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"Controlled" Synthesis and Characterization of Model Methyl Methacrylate/*tert*-Butyl Methacrylate Triblock Copolymers via ATRP

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ABSTRACT: The heterogeneous atom transfer radical polymerization (ATRP) of *tert*-butyl methacrylate (tBMA) using CuX/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) catalytic system with various initiators R−X (X = Br, Cl) was investigated. The importance of the structure of the initiator on the polymerization of tBMA was briefly examined. Polymerization of tBMA with ethyl 2-bromoisobutyrate resulted in uncontrolled polymerization due to slow initiation because of the low back strain effect and relatively high propagation rate constant of tBMA. Well-controlled polymers were obtained with *p*-toluenesulfonyl chloride and 2,2,2-trichloroethanol initiators. This can be explained by the fast initiation coupled with the rapid establishment of the equilibrium between the active and dormant species in the polymerization. Poly(methyl methacrylate) macroinitiators were used to synthesize poly(tBMA-*b*-MMA-*b*-tBMA) triblock copolymers in a range of tBMA compositions. The use of a mixed halogen system in the block copolymer synthesis leads to fast initiation and fast deactivation, resulting in controlled molecular weights and a low polydispersity index. Gradient polymer elution chromatography was used to confirm the block copolymer structure. The retention time of the block copolymers lie in between the retention times of the two homopolymers, indicating the existence of a (block) copolymer structure. This technique was successfully used to identify the influence of the ATRP reaction conditions on the final block copolymer structure.

Introduction

Ionomers[1] are a class of polymers with up to 15 mol % of ionic groups along a nonionic polymer backbone. The ionic groups tend to microphase-separate and form ion-rich domains or ionic aggregates with sizes in the range of nanometers. These ionic aggregates can act as thermoreversible cross-links. Considerable research has been carried out on understanding the structure−property relationships[2−4] of random ionomers for which the ionic groups are randomly distributed along the polymer backbone. Compared to crystalline ionomers, amorphous ionomers are more suitable for studying the effect of ionic interactions on the morphology and on structure−property relationships to avoid the complexities arising from the crystalline domains. Among the amorphous polymers, polystyrene ionomers are studied extensively,[5,6] while studies on poly(methyl methacrylate) (PMMA)[7] based ionomers appear less frequently. These ionomers were all prepared via conventional free-radical polymerization and subsequent functionalization. For a better understanding of the structure−property relationships of ionomers, materials with a more specific architecture, defined molecular weight, and low polydispersity index (PDI) are required. The synthesis of model ionomers has been focused on telechelic ionomers,[8] segmented ionomers,[9] those which contain one ionic group per segment and block ionomers,[2] and those which contain an ionic block with regular ionic functionalities. Only a few reports related to the study of block ionomers with a PMMA backbone were published.[10] McGrath and co-workers[10,11] reported on the synthesis and characterization of methacrylate block ionomers by using living anionic polymerization, where the ionomer block was prepared by the hydrolysis and subsequent neutralization of poly(*tert*-butyl methacrylate). However, the need for high-purity monomers, solvents, and reagents, coupled with the low temperatures usually required, makes anionic polymerization of (meth)acrylates a relatively difficult process.[12] In the past decade the development of the controlled/living radical polymerization techniques allows the synthesis of block copolymers under less vigorous conditions. Stable free radical polymerization (SFRP),[13] atom transfer radical polymerization (ATRP),[14,15] and reversible addition−fragmentation chain transfer[16] polymerization (RAFT) are the most studied techniques. These techniques are based on a reversible activation/deactivation cycle of propagating polymer radicals, resulting in a small fraction of polymer radicals and a large fraction of reversibly deactivated "dormant" polymer chains. The low concentration of radicals suppresses possible termination reactions to a large extent. Among the available techniques, ATRP has emerged as a very versatile and convenient strategy for polymer synthesis with good control of the molecular weight and relatively low polydispersities (PDI < 1.3). However, the sensitivity of ATRP catalyst systems to the acid functionalities forces us to protect acid functionalities in the polymers.

Several research groups[17,18] used *tert*-butyl acrylate (tBA) as a suitable monomer for introducing acrylic acid units in synthesizing block copolymers with various architectures. However, the corresponding methacrylate, i.e., *tert*-butyl methacrylate (tBMA), is rarely used to introduce methacrylic acid units by ATRP. Matyjaszewski[19] and co-workers were the first to report the polymerization of tBMA by ATRP using the CuCl/HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine) catalyst system with an ethyl 2-bromoiso-

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butyrate (EBriB) initiator. The polymerization was carried out at 90 °C in 50 vol % anisole. The semilogarithmic plot of conversion vs time was nonlinear, but high initiation efficiency was claimed for this system. Haddleton[20] systematically studied ATRP of sterically hindered methacrylates at 90 °C in 50 vol % xylene using EBriB/CuBr/imine systems. The increased steric hindrance at the α-carbon of the side chain in the methacrylates apparently results in low rates of polymerization and high rates of termination. Especially in the case of tBMA, uncontrolled molecular weight and high PDI were reported. These results were explained on the basis of possible hydrolysis of tBMA monomer to the acid, leading to catalyst poisoning. Recently, Hadjichristidis[21] reported the synthesis of graft copolymers of PtBMA on polystyrene by the CuBr/bipyridine catalyst system. In this case, the backbone was produced with a 2,2,6,6-tetramethylpiperidine-*N*-oxyl-mediated stable free-radical polymerization process from the copolymerization of styrene and *p*-(chloromethyl)styrene, but so far, block copolymerizations of tBMA with available methacrylic, acrylic, and styrenic monomers by ATRP are not reported. Our aim is to introduce a more rigid methacrylic acid block compared to less rigid acrylic acid block in the PMMA matrix, resulting in methacrylic triblock ionomer precursors. The rigid methacrylic block may result in better mechanical and thermal properties.

In this paper, we report on the importance of initiator selection, when a heterogeneous catalyst like PMDETA/CuX is employed in the controlled radical polymerization of tBMA. The effect of the structure of the initiator and initiation mechanism on the control achieved in the polymerization is briefly discussed. Furthermore, the synthesis of well-defined difunctional (bromine end groups) PMMA macroinitiators and their block copolymerization with tBMA to obtain triblock copolymers in various compositions with controlled molecular weight and relatively low PDI using PMDETA/CuCl catalyst system is discussed. The absorbance ratio method was used to determine the composition of the block copolymers by FTIR spectroscopy. Results of the synthesis and characterization by spectroscopic and chromatographic techniques of block copolymers are presented. Gradient polymer elution chromatography (GPEC) is applied to characterize the block copolymers and to evaluate the effectiveness of block copolymerization reaction conditions during ATRP. These block copolymers are precursor materials for block ionomers, which can be used to understand the influence of chemical structure and composition on the morphology of the block ionomers. The morphological features and the effect of chlorine-functionalized PMMA macroinitiators on tBMA polymerization will be published in a forthcoming paper. These materials may also be used as potential precursors to synthesize well-defined polyelectrolytes,[22] stabilizers in emulsion polymerization,[23] amphiphilic block copolymers,[24] and resins for powder coating applications.

Experimental Section

Materials. Methyl methacrylate (Aldrich, 99%), *tert*-butyl methacrylate (Aldrich, 99%), toluene (Aldrich, 99%), dichloromethane (Biosolve, 99%), and methyl ethyl ketone (Aldrich, 99%) were vacuum-distilled and stored at −15 °C. Ethylene glycol (99%), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (99%), ethyl-2-bromoisobutyl bromide (99%), 2,2,2-trichloroethanol, butyl acetate (99%), triethylamine (99%), *p*-toluenesulfonyl chloride (97%), 1,1,1-trichloroethanol (98%), and silica (0.04−0.6 mm) were obtained from Aldrich and used without further purification. Cu^IBr (98%) and Cu^ICl (98%) were obtained from Aldrich and purified as given below. Copper halides were stirred with glacial acetic acid for 24 h under a nitrogen atmosphere, later washed consecutively with glacial acetic acid, ethanol, and diethyl ether, and dried at 40 °C for 3 days and stored under an argon atmosphere.

