"Controlled" Synthesis and Characterization of High Molecular Weight Methyl Methacrylate/*tert*-Butyl Methacrylate Diblock Copolymers via ATRP

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ABSTRACT: Atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) using CuCl/*N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetramine (HMTETA) as a catalyst system with 2,2,2-trichloroethanol (TCE) as initiator was investigated. Poly(methyl methacrylate) (PMMA) macroinitiators with defined molecular weight, low polydispersity index (PDI), and a high end-group functionality were obtained. These PMMA macroinitiators successfully initiate block copolymerization of *tert*-butyl methacrylate (tBMA), resulting in poly(MMA-*b*-tBMA) diblock copolymers with low PDI for a range of tBMA block lengths. Gradient polymer elution chromatography (GPEC) was used to confirm the block copolymer structure. Furthermore, the effect of molecular weight of the macroinitiator, nature of catalyst system (heterogeneous/homogeneous), and the amount of solvent on the degree of control achieved in the block copolymerization was studied. The GPEC technique was successfully used to demonstrate the effect of the aforementioned parameters on the block copolymer structure. In particular, the use of a homogeneous catalyst system, CuBr/4,4′-di-5-nonyl-2,2′-bipyridine (dNbpy), and a large ratio of methyl ethyl ketone (MEK) to PMMA macroinitiator led to the synthesis of well-controlled high molecular weight diblock copolymers. This can be explained by the complete solubility of the Cu(II) complex, the deactivating species in the ATRP mechanism. The use of the dNbpy ligand and the polar solvent (MEK) promotes the homogeneous catalyst conditions. The homogeneous condition leads to efficient activation/deactivation exchange reactions between the growing polymer chains and the dormant polymer chains, resulting in well-controlled block copolymers.

Introduction

Ionomers are polymers bearing a small amount of ionic functionality (such as metal carboxylate groups) covalently bound to the polymer chain. These ionic groups aggregate into nanometer-scale domains, acting as transient physical cross-links.[1] Several properties[2−4] such as the modulus, glass transition temperature, viscosity, melt strength, and fatigue can be influenced dramatically by incorporating ionic cross-links. It is now well established that the physical, mechanical, and viscoelastic properties of the ionomers are strongly dependent on the morphology of the ionomers. The architecture of the ionomer is one of the most important parameters that determine the morphology of the ionomer. 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. McGrath and co-workers used living anionic polymerization to synthesize the PMMA block ionomers,[5,6] where the undertaken synthetic strategy involves the introduction of an ionic block via poly(*tert*-butyl methacrylate) (PtBMA) block (protected form of poly(methacrylic acid) block), which is further hydrolyzed and neutralized to generate the ionic block in the block copolymer. However, the stringent conditions required for the anionic polymerization limit the range of monomers and functionalities that can be used.[7] In recent years, controlled/"living" radical polymerizations, such as stable free radical polymerization (SFRP),[8] atom transfer radical polymerization (ATRP),[9,10] and reversible addition−fragmentation chain transfer[11] (RAFT) polymerization, have widened the opportunities for block copolymer synthesis considerably. This expansion is primarily due to the use of free radical intermediates during the polymerization; thus, a large range of vinyl monomers may be utilized, and the polymerization can take place under less demanding reaction conditions. In a continuous effort of employing controlled radical polymerizations for block copolymer synthesis, we successfully demonstrated the synthesis and characterization[12] of low molecular weight poly(tBMA-*b*-MMA-*b*-tBMA) block copolymers, the precursor materials for triblock ionomers, via ATRP. The CuCl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) heterogeneous catalyst system with the bromine functionalized PMMA macroinitiators and polar solvent methyl ethyl ketone was used in that study.

Block copolymers can be synthesized in two ways. The first one, known as one pot synthesis, consists of the sequential addition of a second monomer to the reaction medium, after nearly complete consumption of the first monomer. The second method involves the isolation and purification of the first polymer, which is utilized as a macroinitiator for the second block. Several research groups[13−18] used ATRP successfully to synthesize block copolymers of methacrylates and acrylates involving these two approaches. However, there are only limited reports in the literature concerning the synthesis of (meth)acrylic block copolymers from high molecular weight (meth)acrylic macroinitiators via ATRP. Jerome et al.[18] reported the synthesis of ABA triblock copoly-

