poly(methyl acrylate)-Br reacted with an excess of 4-aminobutanol resulted in poly(methyl acrylate)-NH—$(CH_2)_4$—OH, as indicated by the ESIMS spectrum (Fig. 5).

In conclusion, nucleophilic substitution of the bromine end groups of polystyrene with 2-aminoethanol is a convenient way to obtain hydroxyl groups on polystyrene chain ends. To obtain hydroxyl terminated polyacrylate, 4-aminobutanol had to be used as a nucleophile because with 2-aminoethanol, multiple alcohol functionalities were incorporated in the polyacrylate chain.

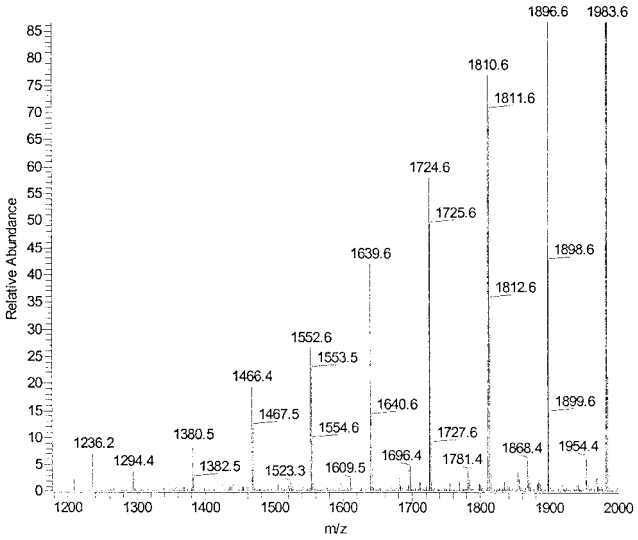
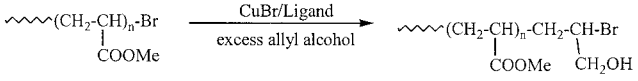


Fig. 5. ESIMS spectrum of poly(methyl acrylate)-NH—$(CH_2)_4$—OH

Scheme 3: Incorporation of allyl alcohol at the chain end of poly(methyl acrylate)



Reaction with less reactive monomer

Polymers synthesized with ATRP contain halogen end groups that can be re-activated in the presence of a metal/ligand complex with the formation of radicals. Upon addition of a second monomer, the polymer chain can be extended with that monomer, resulting in a block copolymer[22]. However, when allyl alcohol is added, a monomer which is not polymerizable by ATRP due to a very low equilibrium constant, radical addition will take place, followed by deactivation of the chain end (k_p(allyl alcohol) $\ll k_d$) (Scheme 3). Reactivation of the resulting chain end becomes impossible, due to the absence of a stabilizing group near the radical center.

Poly(methyl acrylate) was synthesized in bulk with CuBr/2,2′-dipyridyl and when high conversion was reached, the polymer was dissolved in allyl alcohol and a small amount of Cu(0) was added. The addition of Cu(0) enhances the radical generation as Cu(0) and Cu(II)

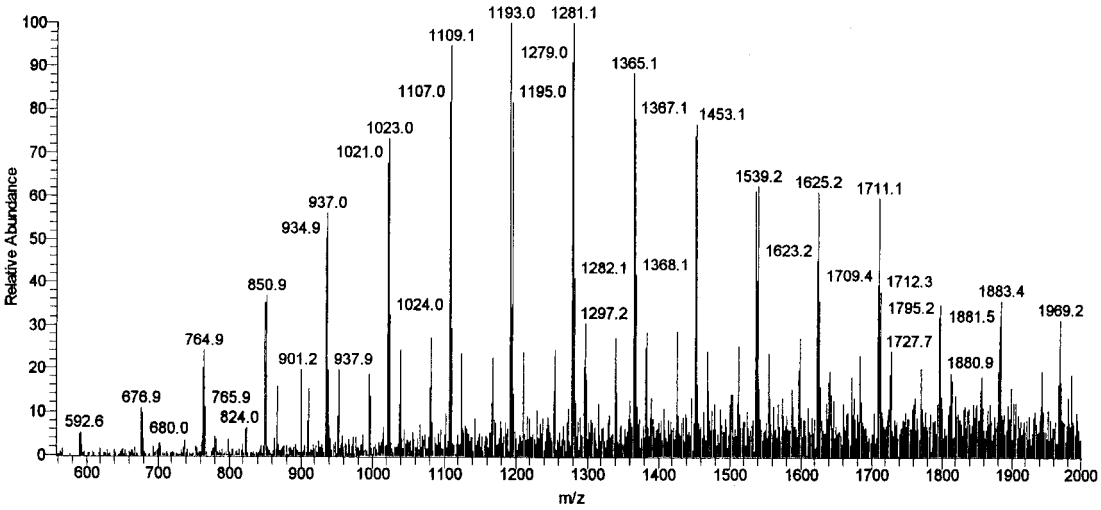
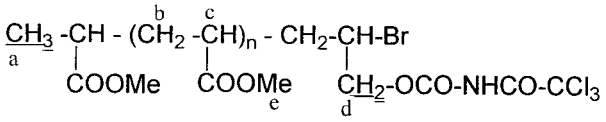