Analysis and Measurements. *Determination of Conversion and Molecular Weight Distribution.* The conversion of the monomer during the polymerization was determined by gas chromatography (GC) analysis. GC measurements were carried out on a Hewlett-Packard 5890 SII, equipped with an AT-Wax capillary column (30 m × 0.53 mm × 10 μm), using a HP 3393a integrator to obtain the chromatogram. Dilute polymer solutions in tetrahydrofuran (THF) were made in 1.5 mL crimp neck vials and measured using an autosampler. The injection temperature was 200 °C, and a 10 °C min^{-1} heating ramp was used. SEC measurements were carried out using a Waters GPC equipped with a Waters 510 pump, a Waters 410 differential refractometer (40 °C), a Waters WISP 712 autoinjector (50 μL injection volume), a PL gel (5 μm particles) 50 × 7.5 mm guard column, and two PLgel mixed-C (5 μm particles) 300 × 7.5 mm columns (40 °C). Data acquisition and processing were performed using Waters Millennium 32 version 3.05 software. Tetrahydrofuran (THF, Biosolve, stabilized with BHT) was used as eluent at a flow rate of 1.0 mL/min, dilute polymer solutions of 2 mg/mL were made, and a 50 μL solution was injected for analysis. Calibration was done using polystyrene (PS) standards (Polymer Laboratories, 580−7.1 × 10^6 g mol^{-1}), and molecular weights are calculated using the universal calibration principle with Mark−Houwink parameters for PMMA[25] (PMMA: $K = 0.944 \times 10^{-4}$ dL g^{-1}, $a = 0.719$).

Spectroscopic Analysis. The FTIR spectra were recorded with a Bio-Rad Excalibur 3000 series spectrometer. One hundred scans at a resolution of 4 cm^{-1} were signal-averaged, and the Bio-Rad Merlin software was used to analyze the spectra. Samples were prepared by casting films from a dilute polymer solution on KBr pellets for FTIR measurements. These films were thin enough to be within the range where the Beer−Lambert[26] law can be applied. The carbonyl (C=O) stretch in the two homopolymers PMMA and PtBMA are observed at 1732 and 1726 cm^{-1}, respectively. In the block copolymer the separate carbonyl peaks were observed as one single peak. We used an absorbance ratio method[27] to estimate the chemical composition of the block copolymers. A1 and A2 are the absorbance of the band at 847 cm^{-1} (assigned to the skeletal vibration of *tert*-butoxy group in PtBMA homopolymer) and the carbonyl ester peak at 1730 cm^{-1}, respectively. The ratio A1/A2 is proportional to the mole percentage of tBMA present in the block copolymer. A calibration curve was constructed between the ratio A1/A2 and mole percentage of tBMA by preparing blends of PMMA and PtBMA of various known concentrations. The data can be fitted well with a linear relation (see Supporting Information). The validity of the calibration curve was verified by making blends with intermediate concentrations. FT-NMR spectra were recorded with a Varian 400 MHz spectrometer. NMR spectra were recorded in $CDCl_3$ at 25 °C. All chemical shifts are reported in ppm downfield from tetramethylsilane (TMS), used as an internal standard ($\delta = 0$ ppm).

GPEC Analysis. GPEC measurements were carried out on a Waters Alliance 2690 separation module with a Waters 2487 dual λ absorbance detector and a PL-EMD 960 ELSD detector (nitrogen flow 5.0 mL/min, temperature 70 °C). A Zorbax silica 5 μm column (4.6 mm × 150 mm, Dupont Chromatography) was used at 30 °C. A linear binary gradient starting from heptane (volume fraction, $\Phi = 1$; 0 min nonsolvent for polymers used in analysis) to THF (volume fraction, $\Phi = 1$; 60 min good solvent for polymers used in analysis) was used and is shown in Table 1. The column was reset at the end of the gradient to initial conditions between 60 and 70 min. A gradient steepness, i.e., gradient change in fraction solvent per minute ($\Delta\Phi_{gradient}$), of 0.02 was applied. HPLC grade

Table 1. Linear Binary Gradient Used for GPEC[a]

step	time (min)	Φ_{heptane}	Φ_{THF}	$\Delta\Phi_{\text{gradient}}$ (min^{-1})	flow (mL/min)
1	0	1	0		0.5
2	50	0	1	0.02	0.5
3	60	0	1		1.5
4	65	1	0	0.2	1.5
5	70	1	0		0.5

[a] The eluent compositions are given in volume fraction (Φ) and $\Delta\Phi_{\text{gradient}}$ steepness of the applied step.

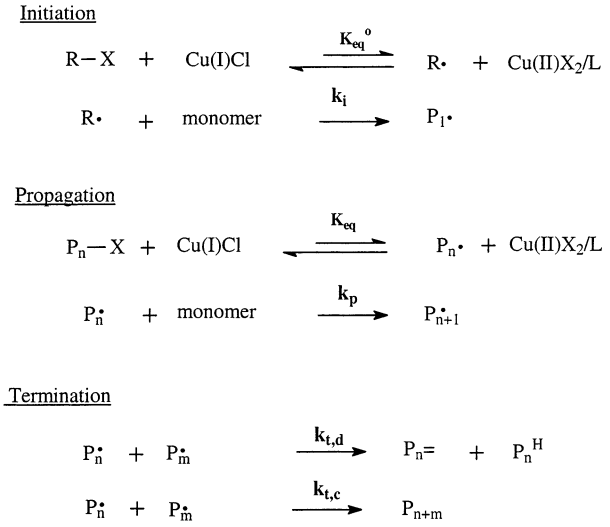
solvents obtained from BioSolve were used. A Varian 9010 solvent delivery system was used to maintain a stable flow rate of the eluents. Dilute polymer solutions were made in THF (10 mg/mL), and a sample of 25 μL was used for analysis. Data were acquired by Millenium 32 3.05 software.[28]

*Synthetic Procedures. tBMA Polymerization***.** A typical ATRP was carried out as follows. CuCl (0.082 g, 0.82 mmol), PMDETA (0.143 g, 0.82 mmol), and tBMA (5.014 g, 0.036 mol) were charged in a dry 50 mL three-neck round-bottom flask, and the flask was sealed with a rubber septum. The reaction mixture was bubbled with argon for 30 min to remove traces of oxygen. In a second, dry 25 mL three-neck round-bottom flask pTsCl (0.157 g, 0.82 mmol) and MEK (2.312 g, 0.03 mol) were charged, and the flask was sealed with a rubber septum. This initiator solution was also bubbled with argon for 30 min to remove traces of oxygen. Finally, the initiator solution was added via a degassed syringe to the monomer solution flask and immersed in an oil bath at 90 °C to start the polymerization. To study the kinetics of the polymerization, samples were drawn using a degassed syringe during the course of the reaction and diluted with THF. Part of the solution was used for gas chromatography (GC) to determine the monomer conversion, and the remaining part was used for SEC analysis. After completion of the reaction, THF (100 mL) was added to the flask, and a magnetic stirrer was used to dissolve the polymer. The resulting green (Cu^{II} complex) polymer solution was passed through a silica column (SiO_2) to remove the copper complex. The resulting colorless polymer solution was concentrated by rotaevaporation, after which the polymer was collected and dried under vacuum for 3 days at 50 °C.