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mers ($M_n \approx$ 90K, 140K, and 156K, from SEC measurements) of methyl methacrylate (MMA, A block) and *n*-butyl acrylate (BA, B block) using the homogeneous $NiBr_2(PPh_3)_2$ ATRP polymerization of MMA with a bromine end-functionalized poly(*n*-butyl acrylate) (PBA-Br, $M_n \approx$ 60K and 105K, from SEC measurements) macroinitiator. The mechanical and viscoelastic properties of these block copolymers were inferior to those of similar block copolymers synthesized by anionic polymerization. The origin of these differences in the properties was related to the polydispersity of the PMMA outer blocks (large diversity in the length of the PMMA outer blocks), arising from the slow initiation of MMA by the PBA−Br macroinitiator used in ATRP. Matyjaszewski et al.[19] synthesized similar high molecular weight ($M_n \approx$ 90K, PDI < 1.35) ABA triblock copolymers utilizing the halogen exchange technique, which improved the cross-propagation between PBA macroinitiators and MMA resulting in better control of molecular weights and PDI. They reported the successful copper-mediated homogeneous (CuCl/dNbpy catalyst) and heterogeneous (CuCl/HMTETA catalyst) ATRP polymerization of MMA with a high molecular weight PBA−Br ($M_n \approx$ 67K) macroinitiator. A lower PDI of the triblock copolymer was obtained with the homogeneous catalyst compared to the heterogeneous catalyst indicating that polymerization is better controlled under homogeneous catalyst conditions. Important conclusions of these studies were that (a) the use of a homogeneous catalyst system coupled with halogen exchange leads to well controlled high molecular weight ABA triblock copolymers of MMA and BA, (b) SEC analysis of the triblock copolymers can not provide a chemical composition distribution of the block copolymers, particularly, in this case, of shorter PMMA outer blocks compared to the middle longer PBA block, and (c) the importance of the analysis of the accurate block copolymer structure, specifically in terms of differences in the chemical composition and its influence on the measured mechanical properties. So far, reports concerning the synthesis of high molecular weight PMMA macroinitiators and their successful initiation of *tert*-butyl methacrylate (tBMA) to obtain high molecular weight poly(MMA-*b*-tBMA) diblocks via ATRP have not been available. Moreover, the chemical composition analysis of such high molecular weight all-methacrylate A−B diblock copolymers with short "B" block lengths has not been reported.

In this paper, we report on the synthesis of highly chlorine end-functionalized poly(methyl methacrylate) (PMMA) macroinitiators with well-defined molecular weight and low polydispersity index (PDI) using a CuCl/HMTETA catalyst system and 2,2,2-trichloroethanol (TCE) as initiator. These PMMA macroinitiators successfully initiate block copolymerizations of *tert*-butyl methacrylate (tBMA), resulting in poly(MMA-*b*-tBMA) diblock copolymers with low PDI for a range of tBMA block lengths. More specifically, 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. Furthermore, the effect of molecular weight of the macroinitiator, nature (heterogeneous/homogeneous) of catalyst system, and the amount of solvent on the degree of control achieved (PDI and the chemical composition of the final block copolymer) in the block copolymerization are presented. Gradient polymer elution chromatography (GPEC) was used to confirm the block copolymer structure. 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 of the precursor block copolymers and corresponding ionomers will be published in a forthcoming paper.

Experimental Section

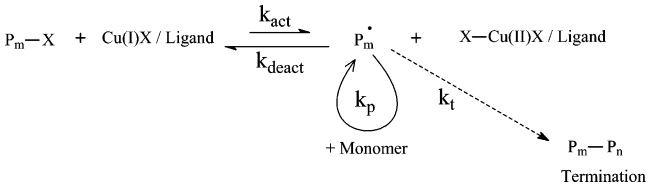
Materials. Methyl methacrylate (Aldrich, 99%), *tert*-butyl methacrylate (Aldrich, 99%), *p*-xylene, and methyl ethyl ketone (Aldrich, 99%) were vacuum-distilled and stored at −15 °C. 2,2,2-Trichloroethanol (98%), butyl acetate (99%), silica (0.04−0.6 mm), *N*,*N*,*N*′,*N*″,*N*‴,*N*‴-hexamethyltriethylenetetramine (HMTETA), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) were obtained from Aldrich and used without further purification. Cu^IBr (99%) and Cu^ICl (99%) were obtained from Aldrich and purified as follows. Copper halides were stirred with glacial acetic acid for 24 h under a nitrogen atmosphere, washed consecutively with glacial acetic acid, ethanol, and diethyl ether, 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[12] 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 auto sampler. An injection volume of 3 μL was used. A temperature range of 40−200 °C was used. 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 PL gel mixed-C (5 μm particles) 300 × 7.5 mm columns (40 °C). A flow rate marker was used to detect and correct for possible small flow rate fluctuations. Data acquisition and processing were performed using the Waters Millennium 32 (v3.05) software. Tetrahydrofuran (THF, Biosolve, stabilized with butylated hydroxytoluene, BHT) was used as eluent at a flow rate of 1.0 mL/min; dilute polymer solutions of 2 mg/mL were made and injected for analysis. The solvent was degassed to avoid any bubble formation during the 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[20] (PMMA: $K = 0.944 \times 10^{-4}$ dL g^{-1}, $a = 0.719$; PS: $K = 1.14 \times 10^{-4}$ dL g^{-1}, $a = 0.716$).

