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Chloro-telechelic poly(ethylene oxide)s as initiators for the atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate

Structural features that affect the initiation efficiency

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Abstract

The atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate with differently substituted model and macroinitiators was performed, in order to evaluate qualitatively the structural features which affect the efficiency of the initiation step. It was found that substituents which stabilize radicals enhance the dissociation of the halogen atom and lead to high initiation efficiencies of the model initiators and macroinitiators. The phenyl group and the oxycarbonyl group result in the efficient initiators **1a** and **3a** for the initiation of both styrene and methyl methacrylate. Further, it was shown that the poly(ethylene oxide) moiety in the initiator, because of its low solubility, e.g. in styrene/poly(styrene) mixtures, leads to phase separation that effects the reactivity of the initiating group. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Chloro-telechelic poly(ethylene oxide)s; Atom transfer radical polymerization; Styrene

1. Introduction

‘Living’ polymerization procedures in the ideal case exert immediate initiation followed by propagation without termination and transfer reactions [1]. Therefore these procedures are qualified synthetic tools for obtaining polymers with well defined architecture, e.g. block copolymers [2–5]. Vinylic, acrylic, and cyclic monomers are to a certain extent prone to living polymerizations which may proceed via an anionic [2], cationic [3], group transfer [4] or coordination [5] mechanisms. More recently block copolymers were obtained also by ‘living’ or ‘controlled’ radical polymerization [6]. In anionic ‘living’ polymerization different procedures were developed for block copolymer syntheses, the sequential addition of monomers being the most common way. With monofunctional initiators A–B block copolymers are obtained, with bifunctional initiators A–B–A triblock copolymers are obtained, the B-block being formed first. The rate of polymerizing is determined by the nucleophilicity of the initiator and the growing chain end and the electrophilicity of the monomer. If the nucleophilicity of the initiator is too low, initiation may be slow and/or incomplete, which implies broadening of the molecular weight distribution and loss of control of the molecular weight and block structure of the polymer.

Another strategy for the preparation of A–B and A–B–A block copolymers is to use terminal functional groups of polymers (here block B) to prepare the macroinitiator for the polymerization of the second monomer and the formation of A block(s). This strategy is especially applied when the two monomers polymerize according to different mechanisms.

The purpose of this study is to prepare poly(ethylene oxide) (PEO) macroinitiators for the atom transfer radical polymerization of styrene (St) and methyl methacrylate (MMA) and to find optimum conditions for the preparation of A–B block copolymers. (The efficiency of the macroinitiators is evaluated on the basis of the molecular weight and the polydispersity of the block copolymers obtained.) In order to estimate the influence of the PEO chain on the polymerization low molecular weight model initiators were used for the polymerization of St and MMA. Initiators for ‘living’ radical polymerization have been the object of intense studies recently [7–9]. We have studied the initiation efficiency of α-halogeno esters **1a–c** as a function of the substitution pattern in α-position to the initiating radical. Hereby the initiator **1a** was used for the first time in ATRP. Conclusions on the nature and reactivity of the initiating active species are presented.

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Table 1
^{1}H n.m.r. data of modelinitiators **1a–c, 2a** and of macroinitiators **3a–c**

Compound	^{1}H n.m.r. data[a]
1a	$\delta = 1.21$ ppm (t, $J = 5.99$ Hz, 3H, CH_3); 4.19 ppm (m, 2H, CH_2); 5.34 ppm (s, 1H, CH); 7.33 ppm (m, 3H, H_{ar}); 7.47 ppm (m, 2H, H_{ar})
1b	$\delta = 1.31$ ppm (t, $J = 5.99$ Hz, 3H, CH_3); 1.70 ppm (d, $J = 5.99$ Hz, 3H, CH_3); 4.23 ppm (q, $J = 5.99$ Hz, 2H, CH_2); 4.39 ppm (m, 1H, CH)
1c	$\delta = 1.31$ ppm (t, $J = 5.99$ Hz, 3H, CH_3); 4.08 ppm (s, 2H, CH_2); 4.25 ppm (q, $J = 5.99$ Hz, 2H, CH_2)
2a	$\delta = 4.28$ ppm (m, 4H, CH_2); 5.27 ppm (d, $J = 3.00$ Hz, 2H, CH); 7.33 ppm (m, 6H, H_{ar}); 7.43 ppm (m, 4H, H_{ar})
3a	$\delta = 3.64$ ppm (s, PEO); 4.32 ppm (m, 2H, α–CH_2); 5.39 ppm (s, 1H, CH); 7.38 ppm (m, 3H, H_{ar}); 7.50 ppm (m, 2H, H_{ar})
3b	$\delta = 1.70$ ppm (d, $J = 5.99$ Hz, 3H, CH_3); 3.65 ppm (s, PEO); 4.32 ppm (m, 2H, α–CH_2); 4.43 ppm (q, $J = 6.89$ Hz, 1H, CH)
3c	$\delta = 3.65$ ppm (s, PEO); 4.11 ppm (s, 2H, CH_2); 4.34 ppm (m, 2H, α–CH_2)

[a] Solvent $CDCl_3$.

2. Experimental

2.1. Materials

α-Chlorophenylacetylchloride (95%, Fluka) was distilled over a Vigreux column, and 2-chloropropionylchloride and chloracetylchloride (Aldrich) were used as received. PEO monomethyl ether (MePEO) 1900 (Aldrich) was dried by removing residual water by azeotropic distillation with toluene on a water separator.

Inhibitors in St and MMA were removed by passing the monomers over an aluminium oxide column. CuBr (98%, Aldrich) and 2,2′-bipyridine (bipy) (ABCR) were used as received without purification. Polymerizations were carried out in an inert gas atmosphere. Nitrogen (Linde) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminium oxide.