(A) Synthesis of Difunctional Initiator. 1,2-Bis(bromoisobutyryloxy)ethane, a difunctional initiator, was synthesized in dichloromethane (DCM, 189 mL, 3.17 mol) through a coupling reaction of 2-bromoisobutyryl bromide (BIBB, 13.7 mL, 0.11 mol) with ethylene glycol (EG, 2.79 mL, 0.05 mol) in the presence of triethylamine (17.1 mL, 0.12 mol) at 0 °C under an argon atmosphere. Unreacted BIBB and EG were removed by sequential extraction with water, 1 M $NaHCO_3$, and a saturated NaCl solution. DCM was removed by rotaevaporation. The initiator was purified by dissolving in methanol at 50 °C and recrystallizing at −5 °C (this procedure was repeated at least three times) and characterized by ^{1}H NMR. Yield: 85%. ^{1}H NMR ($CDCl_3$): $\delta = 1.93$ (6H, s), 4.43 (4H, s).

(B) Synthesis of PMMA Macroinitiators. To a dry 50 mL three-neck round-bottom flask CuBr (0.122 g, 0.83 mmol), $CuBr_2$ (when necessary), PMDETA (0.144 g, 0.83 mmol), and MMA (5.012 g, 0.05 mol) were charged, and the flask was sealed with a rubber septum. The reaction mixture was bubbled with argon gas for 30 min to remove traces of oxygen. In a second dry 25 mL three-neck round-bottom flask difunctional initiator (0.299 g, 0.83 mmol) and toluene (1.823 g, 0.02 mol) were charged, and the flask was sealed with a rubber septum. This initiator solution was also bubbled with argon for 30 min to remove traces of oxygen. Finally, the initiator solution was added via a degassed syringe to the monomer solution and immersed in an oil bath at 90 °C to start the polymerization. To study the kinetics of the polymerization, samples were drawn using a degassed syringe during the course of reaction and diluted with THF. Part of the solution was used for gas chromatography (GC) to determine the monomer conversion, and the remaining part was used for SEC analysis. The polymer was purified as described in the tBMA homopolymerization section.

Scheme 1. General Scheme for Atom Transfer Radical Polymerization



*(C) Synthesis of Block Copolymers***.** The halide exchange technique was used to synthesize the block copolymers. The procedure was the same as discussed in the previous section except that a macroinitiator (1.023 g, $M_n = 6005$, 0.16 mmol) and solvent (methyl ethyl ketone, 2.5 mL) were added to the flask initially. Once the macroinitiator was dissolved completely, the monomer (tBMA, 1.07 mL, 3.38 mmol) and PMDETA (0.022 g, 0.16 mmol) were added. The solution was bubbled with argon for 30 min, and finally CuCl (0.023 g, 0.16 mmol) was added. The flask was immersed in an oil bath at 90 °C to start the polymerization. Samples were taken at regular intervals and analyzed for monomer conversion by GC. The polymer was purified as described above.

Nomenclature. The nomenclature used for the polymers can best be explained using examples. The designation MD6 refers to the difunctional poly(methyl methacrylate) macroinitiator with a molecular weight of 6000. The notation BM6B refers to a triblock copolymer with PMMA middle block of molecular weight 6000 and PtBMA outer blocks synthesized by block copolymerization of MD6 with tBMA. Similarly, the designation MM4M refers to the chain extension of the MD4 macroinitiator with methyl methacrylate.

Results and Discussion

ATRP of *tert*-Butyl Methacrylate. Effect of Initiator. The CuBr or CuCl/PMDETA catalyst system was used in the homopolymerization of tBMA. The choice of the appropriate initiator/CuX (X = Cl, Br) system is a key parameter, when polymerizing monomers such as MMA with their high observed propagation rate constants ($k_p^{\text{obs}} = k_pK_{\text{eq}}$ according to the terminology defined by Matyjaszewski;[29] cf. Scheme 1) to avoid slow initiation (low observed initiation rate constant $k_i^{\text{obs}} = k_iK_{\text{eq}}^{\circ}$ compared to k_p^{obs}) and/or possible side reactions. This is more important when working with a highly active catalyst system like PMDETA/CuX ($K_{\text{eq}} \sim 10^{-7}-10^{-6}$ for MMA with PMDETA/CuBr). PMDETA was selected because (a) the catalyst complex is highly active, (b) easily available, (c) cost-effective and (d) the catalyst complex can be easily separated from the polymer.[30] The three initiators used were EBriB, *p*-toluenesulfonyl chloride[31] (pTsCl), which is well-known as a universal initiator, and 1,1,1-trichloroethanol.[32] These three initiators were selected to study the effect of chlorine- and bromine-based initiation systems on the controlled polymerization of tBMA. EBriB has been used extensively in the polymerization of a variety of methacrylates.[33] Percec[31] and co-workers

Table 2. ATRP of TBMA with the CuX (X = Br/Cl)/PMDETA Catalyst System, Initiated by Three Initiators in Toluene at 90 °C; [I]/[Cu]/[PMDETA] = 1:1:1[a]

entry	initiator	catalyst	$[M]_0/[I]_0$	solvent[b] (%)	reaction time (h)	conv (%)	M_n(exp)	M_n(theo)[c]	PDI
1	EBriB	CuBr	42	30	5	40	4100	2600	1.65
2	EBriB	CuCl	42	50	6	60	5900	3600	1.50
3	PTsCl	CuCl	42	50	5	80	7000	4900	1.23
4	TCE	CuCl	42	50	5	70	6800	4300	1.22

[a] PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, EBriB = ethyl 2-bromoisobutyrate, PTsCl = *p*-toluenesulfonyl chloride, TCE = 2,2,2-trichloroethanol. [b] Volume percent of solvent in the total volume. [c] $M_{n,theo} = M_w$ of initiator + ([M]/[I] × 142 × conversion).

were the first to demonstrate the use of arenesulfonyl halides as universal initiators for heterogeneous and homogeneous metal-catalyzed living radical polymerization of styrene derivatives, methacrylates, and acrylates.

Polymerization with EBriB. Polymerizations of tBMA with the EBriB initiator and CuBr/PMDETA catalyst system in 30 vol % toluene at 90 °C resulted in uncontrolled polymerization with high polydispersity index (PDI ≤ 1.7, Table 2). The SEC traces of samples taken at regular time intervals during the polymerization showed a long tail toward the low molecular weight region, indicating that a large amount of radical termination occurred during the initial stages of the polymerization. The polymerization stopped after 30 min, with no further increase in molecular weight.

The uncontrolled polymerization of tBMA from EBriB may be due to the following reasons. A successful ATRP initiating system requires the following two important parameters. First, the initiation should be fast compared to propagation, and second, it should minimize the probability of side reactions.[29] Thus, the apparent (observed) initiation rate constant ($k_i^{obs} = k_iK°_{eq}$, Scheme 1) should be larger than the observed propagation rate constant, k_p^{obs} (i.e., $k_iK°_{eq} \geq k_pK_{eq}$). It appears that for the EBriB/CuBr system k_i^{obs} is much smaller than the observed propagation rate constant k_p^{obs}. This would result in slow and inefficient initiation, with a significant portion of the initiator being lost due to termination reactions at the onset of the polymerization. Slow initiation coupled with the high equilibrium constant (K_{eq}) for methacrylates with the PMDETA/CuBr catalyst system would result in an uncontrolled polymerization. Slow initiation with the EBriB/CuBr/dNbpy initiator catalyst system in the polymerization of the MMA was reported[29] earlier. EBriB, though electronically similar to propagating species of methacrylates, is less active due to smaller back strain[29] effect, which apparently results in slow initiation of the tBMA polymerization.

Mixed halogen systems[34,35] (R−Br/CuCl) are used to increase the initiation rate constant in ATRP. A mixed halogen system results in faster initiation, slower propagation, and fast deactivation; as a consequence, the polymerization is more controlled. ATRP of MMA using EBriB/CuCl[29] initiation system leads to a better molecular weight control and lower polydispersity index than the EBriB/CuBr system. Polymerization of tBMA performed with an EBriB/CuCl/PMDETA mixed halogen system in 50 vol % toluene results in a continuous increase of molecular weight with conversion as opposed to the EBriB/CuBr system discussed above. The SEC traces of polymer samples taken at two reaction times are shown in Figure 1.