Fig. 6. ESIMS spectrum of poly(methyl acrylate)-CH_2—CH(CH_2OH)—Br



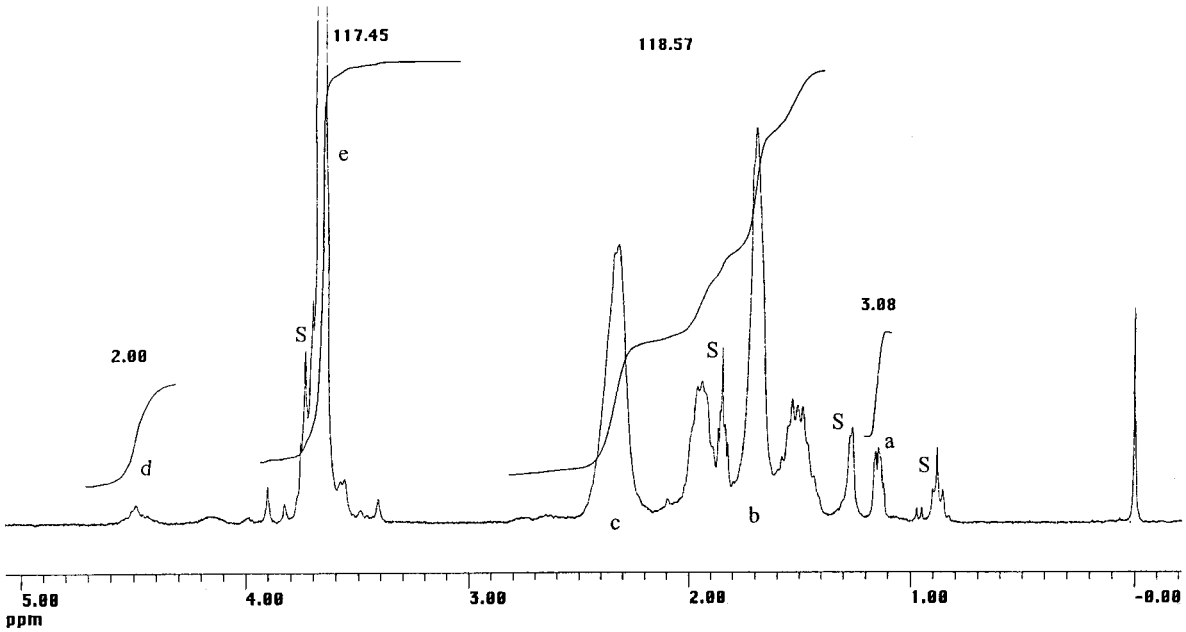


Fig. 7. ^{1}H NMR spectrum of poly(methyl acrylate)-CH_2—CH(CH_2OH)—Br

metathesize, resulting in two Cu(I) molecules[23]. After stirring overnight, the polymer was purified by precipitation and the incorporation of allyl alcohol at the chain end (Scheme 3) was confirmed by ESIMS (Fig. 6). This procedure was improved by using CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (1/1) as metal/ligand complex during the polymerization of acrylate. The use of the triamine as ligand had the advantage that the polymerization mixture was quite homogeneous resulting in the synthesis of well-defined polymer with lower polydispersity. To quantify the incorporation of allyl alcohol at the chain end, ^{1}H NMR was used. Trichloroacetyl isocyanate was added to the NMR-tube to convert the —CH_2OH group, the peak of which was overlapping with the ester peaks of the polymer backbone in the ^{1}H NMR spectrum, into CH_2O-CO—NHCO—CCl_3, visible at 4.50 ppm (Fig. 7).