2.2. Measurements

^{1}H nuclear magnetic resonance (n.m.r.) and ^{13}C n.m.r. spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz and 75 MHz, respectively. Deuterated chloroform ($CDCl_3$) was used as a solvent, and tetramethylsilane (TMS) served as an internal standard.

Gel permeation chromatography (g.p.c.) analyses were carried out using a high pressure liquid chromatography pump (Bischoff), a refractive index detector (Waters), and an ultra-violet (u.v.)-detector (Carlo Erba at $\lambda = 264$ nm). The eluting solvent was dimethylacetamide (DMAc) with 0.12 wt% LiCl and with a flow rate of 0.5 ml min^{-1}. Four columns with PL-gel (Polymer Laboratories) were applied. The length of each column was 300 mm, the diameter 7.5 mm, the diameter of gel particles 5 μm, and the nominal pore widths were 100, 500, 10^3 and 10^4 Å. Calibration with polystyrene (PSt) standards was used for the determination of molecular weights of PSts and PEO/PSt block copolymers, while calibration with poly(methyl methacrylate) (PMMA) standards was used for the corresponding PMMAs.

Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry measurements were carried out on a Hewlett Packard G 2052 spectrometer in linear mode calibrated for molecular weights of up to 8000 with an HP G 2052 A calibration kit containing various peptides. Samples were deposited in a Dithranol (trihydroxyanthracene) matrix from acetone and doped with LiCl (or KCl), which results in each species being observed as a Li^+ (or a K^+) adduct at molecular masses $M + 6.941$ (or $M + 39.098$).

The model initiators **1a–c** and **2a** were obtained commercially or prepared according to general synthetic procedures and characterized by ^{1}H and ^{13}C n.m.r. spectroscopy (cf. Tables 1 and 2).

2.3. Preparation of poly(ethylene oxide) macroinitiators **3a–c**

2.3.1. General procedure

PEO (MePEO, $\bar{M}_n$ 1900) was dissolved in toluene and heated for 12 h at reflux on a water separator. The dry

Table 2
^{13}C n.m.r. data of modelinitiators **1a–c, 2a** and of macroinitiators **3a–c**

Compound	^{13}C n.m.r. data[a]
1a	$\delta = 13.92$ ppm (CH_3); 59.12 ppm (CH); 62.43 ppm (CH_2); 127.93 ppm (C_{ar}); 128.52 ppm (C_{ar}); 128.95 ppm (C_{ar}); 135.91 ppm (C_{ar}); 168.30 ppm (COO)
1b	$\delta = 14.04$ ppm (CH_3); 21.51 ppm (CH_3); 52.60 ppm (CH); 62.04 ppm (CH_2); 170.10 ppm (COO)
1c	$\delta = 14.12$ ppm (CH_3); 41.07 ppm (CH_2); 62.29 ppm (CH_2); 167.38 ppm (COO)
2a	$\delta = 58.72$ ppm (CH); 63.29 ppm (CH_2); 127.89 ppm (C_{ar}); 128.85 ppm (C_{ar}); 129.29 ppm (C_{ar}); 135.39 ppm (C_{ar}); 167.94 ppm (COO)
3a	$\delta = 70.57$ ppm (PEO)
3b	$\delta = 70.57$ ppm (PEO)
3c	$\delta = 70.57$ ppm (PEO)

[a] Solvent $CDCl_3$.

Table 3
Bulk polymerization of styrene and methyl methacrylate with the model initiators in the presence of CuBr/2,2′-bipyridin[a]

No.	I	M	[M]/[I]	$x_p$in %[b]	$\bar{M}_{n,th}$[c]	$\bar{M}_{n,exp}$[d]	Q[d]
1	**1a**	St	192.0	80	16.000	15.700	1.36
2	**1b**	St	218.0	86	19.500	16.700	1.75
3	**1c**	St	183.3	84	16.000	36.800	1.91
4	**2a**	St	192.0	85	17.000	19.800	1.36
5	**1a**	MMA	212.6	86	18.300	16.700	1.15
6	**1b**	MMA	196.9	90	17.700	41.400	1.38
7	**1c**	MMA	247.0	25	6.200	59.800	1.28

[a] Molar ratio of initiator/CuBr/bipy $= 1/1/3$; $T = 130$°C, $t = 24$ h for St and 2 h for MMA.

[b] Determined gravimetrically.

[c] Calculated according to $\bar{M}_{n,th} = [M]/[I]x_pM_{mon}$.

[d] Determined by means of g.p.c.: eluting solvent DMAC with 0.12% LiCl (80°C); calibration with PSt standards for PSt and PEO-*b*-PSt and with PMMA standards for PMMA and PEO-*b*-PMMA.

solution of 7.06 mmol of MePEO in 100 ml toluene was treated with 28.24 mmol of the corresponding acid chloride and heated for 24 h to reflux. The solvents and volatiles were evaporated in high vacuum, the residue was dissolved in 150 ml methylene chloride, stirred over K_2CO_3, and filtered, the solvent was removed, and the residue dried. For purification the macroinitiator was dissolved in 100 ml toluene, reprecipitated into 750 ml hexane, isolated by filtration, and dried to constant weight. Yield: 90%.

^{1}H n.m.r. and ^{13}C n.m.r. data are summarized in Tables 1 and 2.

MALDI-TOF analysis of **3a–c**:

3a: $\bar{M}_n = 2350$. Molecular weight for the peak maximum: calc. 2470.3 amu; found 2471.6 corresponding to $H_3C–(OCH_2–CH_2)_{51}–O–CO–CH(C_6H_5)–Cl/K$.

3b: $\bar{M}_n = 2200$. Molecular weight for the peak maximum: calc. 2199.9 amu; found 2199.0 corresponding to $H_3C–(OCH_2–CH_2)_{47}–O–CO–CH(CH_3)–Cl/Li$.