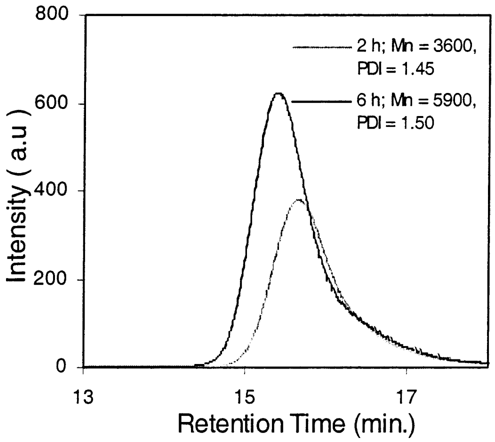


Figure 1. GPC traces of PtBMA at two time intervals during the ATRP polymerization in toluene at 90 °C. $[\text{EBriB}]_0 = [\text{CuCl}]_0 = [\text{PMDETA}]_0 = 0.07$ M, $[\text{tBMA}]_0 = 3.03$ M.

Molecular weights increased with conversion, but PDI was broad and the low molecular weight tail is also present in the SEC traces. The use of a mixed halogen system increased the initiation rate; however, it was not sufficient to achieve a controlled polymerization. The slow initiation also affects the polydispersity index. PDI is inversely related to the concentration of Cu^{II} (see eq 1) and the rate of deactivation. In successfully controlled radical polymerizations, the equilibrium between the dormant (polymeric halides) and active species (growing radicals, cf. Scheme 1) occurs rapidly, and the contribution of termination reactions can be neglected. The ability to regulate the radical levels to low concentrations and thus suppress radical−radical termination via coupling or disproportionation is based on the fast establishment of the following inequality, i.e., $k_d[R^\bullet][Cu(II)/L] \gg k_t[R^\bullet]^2$. If k_d or the Cu^{II} concentration is too low, the latter term $k_t[R^\bullet]^2$ cannot be neglected and irreversible termination reactions will be significant, resulting in uncontrolled polymerization. This is possible because at the beginning of the polymerization the concentration of deactivator is built up until the rate of deactivation of the radical by Cu(II)/L is faster than the rate of radical consumption by coupling or disproportionation. When initiation is slow and continuous, the equilibrium Cu^{II} concentration will be reached slowly, and consequently $k_t[R^\bullet]^2$ might be equal to or higher than $k_d[R^\bullet][Cu(II)/L]$. This may result in significant radical terminations during the polymerization. Similar effects were reported in the polymerization of MMA[29] by 1-PECl/CuCl initiation system, which is a poor initiating system for MMA polymerizations.

$$\frac{M_w}{M_n} = 1 + \frac{k_p[RX]_0}{k_d[X - M_t^{n+1}/L]}\left(\frac{2}{p} - 1\right) \qquad (1)$$

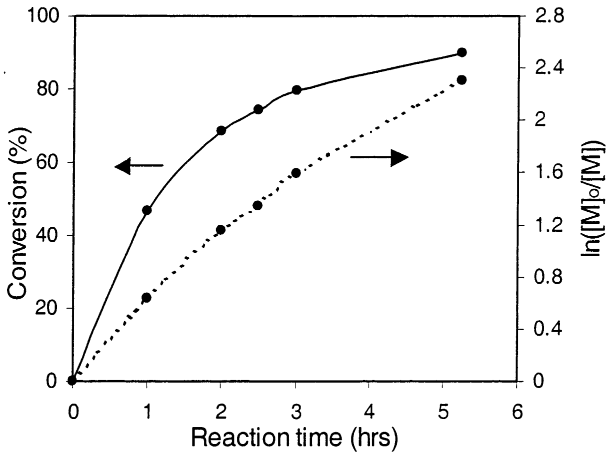


Figure 2. Plots of $\ln([M]_0/[M])$ vs reaction time and monomer conversion vs reaction time for the ATRP of tBMA in toluene at 90 °C. $[pTsCl]_0 = [CuCl]_0 = [PMDETA]_0 = 0.07$ M, $[tBMA]_0 = 3.03$ M.

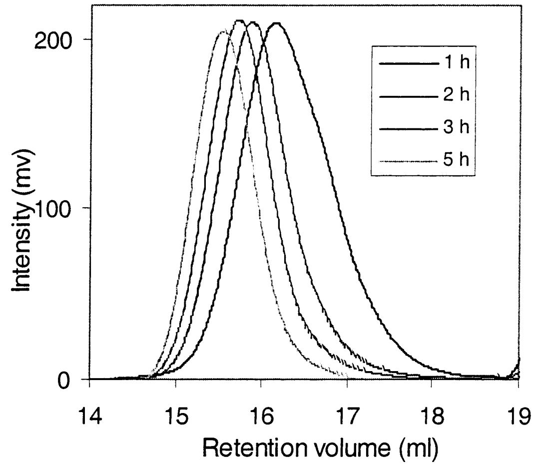


Figure 3. GPC traces of PtBMA polymerized in toluene at 90 °C at various reaction time intervals illustrating the growth of PtBMA chain length: 1 h ($M_n = 2900$, PDI = 1.39); 2 h ($M_n = 4200$, PDI = 1.28); 3 h ($M_n = 5600$, PDI = 1.23); 5 h ($M_n = 7000$, PDI = 1.21); $[p\text{-TsCl}]_0 = [CuCl]_0 = [PMDETA]_0 = 0.07$ M, $[tBMA]_0 = 3.05$ M.

Polymerization with pTsCl. ATRP polymerizations of tBMA using pTsCl initiator and CuCl/PMDETA catalyst system were performed in 50 vol % toluene at 90 °C. The molar ratio of initiator to catalyst to ligand is similar to the one used in the EBriB reaction, and the polymerization results are therefore comparable. A typical semilogarithmic kinetic plot of the homopolymerization of tBMA with pTsCl is shown in Figure 2. The kinetic plot of the conversion vs time is linear up to 60% conversion, indicating that a constant number of growing polymer chains are present. The molecular weight increased linearly with conversion, and the PDI decreased progressively with conversion with a final polydispersity index of less than 1.25 (see Table 2). This is also evident from the SEC traces of polymer samples taken at regular intervals during the polymerization (Figure 3). The peak retention time progressively shifts towards lower values, indicating that the molecular weight gradually increases with conversion. The SEC peak is symmetrical with no tailing in the low molecular weight region. These results show that pTsCl successfully initiates the controlled polymerization of tBMA.

The observed difference in the polymerization behavior may be due to differences in the initiation mechanism[36] involved in the two types of initiators. Percec[37] and co-workers were the first to propose the initiation mechanism for sulfonyl halide initiators in metal-catalyzed radical polymerization. The propagation and reversible termination steps are identical for sulfonyl and alkyl halides. The first difference is that the metal-catalyzed reduction of the arylsulfonyl halide to the corresponding sulfonyl radical is faster than that of corresponding alkyl radical. This may, therefore, facilitate a higher rate of initiation than propagation. In this case, all of the initiator is consumed before significant propagation occurs. The second difference is that the sulfonyl radicals formed from sulfonyl halides are more stable and form sulfonyloxy and/or sulfinyl[37] radicals through a reversible combination process. This stabilization is believed to be due to sulfinyl radicals that do not initiate or dimerize. Therefore, pTsCl results in a fast initiation, which establishes a fast equilibrium between the dormant and active species, thus leading to a controlled polymerization. This is clearly reflected in the narrow MWDs of the poly(tBMA) initiated by pTsCl, indicating that all of the chains are initiated simultaneously during the initiation stage of the polymerization.