Spectroscopic Analysis. The FTIR spectra were recorded with a BioRad Excalibur 3000 series spectrometer. One hundred scans at a resolution of 4 cm^{-1} were signal-averaged, and the BioRad 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[21] law can be applied. The detailed FTIR procedure and analysis of the data were described previously.[12] 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. Normal phase gradient polymer elution chromatography (NP-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 L/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

Scheme 1. Atom Transfer Radical Polymerization



starting from heptane (volume fraction, $\Phi = 1$; 0 min nonsolvent for the polymers used in analysis) to THF (volume fraction, $\Phi = 1$; 60 min good solvent for the polymers used in analysis) was used. 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. A detailed description of the gradient used was reported previously.[12] HPLC grade 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 volume of 25 μL was used for analysis. Data were acquired and analyzed by the Millenium 32 3.05 software.[22]

Synthetic Procedures. *Synthesis of PMMA Macroinitiators.* CuCl (0.164 g, 1.66 mmol), $CuBr_2$ (0.011 g, 0.08 mmol), HMTETA (0.382 g, 1.66 mmol), *p*-xylene (22.031 g, 0.20 mol), and MMA (20.012 g, 0.2 mol) were charged to a dry 250 mL three-neck round-bottom flask, 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, trichloroethanol (0.481 g, 3.32 mmol) and *p*-xylene (8.012 g, 0.07 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 taken 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, while 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) colored 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.

Synthesis of Block Copolymers. CuBr was used as catalyst for the block copolymer synthesis. The procedure was the same as discussed in the previous section except that a macroinitiator (8.056 g, $M_n = 4200$, 1.90 mmol) and solvent (methyl ethyl ketone, 6.02 mL) were added to the flask initially. Once the macroinitiator was completely dissolved, the monomer (tBMA, 13.429 g, 0.094 mol) was added. The solution was bubbled with argon for 30 min to remove traces of oxygen. In a second, dry 25 mL three-neck round-bottom flask, MEK (6.42 mL), PMDETA (0.332 g, 1.91 mmol), and CuBr (0.275 g, 1.91 mmol) were charged, and the flask was sealed with a rubber septum. This catalyst solution was also bubbled with argon for 30 min to remove traces of oxygen. Finally, the catalyst solution was added via a degassed syringe to the monomer solution and immersed in an oil bath at 90 °C to start the polymerization. Initial and final samples were taken and analyzed for monomer conversion by GC. The obtained block polymer was purified as described above.