3c: $\bar{M}_n = 2250$. Molecular weight for the peak maximum: calc. 2273.9 amu; found 2272.7 corresponding to $H_3C–(OCH_2–CH_2)_{51}–O–CO–CH_2–Cl/Li$

2.4. Polymerization of styrene and methyl methacrylate in bulk with model initiators and macroinitiators

2.4.1. General procedure

Into a Schlenk glass tube 0.181 mmol initiator, 0.181 mmol CuBr, 0.543 mmol bipy and 34.76 mmol monomer were filled. The heterogeneous mixture was degassed (three times), and immersed in an oil bath at 130°C under nitrogen. The polymerization was terminated by cooling rapidly to room temperature (RT). The product was dissolved in 40 ml methylene chloride and precipitated into a mixture of 30 ml 0.5 mol% HCl in 450 ml methanol. The polymer was isolated by filtration and dried to constant weight. The mother liquor was concentrated, dried to constant weight and analysed by means of ^{1}H n.m.r. spectroscopy. The results are summarized in Tables 3 and 4.

2.4.2. Investigation of the initiator efficiency

Into a Schlenk glas tube 0.588 mmol initiator, 0.588 mmol CuBr, 1.764 mmol bipy and 8.821 mmol monomer in a molar ratio of 1/1/3/15 were filled and polymerized as described above. After a time, *t*, the reaction mixture was rapidly cooled to room temperature, dissolved in 20 ml CCl_4 and passed over an aluminium oxide column

Table 4
Bulk polymerization of styrene and methyl methacrylate with the macroinitiators in the presence of CuBr/2,2′-bipyridin[a]

No.	I	M	[M]/[I]	x_p (%)[b]	$\bar{M}_{n,th}$[c] $\times 10^{-3}$	$\bar{M}_{n,exp}$[d] $\times 10^{-3}$	Q[d]	$[EO]_o/[M]_o$[e]	$[EO]_p/[M]_p$[f]
1	**3a**	St	192.0	76	15.2	21.5(17.2)$^{\wedge\{g}$}	1.36(1.29)[g]	0.24	0.21
2	**3b**	St	211.5	82	18.1	20.2(16.4)$^{\wedge\{g}$}	1.53(1.47)[g]	0.22	0.21
3	**3c**	St	208.0	65	14.1	20.3(17.6)$^{\wedge\{g}$}	1.45(1.40)[g]	0.22	0.19
4	**3a**	MMA	216.8	91	20.7	20.7	1.15	0.22	0.17
5	**3b**	MMA	199.1	87	17.3	33.9	1.38	0.23	0.06
6	**3c**	MMA	216.1	90	19.4	50.1	1.28	0.21	0.03

[a] Molar ratio of initiator/CuBr/bipy $= 1/1/3$; $T = 130$°C, $t = 24$ h for St and 2 h for MMA.

[b] Determined gravimetrically.

[c] Molecular weight of the PSt resp. PMMA block: $\bar{M}_{n,th} = [M]/[I]x_pM_{mon}$.

[d] Determined by means of g.p.c.: eluting solvent DMAC with 0.12% LiCl (80°C); calibration with PSt resp. PMMA standards.

[e] Introduced in the feed.

[f] Determined by means of ^{1}H n.m.r.

[g] These values refer to the PSt block obtained after reduction with $LiAlH_4$.

in order to remove the catalyst. The conversion was determined by means of n.m.r. measurements of the obtained solutions. The results are summarized in Fig. 1.

2.5. Reductive cleavage of poly(styrene)-block-poly(ethylene oxide)s

2.5.1. General procedure

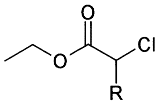
To a solution of 0.90 mmol lithium aluminum hydride in 50 ml THF a solution of the block copolymer containing 0.09 mmol ester in 100 ml THF was added and heated to reflux for 24 h. The reaction mixture was then cooled to 0°C and treated successively with water and a 10% aqueous solution of sulfuric acid. Finally, sodium bicarbonate was added until pH 7 was reached. The organic phase was separated and the water phase was extracted (three times) with methylene chloride. The combined organic layers were separated from residual water and dried over sodium sulfate. The organic phase was concentrated and then poured into 0.5 mol% HCl in methanol. The precipitate (fr.1) was isolated by filtration and dried to constant weight. Evaporation of the solvent from the mother liquor gave a second polymer fraction (fr.2).

^{1}H n.m.r. analysis proved fr.1 to be pure PSt (Section 3.3) and fr.2 to be PEO.

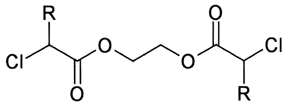
3. Results and discussion

In recent years the ‘controlled’ radical polymerization has been developed to become an efficient method for the synthesis of polymers with low polydispersity and a degree of polymerization predetermined by the monomer to initiator ratio under consideration of the conversion [6]. The atom transfer radical polymerization (ATRP) being one type of ‘living’ radical polymerization that is based on a rapid and reversible exchange between a low concentration of growing radicals ($[R] = 10^{-7}$ to 10^{-8} mol l^{-1}) and dormant species[10]. By using activated alkyl halides as initiators and CuCl or CuBr/bipy as catalyst a variety of vinyl monomers, e.g. St and MMA were polymerized in a ‘living’ manner.

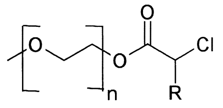
For our investigations we applied the model initiators **1a–c** and **2a** and the PEO macroinitiators **3a–c**.