Trichloroethanol (TCE) was also used as an initiator for polymerization of tBMA with CuCl/PMDETA catalyst system to further verify the importance of fast initiation in controlled polymerization of tBMA. Destarac[32] showed that using TCE as initiator resulted in a fast and nearly quantitative initiation of MMA using a CuCl/bpy catalyst system. Polymerization of tBMA using TCE/CuCl/PMDETA initiator catalyst system led to low PDI and controlled molecular weight (entry 4, Table 2).

Synthesis of Block Copolymers. The synthetic strategy to prepare model triblock (A−B−A) ionomer precursors is given in Scheme 2. The scheme involves two steps: (1) synthesis of living difunctional PMMA macroinitiators with well-controlled molecular weight and PDI and (2) copolymerization with tBMA to obtain triblock copolymers. The most important aspect of these polymerizations is that the selected reaction conditions result in living PMMA macroinitiators, which successfully initiate tBMA polymerization, leading to block copolymers with controlled molecular weight and low PDI.

Difunctional PMMA Macroinitiators. MMA was polymerized in toluene with a difunctional initiator, CuBr, and PMDETA catalyst system at 90 °C via ATRP in 30 vol % toluene solution. The choice of bromine initiator was due to the easy synthetic accessibility of the difunctional bromine initiator by a simple coupling reaction between ethylene glycol and 2-bromoisobutyryl bromide (BIBB). The kinetic plots of $\ln([M]_0/[M])$ vs reaction time (t) and monomer conversion vs reaction time for the ATRP of MMA using this system are shown in Figure 4. The plots are linear up to 80% conversion, indicating that the number of propagating species is constant during polymerization. It is necessary to stop the reaction around 90% conversion to maintain high chain-end functionality. Table 3 summarizes the results of the macroinitiator synthesis. Fast polymerizations and a good correlation between the theoretical (from conversion measurements) and experimental (from SEC analysis) molecular weight indicates high initiation efficiency. PDI was between 1.2 and 1.3 under these heterogeneous catalyst[38] conditions due to the low solubility of Cu^{II} species (deactivator in ATRP equilib-

Scheme 2. Synthetic Strategy for Methyl Methacrylate and *tert*-butyl Methacrylate Block Copolymers

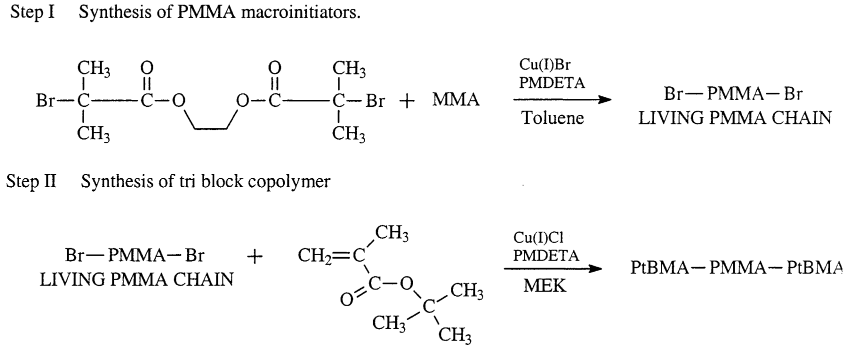


Table 3. ATRP of MMA Initiated by the Difunctional Initiator Catalyzed by the CuBr/PMDETA System: Preparation of Difunctional Macroinitiators

		reaction	conversion	theoretical	experimental		
expt	M:I:Cu:L	time (min)	(%)	M_n [a]	M_n[b]	M_w	PDI
MD15	150:1:1:1	170	94	14500	15900	20500	1.25
MD8	80:1:1:1	140	85	7200	8000	10100	1.27
MD6	60:1:1:1	125	95	6200	6000	7800	1.25
MD4[c]	40:1:1:1	100	88	3800	4100	5500	1.31
MD2[c]	20:1:1:1	110	80	2050	2600	3500	1.32

[a] M_w initiator + 100 ($[MMA]_0/[I]_0$ × conversion). [b] From SEC analysis in THF using universal calibration for PMMA with PS standards. [c] Additional toluene and Cu(II) are added to dilute the radical concentration.

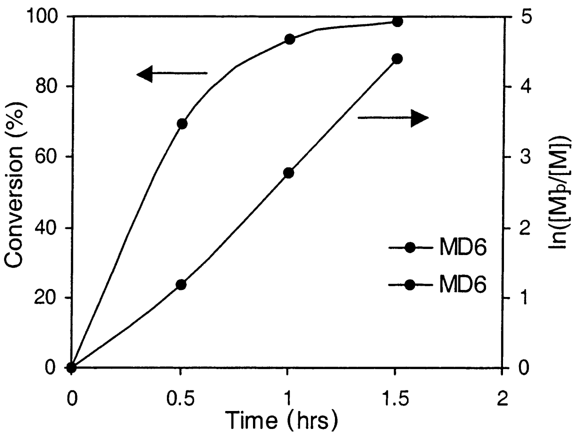


Figure 4. Plots of $\ln([M]_0/[M])$ vs reaction time and monomer conversion vs time for the ATRP of MMA in toluene at 90 °C. $[\text{Initiator}]_0 = [\text{CuBr}]_0 = [\text{PMDETA}]_0 = 0.107$ M, $[\text{MMA}]_0 = 6.443$ M.

rium). For low molecular weight PMMA macroinitiators (coded as MD4 and MD2) polymerizations were done in 50 vol % toluene to decrease the initiator and catalyst concentration. This will reduce the high initial radical concentration, thereby suppressing excessive termination reactions.

ATRP Initiated by PMMA Macroinitiators. Chain Extension with MMA. The prepared polymers were used as macroinitiators for block copolymerizations. The resulting molecular weights and polydispersities are summarized in Table 4. The halogen exchange[34] technique was used for all polymerizations to improve the macroinitiator efficiency. Recent studies have used Cu^{I} chloride complexed with simple linear amine ligands in conjunction with bromo-terminated macroinitiators to successfully prepare several block copolymers.[34] This is due to the fact that the Br group initially provides a fast initiation, but the replacement of the bromine atom at the chain end by chlorine shortly after the polymerization is started suppresses undesirable secondary reactions by decreasing the radical concentration, while the initiation remains fast compared to propagation. Methyl ethyl ketone was used as solvent to increase the solubility of the Cu^{II} complex (deactivator) to obtain a good control on the PDI. The living character of the polymerization is demonstrated by chain extension of MD4 by MMA (entry MM4M in Table 4). Figure 5a shows the SEC traces of MD4 and the chain extended macroinitiator MM4M. The clear shift of the SEC peak of MM4M to shorter retention times and the absence of a tail or shoulder at higher retention times show that the efficiency of the macroinitiator is high, which is characteristic of a living polymerization. The theoretical molecular weight matches well with the experimental molecular weight.