Addition of allyl alcohol at the end of the polymerization of poly(methyl acrylate) is a convenient way to obtain alcohol end groups at the chain end.

Conclusions

Polymers with hydroxyl end functionalities were prepared using different approaches. Hydroxyl end groups were incorporated using 2-hydroxyethyl 2-bromopropionate as initiator for the ATRP of styrene and acrylate. Solvolysis of halogen end groups of polymers prepared by ATRP was not successful because of the occurrence of side reactions. Substitution of the halogen end groups of polystyrene with 2-aminoethanol resulted in hydroxyl end functionalized polystyrene. To obtain hydroxyl terminated poly(methyl acrylate) 4-aminobutanol was used as nucleophile, while 2-aminoethanol led to a multiple substitution product. Addition of allyl alcohol at the end of the ATRP of methyl acrylate resulted also in hydroxyl terminated poly(methyl acrylate).

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[1] K. Matyjaszewski, Ed., "*Controlled Radical Polymerization*", American Chemical Society, Washington, D.C. 1998
[2] K. Matyjaszewski, J. S. Wang, *Macromolecules* **28**, 7901 (1995)
[3] K. Matyjaszewski, T. Patten, J. Xia, T. Abernathy, *Science (Washington, D.C.)* **272**, 866 (1996)
[4] J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc*. **117**, 5614 (1995)
[5] K. Matyjaszewski, V. Coessens, Y. Nakagawa, J. Xia, J. Qiu, S. Gaynor, S. Coca, C. Jasieczek, *ACS Symp. Ser.* **704**, 16 (1998)
[6] K. L. Beers, S. Boo, K. Matyjaszewski, *Polym. Mat. Sci. Eng.* **79**, 407 (1998)
[7] S. Coca, C. B. Jasieczek, K. L. Beers, K. Matyjaszewski, *J. Polym. Sci., Part A: Polym. Chem.* **36**, 1417 (1998)
[8] K. Matyjaszewski, S. Coca, C. B. Jasieczek, *Macromol. Chem. Phys.* **198**, 4011 (1997)
[9] X. Zhang, J. Xia, K. Matyjaszewski, *Macromolecules* **31**, 5167 (1998)
[10] K. Matyjaszewski, S. Coca, Y. Nakagawa, J. Xia, *Polym. Mat. Sci. Eng.* **76**, 147 (1997)
[11] D. M. Haddleton, C. Waterson, P. J. Derrick, C. B. Jasieczek, A. J. Shooter, *Chem. Commun*. 683 (1997)
[12] V. Coessens, Y. Nakagawa, K. Matyjaszewski, *Polym. Bull. (Berlin)* **40**, 135 (1998)
[13] J. Qiu, K. Matyjaszewski, *Macromolecules* **30**, 5643 (1997)
[14] T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **31**, 6708 (1998)
[15] S. Coca, K. Davis, P. Miller, K. Matyjaszewski, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **38**(1), 689 (1997)
[16] J. Alexander, M. L. Renyer, H. Veerapanane, *Synth. Commun.* **25**, 3875 (1995)
[17] J. G. Smith, P. W. Dibble, R. E. Sandborn, *J. Org. Chem.* **51**, 3762 (1986)
[18] A. McKillop, M. E. Ford, *Tetrahedron* **30**, 2467 (1974)
[19] K. Matyjaszewski, Y. Nakagawa, S. G. Gaynor, *Macromol. Rapid Commun*. **18**, 1057 (1997)
[20] V. Coessens, K. Matyjaszewski, *J. Macromol. Sci.*, submitted
[21] A. Akelah, A. Moet, "*Functionalized Polymers and their Applications*", Chapman and Hall, London 1990, p. 38
[22] D. A. Shipp, J.- L. Wang, K. Matyjaszewski, *Macromolecules* **31**, 8005 (1998)
[23] K. Matyjaszewski, S. Coca, S. G. Gaynor, M. Wei, B. E. Woodworth, *Macromolecules* **30**, 7348 (1997)