1a-c



2a



3a-c

a: R = C_6H_5; b: R = CH_3; c: R = H

The monofunctional initiators **1a–c** were chosen in order to obtain information on the efficiency of the initiation as a function of the substituent R. The bifunctional initiator **2a** in addition is expected to give information on the influence of two active sites in one molecule. The polymeric initiators **3a–c** are expected to give information

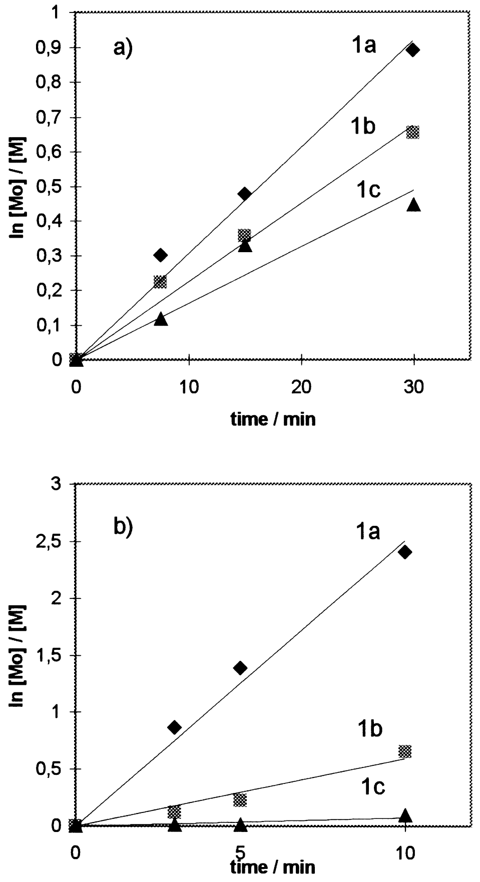


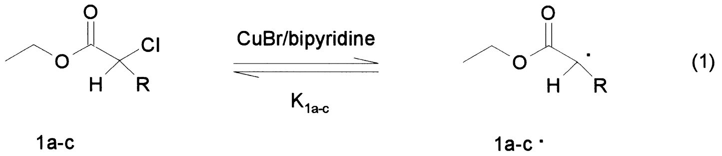
Fig. 1. Plots of ln$[M_0]/[M]$ versus reaction time for the polymerization of a) styrene with **1a–c** (k_{app}(**1a**) = $5.1 \times 10^{-4} s^{-1}$, k_{app}(**1b**) = $3.8 \times 10^{-4} s^{-1}$, k_{app}(**1c**) = $2.7 \times 10^{-4} s^{-1}$) and b) methyl methacrylate with **1a–c** (k_{app}(**1a**) = 41.8×10^{-4} s^{-1}, k_{app}(**1b**) = 10.0×10^{-4}s^{-1}, k_{app}(**1c**) = 1.3×10^{-4}s^{-1}).

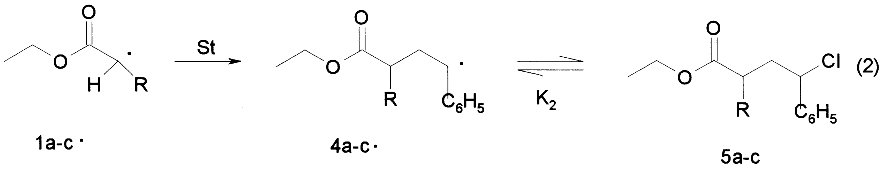
on the influence of the PEO moiety on the reactivity of the active site.

3.1. Investigation of the initiation efficiency

Model initiators **1a–c** were studied with respect to their initiation efficiency on both St and MMA. The reactions were performed in a heterogeneous system with an initiator/CuBr/bipy/monomer ratio of 1/1/3/15 at 130°C for various times, *t*. The conversion was determined by means of ^{1}H n.m.r. spectroscopy. From first-order kinetic plots the apparent rate constant $k_{app} = k_p \times [P\bullet]$, where k_p is the rate constant of propagation and $[P\bullet]$ the radical concentration, was determined for St and MMA polymerization with the initiators **1a–c** (Fig. 1). The apparent rate constant for both monomers have different values; the highest values are observed for the phenyl substituted initiator **1a**, and the lowest for the unsubstituted initiator **1c**. Since the rate constant of propagation k_p is a monomer-specific constant the different slopes in Fig. 1 (different k_{app} values) must result from different radical concentrations.

For a controlled polymerization the initiation rate should be larger than or at least equal to the propagation rate. Both rates depend on the respective rate constants, the monomer concentration, and the concentration of free radicals. The concentration of free radicals is linked with the dissociation constant K_1 (Eq. (1)). The radicals are formed upon dissociation of **1a–c** catalysed by CuBr/bipy. The dissociation constant strongly depends on the nature of R; the better the radical is stabilized, the higher is the dissociation constant, and the faster the initiation. For the polymerization of St, once the initiating radicals **1a–c·** are trapped by St (Eq. (2)) and the radicals **4a-c·** are formed the rate of further monomer addition (rate of propagation) becomes equal for all types of initiators neglecting the penultimate effect. The propagation rate depends on the dissciation constant, K_2. Assuming the same monomer concentration and rate constant for the initiation and propagation step, a fast initiation is expected for $K_1 \geqslant K_2$ (and inversely a slow initiation for $K_1 < K_2$).





For the polymerization of St the equilibrium concentration of the initiating radical **1a·** is higher or equal to the equilibrium concentration of the active growing species **4a·**, for **1c·** the equilibrium concentration is lower than for **4c·**.

Further, the kinetic measurements in Fig. 1 reveal that, for example, the ratio of k_{app}(**1a**,St)/k_{app}(**1b**,St) ≠ k_{app}(**1a**,MMA)/k_{app}(**1b**,MMA). This result reflects the reactivity of the monomers and reveals the lower reactivity of St in comparison to MMA.