Copolymerization with tBMA. Copolymerizations with *tert*-butyl methacrylate were performed to obtain triblock copolymers with a range of molecular weights (Table 4). Low molecular weight tBMA blocks were targeted since ionomers with a high mole percentage of ionic groups are difficult to process due to strong ionic interactions.[2] Figure 5b shows the SEC traces of MD6 and the triblock copolymer BM6B. The SEC traces are unimodal and symmetrical, and there is very little tailing to lower molecular weights in the block copolymer trace, which could have been indicative of unreacted macroinitiator. The large overlap of the SEC peaks is due to the lower targeted molecular weight of the tBMA block. The measured molecular weights are not absolute molecular weights, since the hydrodynamic volume of the block copolymer may differ considerably from the corresponding PMMA macroinitiators in THF solution. However, there is a relatively good agreement between the theoretical molecular weights and experimental molecular weight values as measured by SEC with universal calibration curve for PMMA (Mark–Houwink–Sakurada constants[25] for PMMA: $K = 9.4 \times 10^{-4}$ dL g^{-1}, $a = 0.719$) based on linear PS standards. Polymerization was stopped before 100% conversion of monomer to avoid side reactions, which could lead to high PDI. The block copolymers were purified, dried, and analyzed by ^{1}H NMR to verify incorporation of the

Table 4. Summary of ATR Block Copolymerizations of TBMA Initiated by PMMA Macroinitiators Catalyzed by CuCl/PMDETA[a] in Methyl Ethyl Ketone (Temperature of Reaction = 90 °C; Macroinitiator:MEK = 1:2 (Weight Ratio)

expt	macro-initiator	mol wt (PDI)	DP[c] of second block [reaction time (min), conversion (%)]	theor M_n [d] of block PMMA/PtBMA	exptl M_n [e] of PMMA/PtBMA	MW's from GPC		mol % of tBMA from FTIR
						M_n	PDI	
MM4M	MD4	4100 (1.31)	30 [120, 85]	3000 (PMMA)	2700	6800	1.28	NA
BM6B[b]	MD6	6000 (1.25)	28 [180, 72]	1800 (PtBMA)	2200	8200	1.20	21.3
BM8B	MD8	8000 (1.27)	28 [150, 73]	2400 (PtBMA)	2700	10700	1.31	23.0
BM15B	MD15	15900 (1.25)	28 [240, 80]	3090 (PtBMA)	3100	19000	1.35	16.2
BM7B	MD7	7300 (1.25)	42 [180, 56]	3370 (PtBMA)	4300	11600	1.35	28.2
BM2B	MD2	2600 (1.32)	28 [120, 74]	3100 (PtBMA)	3400	6000	1.39	52

[a] I:Cu(I)Cl:PMDETA = 1:1:1. [b] Where B is PtBMA and M is PMMA. [c] DP is targetted degree of polymerization of the second block PMMA or PtBMA. [d] (Monomer MW)($[M]_0/[I]_0$ × conversion). [e] From SEC analysis in THF using universal calibration for PMMA with PS standards.

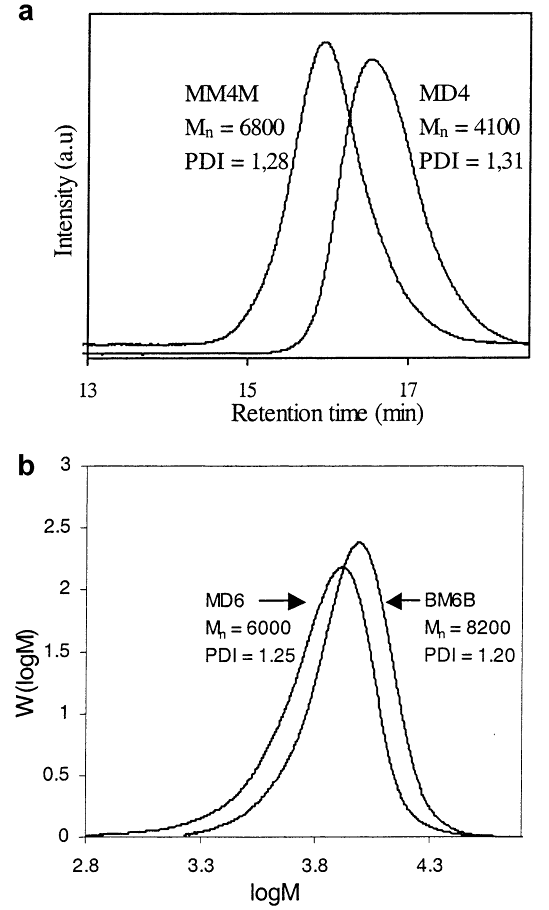


Figure 5. (a) SEC traces of macroinitiator MD4 (difunctional PMMA macroinitiator; M_n = 4100, PDI = 1.31) and MM4M (chain extended PMMA using MD4 as macroinitiator; M_n = 6800, PDI = 1.28). $[PMMA-Br]_0 = [CuCl]_0 = [PMDETA]_0$ = 0.124 mol/L; $[MMA]_0$ = 3.71 mol/L. (b) SEC traces of macroinitiator MD6 (difunctional PMMA macroinitiator; M_n = 6000, PDI = 1.25) and block copolymer BM6B (triblock with PMMA middle block of molecular weight 6000 and PtBMA outer blocks; M_n = 8200, PDI = 1.20). $[PMMA-Br]_0 = [CuCl]_0 = [PMDETA]_0 = 0.04 \times 10^{-2}$ mol/L; $[tBMA]_0$ = 0.946 mol/L.

tBMA monomer. Partial NMR spectra of a macroinitiator and a block copolymer are shown in Figure 6. The peak at 1.4 ppm verifies the incorporation of the *tert*-butyl group in the block copolymers. The α-methyl protons are observed at 0.8−1.2 ppm, and methylene protons from backbone are seen at 1.7−3.1 ppm. The sharp peak at 1.62 ppm is due to water present in the deuterated chloroform.

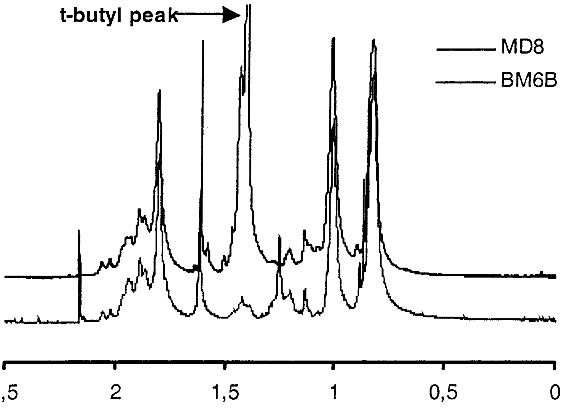


Figure 6. Partial NMR spectra of macroinitiator MD8 (difunctional PMMA macroinitiator with M_n = 8000) and block copolymer BM8B (triblock with PMMA middle block of molecular weight 8000 and PtBMA outer blocks).

Chemical Composition of Block Copolymers: FTIR Analysis. NMR spectra cannot be used to determine the composition of the block copolymers because of the very similar backbone structure of the polymers, which leads to overlap of the signals, especially in the *tert*-butyl group region. Therefore, the chemical composition of the block copolymers was determined by FTIR spectroscopy. Horace[39] reported on the characteristic infrared absorptions of the *tert*-butoxy group present in various organic molecules. The spectrum can be divided into four spectral regions, i.e., 720−770, 820−920, 1000−1040, and 1155−1200 cm^{-1}. The 820−920 cm^{-1} absorptions originate from the skeletal vibration of the *tert*-butoxy group.[39] The absorption at 847 cm^{-1} can be assigned to the above-mentioned skeletal vibration in the FTIR spectrum of PtBMA. Since this band is well-resolved and separated in the block copolymer spectrum, we used this peak to estimate mole percentage of the tBMA in the block copolymer. Table 4 lists the mole percentage of tBMA for the various block copolymers. It is evident that a broad range of tBMA composition is incorporated in the block copolymers.