3.2. Polymerization with model initiators

In our laboratory the kinetics of the atom transfer radical polymerization of St and MMA was studied both in bulk and in solution at different concentrations [11]. Accordingly the polymerization of St with model initiators in bulk was performed in a heterogeneous system with an initiator/CuBr/bipy/monomer ratio of 1/1/3/192 at 130°C for 24 h.

With the initiator **1a** (Table 3, No. 1) a good agreement of theoretical and experimental number-average molecular weight $\bar{M}_{\mathrm{n,th}}$, $\bar{M}_{\mathrm{n,exp}}$) and a polydispersity index $Q \approx 1.3$ was obtained. The PSt obtained with **1c** as initiator (Table 3, No. 3) shows $\bar{M}_{\mathrm{n,exp}}$ more than twice as high as $\bar{M}_{\mathrm{n,th}}$ and a polydispersity index of 1.91. We consider the rate of initiation to be lower than the rate of propagation. This leads to the coexistence of initiation and propagation reaction and explains the tailing toward lower molecular weights in the g.p.c. trace (Fig. 2A, trace 1c). The fact that $\bar{M}_{\mathrm{n,th}} < \bar{M}_{\mathrm{n,exp}}$ reveals that after termination some unreacted **1c** is still in the reaction mixture. With **1b** as initiator (Table 3, No. 2) $\bar{M}_{\mathrm{n,th}}$ is nearly as large as $\bar{M}_{\mathrm{n,exp}}$; the polydispersity index, however, is exceptionally large. From this we conclude that the rate of initiation is only slightly smaller than the rate of propagation and that the initiator is just consumed at the given conversion.

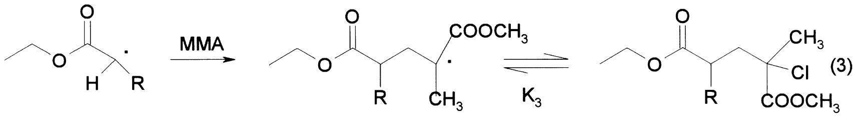
The g.p.c. traces (Fig. 2) of the polymer samples prepared with **1a** and **1b** as initiator are unsymmetrical with a tailing toward lower molecular weights. A further explanation of this experimental result is a thermal initiation of St polymerization which becomes evident at high polymerization temperatures and times. These chains grow also in a living manner, but reach a lower final molecular weight. Termination also may have a broadening effect on the molecular weight distribution, this effect should be low, however, as the results for the polymerization initiated with **1a** are in full accordance with those expected of a 'living' radical polymerization, with respect to control of molecular weight and polydispersity.

Polymerization of St with the initiator **2a** (Table 3, No. 4) shows a molecular weight of PSt which is slightly higher than expected, the polydispersity index, however, being rather low ($Q \approx 1.3$). Taking into consideration the good results obtained for the polymerization of St with the initiator **1a,** for initiator **2a,** due to the proximity of the two active sites in one molecule, side reactions of parts of the initiator or dimerization of a small fraction of initiating species during the pre-equilibrium phase have to be considered.

The polymerization of MMA with the model initiators **1a–c** was performed at 130°C for 2 h. Only initiator **1a**

(Table 3, No. 5) results in a PMMA with theoretical molecular weight and rather low polydispersity index. The g.p.c. elution curve (Fig. 2B, trace 1a) shows a symmetrical shape. With **1b** (Table 3, No. 6) as initiator $\bar{M}_{\mathrm{n,exp}}$ is more than two times higher than $\bar{M}_{\mathrm{n,th}}$ and with **1c** (Table 3, No. 7) the polymerization is completely out of control with respect to the molecular weight, although the polydispersity index is still quite low. This can be explained by investigations of imperfections such as slow intiation, termination, transfer, and slow exchange and their effects on kinetics, molecular weight, and polydispersities of ‘living’ chain growth polymerization [12]. The polydispersity is described to be < 1.3, considering slow initiation while excluding any further imperfections. We therefore assume that in the absence of side reactions only a small amount of **1c** initiates the polymerization, causing $\bar{M}_{\mathrm{n,exp}}$ of the product to be much higher than $\bar{M}_{\mathrm{n,th}}$ and the molecular weight distribution to be relatively narrow. Termination in our experiment can be neglected, as the polymerization with the highest concentration of radicals, that is the one initiated with **1a**, does not show any irregularities that could be related to termination reactions.

For the polymerization of MMA the equilibrium concentration of the initiating species **1b·** and **1c·** is lower than the concentration of the propagating species **6b,c·** (Eq. (3)). The result is slow initiation with all its consequences, mainly $\bar{M}_{\mathrm{n,th}} < \bar{M}_{\mathrm{n,exp}}$. For the initiating species **1a·** the equilibrium concentration is higher than or equal to the propagating species **6a·**; the result is a fast initiation, and a good agreement between $\bar{M}_{\mathrm{n,th}}$ and $\bar{M}_{\mathrm{n,exp}}$ is observed.



1a-c · 6a-c· 7a-c (3)

3.3. Polymerization with macroinitiators

The molecular weights of the macroinitiators were determined by means of MALDI-TOF analyses; an average value of $\bar{M}_{\mathrm{n}} = 2250$ was determined. The MALDI-TOF for the macroinitiator **3c** (Fig. 3), for example shows a single major peak series with a peak difference of 44.1 amu (CH_2CH_2O), confirming the proposed structure and the purity of this initiator. The experimental mass of 2272.7 amu corresponds within the limits of accuracy of MALDI-TOF measurements (±4 amu) [13] to the expected structure of **3c**, CH_3O–$(CH_2CH_2O)_{49}$–$COCH_2Cl/Li$ (2273.92 amu). Based on the results obtained from the MALDI-TOF analysis the quantitative chain analogous transformation of MePEO with the acid chlorides to result in **3a–c** was confirmed by ^{1}H n.m.r. measurements. G.p.c. measurements of the macroinitiators **3a–c** in DMAc with 0.12 wt% LiCl at 80°C, however, revealed much higher molecular weights with respect to PSt or PMMA standards; average values of $\bar{M}_{\mathrm{n}} = 4000$ ($Q = 1.05$–1.10) are obtained. These results have to be taken into account when the block copolymers—poly(ethylene oxide)-*block*-poly(styrene) (PEO-*b*-PSt) and poly(ethylene oxide)-*block*-poly(methyl methacrylate) (PEO-*b*-PMMA)—are characterized by means of g.p.c. measurements (Tables 4 and 5).

The results obtained from polymerization of both St and MMA with the model initiators **1a–c** have shown that **1a** gives the best control. In consequence, the macroinitiator **3a** was used for a time dependent analysis of St polymerization. At 130°C **3a** is soluble in St, however, during polymerization the melt becomes turbid, indicating a phase separation. It proved to be difficult to determine the conversion of these polymerizations gravimetrically as the obtained block copolymers showed partial solubility in methanol due to the hydrophilic PEO block.

In order to analyse the PSt block with respect to its molecular weight and polydispersity index the A–B block copolymer was treated with $LiAlH_4$ to reduce the ester bond between the blocks and to detach the PEO segment. A comparison of the ^{1}H n.m.r. spectrum of PEO-*b*-PSt (Fig. 4A) and that of the PSt block (Fig. 4B) obtained after treatment with $LiAlH_4$ clearly demonstrates the successful disconnection of the two blocks (complete disappearance

Table 5
G.p.c. data of poly(ethylene oxide)-*block*-poly(styrene)[a] samples obtained at different polymerization times and of the corresponding poly(styrene) block obtained after reduction with $LiAlH_4$[b]

No.	*t* (h)	$\bar{M}_{\mathrm{n}}$[c] PEO-*b*-PSt	*Q*[c] PEO-*b*-PSt	$\bar{M}_{\mathrm{n}}$[d] PSt	*Q*[d] PSt
1	3	6 800	1.62	4 900	1.49
2	5	10 600	1.53	7 400	1.41
3	7	14 700	1.42	9 800	1.36
4	9	16 500	1.43	12 100	1.38
5	23	21 500	1.36	17 200	1.29

[a] Molar ratio of initiator/CuBr/bipy = 1/1/3; *T* = 130°C, bulk.

[b] Cf. Section 2.

[c] Determined by means of g.p.c.: eluting solvent DMAC with 0.12% LiCl (80°C); calibration with PSt standards.

[d] These values refer to the PSt block obtained after reduction with $LiAlH_4$ determined by means of g.p.c.: eluting solvent DMAC with 0.12% LiCl (80°C); calibration with PSt standards.

of the resonance lines of MePEO). Analysis of the PSt block by means of g.p.c. reveals a linear increase of the molecular weight and a decrease of the polydispersity index with increasing conversion. This is expected for a living polymerization (Table 5).

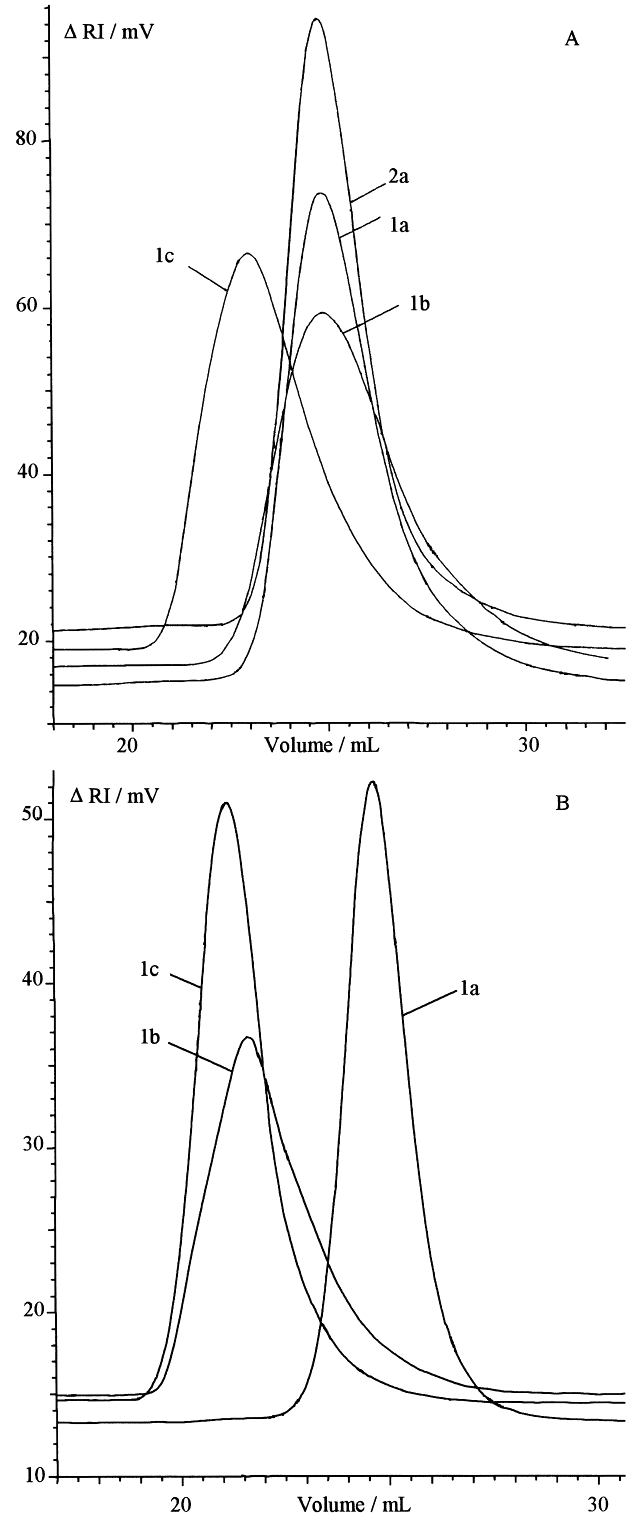


Fig. 2. G.p.c. traces of polymer samples prepared with the model initiators **1a–c** and **2a**: (A) Poly(styrene); (B) Poly(methyl methacrylate).