GPEC Analysis of Block Copolymers. Characterization techniques such as NMR and IR can give information about the overall chemical composition of copolymers but cannot distinguish between a polymer blend and a copolymer with the same overall chemical composition. On the other hand, SEC can give an indication of the existence of block copolymer by measuring the increase of the hydrodynamic volume of the copolymer vs the hydrodynamic volume of the macroinitiator. However, SEC cannot be used as a direct proof for the existence, purity, and determination of the chemical composition distribution (CCD) of the block copolymer. High-performance liquid chromatography (HPLC)[40] is an established technique for selective separation and characterization of block and random

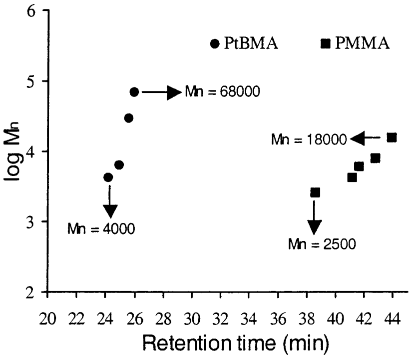


Figure 7. Molar mass dependence of poly(*tert*-butyl methacrylate) (PtBMA, ●, 4000, 6300, 30 200, 68 000 g/mol) and poly(methyl methacrylate) (PMMA, ■, 2500, 4300, 6000, 8000, 18 000 g/mol) homopolymers on the retention time in the GPEC under heptane–THF (2%/min) gradient on silica column.

copolymers. Separation of polymers in HPLC is based on a combination of adsorption/partitioning, precipitation/redissolution, and exclusion effects. Since the contribution of these separate mechanisms can be different in each specific case, we prefer to use the name gradient polymer elution chromatography[41] (GPEC is a registered trademark of Waters Chromatography). In GPEC, separation of polymers is based on differences in column interactions, as is the case in isocratic chromatography, but also on precipitation and redissolution mechanisms as the eluent composition changes gradually in time. Application of GPEC therefore provides the possibility to separate polymeric compounds according to molar mass, chemical composition, and chain(-end) functionality. For example, GPEC recently has been applied to characterize random and block copolymers.[42] In the current study, we used normal phase GPEC with THF and *n*-heptane as eluents. The gradient used is shown in Table 1. The retention times under these chromatographic conditions for a number of PMMA and PtBMA samples prepared via ATRP are shown in Figure 7. The following conclusions are drawn from Figure 7. The molecular weight (M_n) dependency of PMMA on the retention time ranges from 38 min (M_n = 2500) to 44 min (M_n = 18 000). The large dependence of retention time on molecular weight may result in broad peaks for PMMAs with this gradient. Similarly, the molecular weight (M_n) dependency of PtBMA on the retention time ranges from 24 min (M_n = 4000) to 26 min (M_n = 60 000). The two homopolymers are well-separated at all molecular weights, and a retention time difference of 15 min indicates that the effectiveness of the gradient selected is high. PtBMA with its bulky nonpolar ester group elutes first compared to the methyl group of PMMA. The retention time increases with molecular weight and becomes independent of the molecular weight at a certain critical molecular weight that is characteristic of each homopolymer. Although the two homopolymers have different molar mass dependencies, the block copolymer can be separated from the homopolymer. Figure 7 shows that when the retention time is less than 38.5 min PMMA molecules will not elute at this retention time unless the segments are chemically linked to PtBMA as in a (block) copolymer. A difference in the chemical composition of the copolymer leads to a change in retention time of the copolymer, which can be used to establish the block copolymer structure.

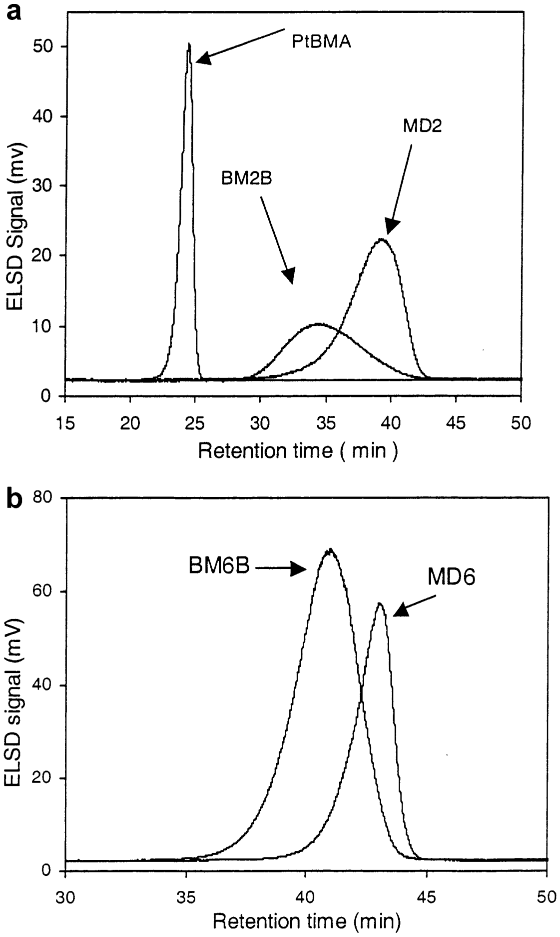


Figure 8. (a) GPEC traces of macroinitiator MD2 (difunctional PMMA macroinitiator with M_n = 2600) and block copolymer BM2B (triblock with PMMA middle block of molecular weight 2600 and PtBMA outer blocks) using heptane–THF gradient (2%/min) on silica column. (b) GPEC traces of macroinitiator MD6 (difunctional PMMA macroinitiator with M_n = 6000) and block copolymer BM6B (triblock with PMMA middle block of molecular weight 6000 and PtBMA outer blocks) using heptane–THF gradient (2%/min) on silica column.

Analysis of Block Copolymers. GPEC traces of BM2B, MD2, BM6B, and MD6 are shown in Figure 8a,b. The presence of the block copolymer peak in between the peaks of two homopolymers is a clear evidence for the block copolymer formation. The retention time of the block copolymer compared to the macroinitiator is lowered and shifted toward the PtBMA homopolymer even though the molecular weight of the block is higher. The difference in the elution behavior is a direct indication of chemical composition difference between the macroinitiator and block copolymer. The sensitivity of the GPEC technique is evident from the elution behavior of BM6B and MD6 in SEC and GPEC, respectively (Figures 5b and 8b). In GPEC, the peaks from the block copolymer and the macroinitiator are well-resolved. The relative shift in the retention time of the block copolymer compared to the corresponding macroinitiator is dependent on the chemical composition (mole percentage of tBMA) of the block copolymer.

Effect of Block Copolymer Reaction Conditions. GPEC Study. There are two factors that govern the success of block copolymer synthesis using ATRP: chain-end functionality and cross-propagation efficiency.[43] Efficient cross-propagation depends on relative reactivity ratios, propagation rate constants, and equilibrium constants of both macroinitiator and growing chains. When well-matched,[44] the molecular weights of

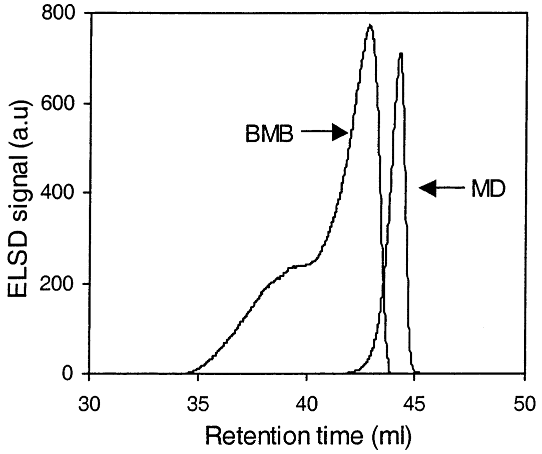


Figure 9. GPEC traces of macroinitiator MD and block copolymer BMB (difunctional PMMA macroinitiator) and block copolymer BMB (triblock with PMMA middle block and PtBMA outer blocks) using heptane−THF gradient (2%/min) on silica column.

the polymers will be predictable with low polydispersity indexes. If the above conditions are not met, initiation will be slower than propagation, resulting in a nonuniform length of the PtBMA block and heterogeneities in the block copolymer. The halogen exchange technique, i.e., R−Br/CuCl, improves the cross-propagation efficiency, resulting in better control of the polymerization. The developed GPEC technique is very sensitive for this block length distribution, i.e., the distribution of the PtBMA block length in the copolymer. Figure 9 shows the GPEC traces of the macroinitiator and block copolymer synthesized by ATRP where no halogen exchange technique is used; i.e., CuBr is used as a catalyst rather than CuCl. Though the peak position is shifted toward a lower retention time, the bimodal, asymmetrical peak demonstrates that the polymerization is poorly controlled. SEC analysis gave a unimodal and symmetrical peak for this block copolymer (not shown here). For the first time we demonstrate qualitatively the use of the GPEC technique to study the influence of macroinitiator initiation on the block copolymer structure.