In order to study the influence of the PEO-moiety in the macroinitiator on the initiation and propagation step St and MMA were polymerized with the macroinitiators **3a–c**. Apparently, the solubility of the macroinitiators in MMA and MMA/PMMA mixtures is higher than in St/PSt, since the mixture remains clear up to the end of the polymerization.

From ^{1}H n.m.r. data the ratio of EO/St and EO/MMA repeating units was determined (Table 4). For St polymerization only small deviations from the expected values were observed. For PMMA obtained with **3a** as initiator most of the MePEO introduced in the feed was incorporated in the copolymer (Table 4, No. 4), however, for **3b** and **3c** as initiating species a large discrepancy was found indicating a low initiation efficiency (Table 4, Nos. 5,6). Small deviations in the block copolymer composition from the expected one may have one of the following reasons: (i) incomplete functionalization of MePEO; (ii) loss of parts of the block copolymer with a high EO/St ratio during isolation of the polymer (polymers with a high EO content are soluble in methanol); (iii) inaccuracy of the analytical method (small deviation in the integration of the peaks in the ^{1}H n.m.r. spectra may induce large errors); (iv) for PMMA the resonance lines in the ^{1}H n.m.r. spectra which were analysed are close to each other and not baseline resolved.

The g.p.c. traces of PEO-*b*-PS (Fig. 5A) are unimodal and slightly asymmetrical. An evaluation with PS-standards revealed small deviations of the molecular weight of the PSt block and a polydispersity index between 1.36 and 1.53 (Table 4). Analysis of PEO-*b*-PMMA (Fig. 5B) by g.p.c. with PMMA standards revealed a good agreement between $\bar{M}_{n,th}$ and $\bar{M}_{n,exp}$ for the initiator **3a** (Table 4). The higher values of $\bar{M}_{n,exp}$ than $\bar{M}_{n,th}$ for the PMMA samples prepared with **3b** and **3c** as initiators indicate a slow initiation compared to the chain growth reaction[12].

The experimental results obtained for the polymerization of St and MMA with the macroinitiators **3a–c** do not reveal essential differences to the polymerizations initiated with the model initiators. This is reflected by the ratio $\bar{M}_{n,exp}/\bar{M}_{n,th}$ which for both model and macromolecular initiators increases from **1a** to **1c** and from **3a** to **3c**. Thus, the macroinitiators show an initiation behaviour which is similar to that of the corresponding model initiators.

However, we notice that conversions of the polymerization of stryrene obtained with macroinitiators are slightly lower than the ones obtained with the model initiators, and polydispersities of the PSt blocks are lower than those of the ones initiated with **1a–c**. On the other hand, the polymerization of MMA does not seem to be affected by the presence of a PEO compound. This suggests that there is a minor imperfection in the PEO–PSt system, probably due to incompatibility of the hydrophilic macroinitiator and the hydrophobic St/PSt system, which leads to the phase separation described above and may also affect the initiation reaction itself.

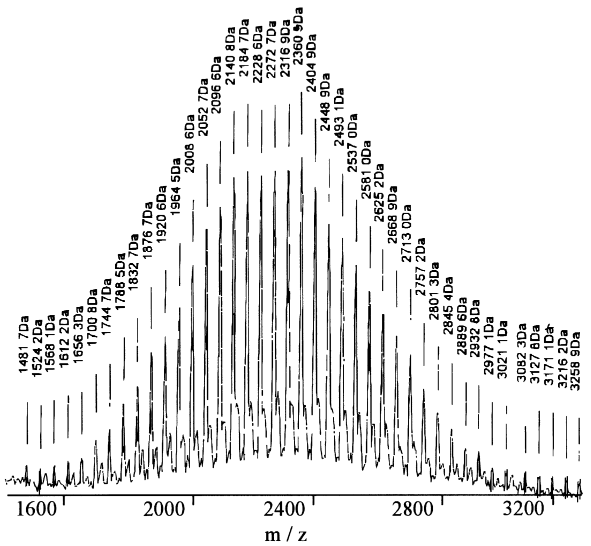


Fig. 3. MALDI-TOF mass spectrometry of the macroinitiator **3c**: $CH_3O-(CH_2CH_2O)_n-COCH_2Cl$.

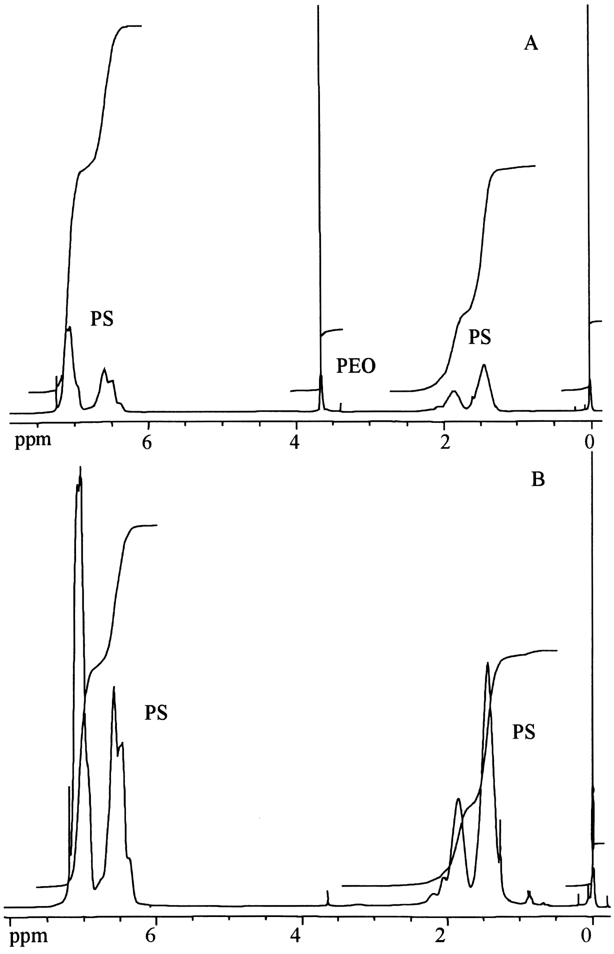


Fig. 4. ^1H n.m.r. spectrum of: (A) poly(ethylene oxide)-*block*-poly(styrene); (B) poly(styrene) obtained after reductive cleavage of the block copolymer with $LiAlH_4$ (sample No. 2 of Table 5).

4. Conclusions

The polymerization of St and MMA with model initiators **1a–c** revealed the substitution of the carbon radical to have a strong influence on the rate of initiation. Substituents which stabilize the radical enhance the dissociation of the initiator, catalysed by CuBr/bipy, producing a higher radical concentration in equilibrium

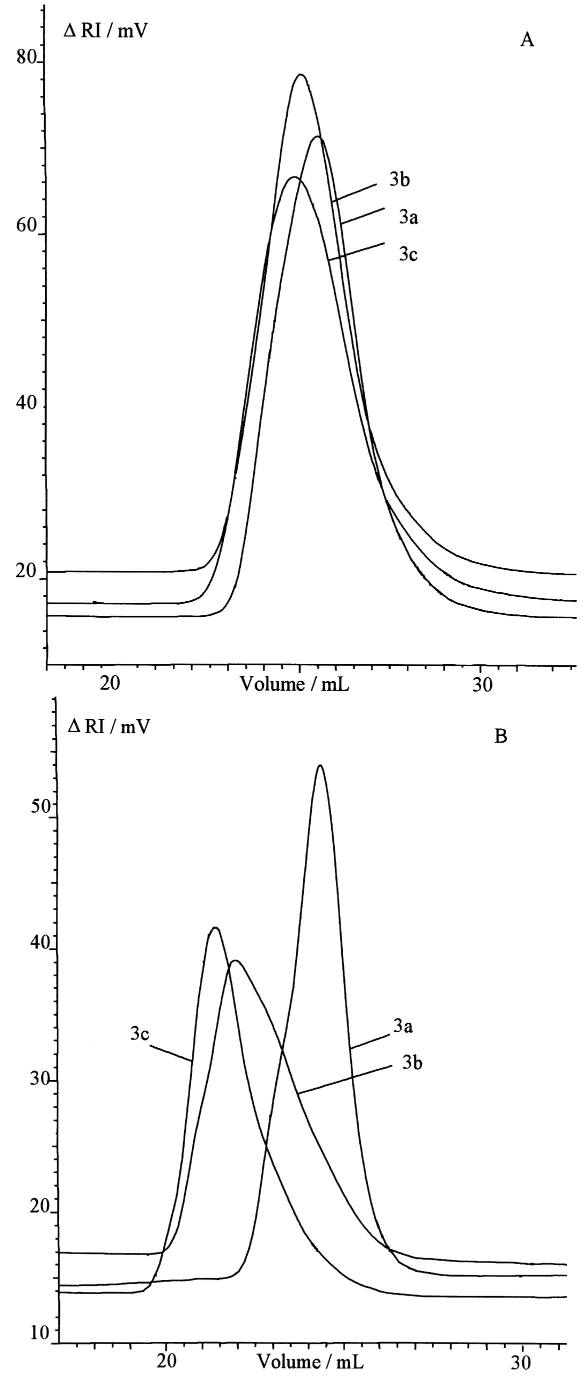
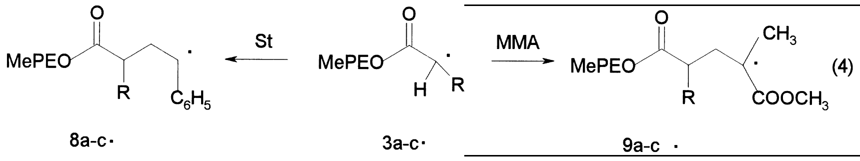


Fig. 5. G.p.c. traces of polymer samples prepared with the macroinitiators **3a–c:** (A) Poly(ethylene oxide)-*block*- poly(styrene); (B) Poly(ethylene oxide)-*block*-poly(methyl methacrylate).

and thus an increased initiation rate. The mesomeric stabilization of the radicals **1a·** and **3a·** by both a phenyl group and an oxycarbonyl group makes the active site in **1a** and **3a** suitable for the initiation of both St and MMA (Eq. (4)).



Two identical functional active sites in a low molecular weight initiator **2a** show a small decrease in the concentration of active sites during the pre-equilibrium phase which, however results in similar initiation efficiencies as their monofunctional analoga. The MePEO moiety in the polymeric initiators **3a–c** exerts its influence on the polymerization by means of its solubility in the mixture St/PSt or MMA/PMMA; a low solubility leads to phase separation and appears to have an equalizing effect on the reactivity of the different initiators. Obviously PEO-sequences interact neither with dormant species by enhancing the dissociation nor with the radical pair enhancing the addition to the monomers. This is in opposition to anionic polymerization [14] where a PEO chain segment enhances the polymerization rate by complexation of the counter cations (Li^+, Na^+, K^+) with the consequence of formation of a loose ion pair and an anion with increased nucleophilicity.

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