Conclusions

The results of the heterogeneous atom transfer radical polymerization of tBMA indicate that the selection of the initiator is an important factor to obtain poly(tBMA) with well-defined molecular weights and low PDI. *p*-Toluenesulfonyl chloride and trichloroethanol were efficient initiators due to higher initiation rates compared to the propagation rate. Dibromo-functionalized living PMMA macroinitiators synthesized using a CuBr/PMDETA catalyst system successfully initiates the tBMA polymerization, resulting in triblock copolymers with controlled molecular weight and narrow molecular weight distribution. PMMA macroinitiators were more effective than the corresponding EBriB initiator in tBMA polymerization. The spectroscopic and chromatographic results of the copolymers reveal the effectiveness of the halogen exchange technique used in the block copolymer synthesis to achieve high macroinitiator efficiency. GPEC analysis of the block copolymers confirms the presence of the block copolymer structure and shows that macroinitiator efficiency is high. The selectivity of the gradient in GPEC to PtBMA length in the block copolymer enables to measure the chemical composition distribution of the block copolymers. GPEC might be effectively used to study the influence of copolymerization reaction conditions on the resulting block copolymer structure. GPEC separation of block copolymers can be improved by optimizing gradient shape and steepness, resulting in quantitative analysis of the block copolymer. These precursor materials can be selectively hydrolyzed and neutralized with metal salts to obtain well-defined block ionomers.

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Supporting Information Available: FTIR spectra of PMMA and PtBMA, calibration curve for percentage tBMA content in block copolymer, plot of $\ln([M]_0/[M])$ vs reaction time for ATRP of tBMA, FTIR spectra of BM6B, GPEC traces of MD4, and schematic plot of gradient (heptane, THF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) See, e.g.: Eisenberg, A.; King, M. *Ion Containing Polymers*; Halsted-Wiley: New York, 1975.
(2) Eisenberg, A.; Kim, J. S. *Introduction to Ionomers*; John Wiley & Sons: New York, 1998.
(3) Tant, M. R., Mauritz, K. A., Wilkes, G. L., Eds.; *Ionomers: Synthesis, Structure, Properties and Applications*, Blackie Academic and Professional: London, 1997.
(4) Schlick, S., Ed.; *Ionomers: Characterization, Theory, and Applications*; CRC Press: Boca Raton, FL, 1996.
(5) Eisenberg, A.; Navratil, M. *Macromolecules* **1974**, *7*, 90.
(6) Hara, M.; Jar, P.; Sauer, J. A. *Polymer* **1991**, *32*, 1622.
(7) Ma, X.; Sauer, J. A.; Hara, M. *Macromolecules* **1995**, *28*, 3953.
(8) Jerome, R.; Broze, G. *Rubber Chem. Technol.* **1985**, *58*, 223.
(9) Feng, D.; Venkateshwaran, L.; Wilkes, G. L.; Stark, J. E.; Leir. C. M. *J. Appl. Polym. Sci.* **1989**, *37*, 1549.
(10) Reporter, C. D.; Long, T. E.; McGrath, J. E. *Polym. Int.* **1994**, *33*, 205.
(11) Venkateshwaran, L. N.; York, G. A.; De Porter, C. D.; McGrath, J. E.; Wilkes, G. L. *Polymer* **1992**, *33*, 2277.
(12) Haddleton, D. M.; Muir, A. V. G.; Richards, S. N. In *Macromolecular Design of Polymeric Materials*; Hatada, K., Kitamyama, T., Vogl, O., Eds.; Marcel Dekker: New York, 1997; p 123.
(13) Solomon, D. H.; Rizzardo, E. Eur. Pat. Appl. 135 280 A2, 1985.
(14) Wang, J. S.; Matyjaszweski, K. *Macromolecules* **1995**, *28*, 7901.
(15) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(16) Chiefari, J. Y. K.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P. T.; Mayadunne, T. R A.; Meijs, G. F.; Moad, G. *Macromolecules* **1998**, *31*, 5559.
(17) Heise, A.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 8647.
(18) Davis, K. A.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 4039.
(19) Zhang, X.; Xia, J.; Matyjaszewski, K. *Poly. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1999**, *40* (2), 440.
(20) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. M.; Kukulji, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110.
(21) Moschogianni, P.; Pispas, S.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 650.
(22) Mengel, C.; Meyer, W. H.; Wegner, G. *Macromol. Chem. Phys.* **2001**, *202*, 1138.
(23) Rager, T.; Meyer, W. H.; Wegner, G. *Macromol. Chem. Phys.* **1999**, *200*, 1672.
(24) Busse, K.; Kressler, J.; Van Eck, D.; Horing, S. *Macromolecules* **2002**, *35*, 178.
(25) Beuermann, S.; Paquet, D. A., Jr.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.

(26) Coleman, M. M.; Painter, P. C. J. *Macromol. Sci., Rev. Macromol. Chem.* **1978**, *C16*, 1975.

(27) Williams, H. L.; Han K. *J. Appl. Polym. Sci.* **1989**, *38*, 73.

(28) Staal, W. J. Ph.D. Thesis, Eindhoven University of Technology, Eindhoven, The Netherlands, 1996.

(29) Matyjaszewski, K.; Wang, J. L.; Grimaud, T.; Shipp, D. A. *Macromolecules* **1998**, *31*, 1527.

(30) Kroll, R.; Eschbaumer, C.; Schubert, U. S.; Buchmeister, M. R.; Wurst, K. *Macromol. Chem. Phys.* **2001**, *202*, 645.

(31) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.

(32) Destarac, M.; Matyjaszewski, K.; Boutevin, B. *Macromol. Chem. Phys.* **2000**, *201*, 265.

(33) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 337.

(34) Matyjaszewski, K.; Shipp, D. A.; Wang, J. L.; Grimaud, T.; Patten, T. E. *Macromolecules* **1998**, *31*, 6836.

(35) Chambard, G.; Klumperman, B.; German, A. L. *Macromolecules* **2000**, *33*, 4417.

(36) Percec, V.; Barboiu, B.; Kim, H, J. *J. Am. Chem. Soc.* **1998**, *120*, 305.

(37) Percec, V.; Barboiu, B.; Bera, K. T.; Sluis, M.; Grubbs, R. B.; Frechet, M. J. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4776.

(38) Snijder, A.; Klumperman, B.; van der Linde, R. *Macromolecules* **2002**, *35*, 4785.

(39) Ory, H. A. *Anal. Chem.* **1960**, *32*, 509.

(40) Katz, E.; Eksteen, R.; Schoenmakers, P.; Miller, N. *Handbook of HPLC*; Marcel Dekker: New York, 1979.

(41) Philipsen, H. J. A.; De Cooker, M. R.; Claessens, H. A.; Klumperman, B.; German, A. L. *J. Chromatogr. A* **1997**, *761*, 147.

(42) Cools, P. J. C. H.; Maesen, F.; Klumperman, B.; van Herk, A. M.; German, A. L. *J. Chromatogr. A* **1996**, *736*, 125.

(43) Robin, S.; Gnanou, Y. *Controlled Radical Polymerization: Progress in ATRP, NMP and RAFT*; American Chemical Society: Washington, DC, 2000; Vol. 768, p 334.

(44) Davis, K. A.; Matyjaszewski, K. *Macromolecules* **2001**, *34*, 2101.

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