Results and Discussion

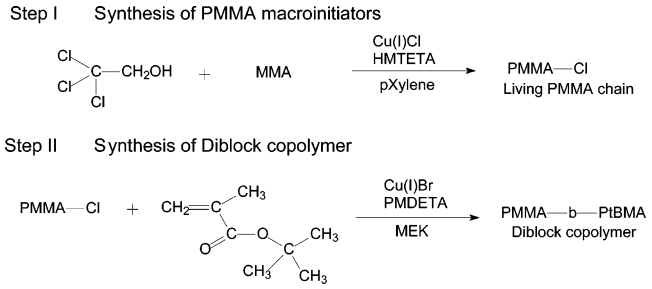
Monofunctional PMMA Macroinitiators. ATRP proceeds via the establishment of a dynamic equilibrium between the active and dormant species as shown in Scheme 1.[9,10] The overall rate of polymerization and the level of control during the polymerization are influenced by several internal variables, such as initiator, catalyst, solvent, ligand, type of transferring halogen (X), and external variables such as temperature.[23,24] The choice of the appropriate initiator/CuX (X = Cl, Br) system is a key parameter, when polymerizing monomers such as MMA with a high equilibrium constant ($K_{eq} \sim 10^{-7}-10^{-6}$), to reduce the termination process (second order with respect to the concentration of radicals) and to establish the dynamic equilibrium between the dormant and active species.[25] This is more important when working with a highly active catalyst system like HMTETA/CuCl. HMTETA 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.[26] MMA was polymerized via ATRP in *p*-xylene with a CuCl and HMTETA catalyst system and trichloroethanol (TCE) as initiator at 90 °C. Only half an equivalent of metal catalyst to initiator was used in solution polymerizations to reduce the radical concentration and the rate of the polymerization. Previously, Destarac et al.[27] showed that the use of 2,2,2-trichloroethanol (TCE) resulted in a fast and nearly quantitative initiation of MMA with a CuCl/bpy catalyst system. TCE was chosen because it is a readily available, fast and efficient initiator. Although three chloride atoms are present per molecule, it is suggested in the literature that only one atom is viable for initiation.[27] The choice for a chloride functional initiator was based on the fact that the ATRP equilibrium constant (K_{eq} for CuCl/TCE/PMDETA $= 3.9 \times 10^{-8}$) is lower than for a bromide-based system.[23,24,28] The lower equilibrium constant may lead to a better controlled polymerization. Furthermore, the more stable chloride bond (R−Cl) may minimize termination reactions at high conversions compared to the less stable bromide bond (R−Br), thereby resulting in highly chlorine end-functionalized PMMA macroinitiators. Snijder et al.[28] showed by electron spin resonance spectroscopy measurements that the ceiling concentration of $Cu^{II}Cl_2$ (CuCl/TCE/PMDETA system) is higher than the ceiling concentration of $Cu^{II}Br_2$ (CuBr/ethyl-2-bromo-2-methylpropionate, EBMP/PMDETA system) concentration, which has a positive effect on the degree of control in the polymerization. A higher deactivator concentration minimizes the side reactions at high conversions, resulting in polymers with low polydispersity index. A clear homogeneous polymerization solution was observed under these polymerization conditions. Table 1 summarizes the results of the PMMA macroinitiator synthesis. A good correlation between the theoretical (from conversion measurements) and experimental (from SEC analysis) molecular weight indicates high initiator efficiency at all molecular weights. PDI was between 1.1 and 1.2, which is comparable to a homogeneous ATRP[29] catalytic system based on CuBr/4,4′-di-5-nonyl-2,2′-bypyridine (dNbpy) in conjunction with *p*-toluenesulfonyl chloride. In the case of a low molecular weight macroinitiator (M1, Table 1), $Cu^{II}Cl_2$ was added to reduce the initial radical concentration due to the high initiator-to-monomer ratio. Less solvent (*p*-xylene) was used in the case of high molecular weight macroinitiators (M5-M7, Table 1) to increase the polymerization rate. All polymerizations were stopped around 90% conversion to avoid side reactions at high conversion and to retain high chlorine end functionality.

Table 1. ATRP of MMA Initiated by Trichloroethanol and Catalyzed by CuCl/HMTETA System: Synthesis of Monofunctional Macroinitiators[a]

						experimental M_n[c]	
expt	M:I	*p*-xylene (vol %)	reaction time (h)	conversion (%)	theoretical M_n[b]	M_n	PDI
M1[d]	120:1	61	8	73	4 500	4 200	1.22
M2	200:1	52	9	88	9 000	11 600	1.14
M3	200:1	52	10	88	8 900	12 800	1.15
M4	300:1	52	10	93	14 100	16 700	1.14
M5	1000:1	45	16	81	40 500	38 600	1.20
M6	1500:1	45	18	71	53 300	53 200	1.17
M7	2000:1	35	19	64	64 000	60 900	1.18

[a] Ratio of initiator to catalyst to ligand is 1:0.5:0.5. [b] MW initiator + 100 ([MMA]$_0$/[I]$_0$ × conversion). [c] From SEC analysis in THF using universal calibration for PMMA with PS standards. [d] $Cu^{II}Cl_2$ added to minimize the radical termination.

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



Synthesis of Block Copolymers. The synthetic strategy to prepare diblock (A−B) ionomer precursors is given in Scheme 2. The scheme involves two steps: (1) synthesis of living monofunctional PMMA macroinitiators with well-controlled molecular weight and PDI and (2) copolymerization with tBMA to obtain diblock 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. There are two factors that govern the realization of block copolymer synthesis using ATRP: chain-end functionality and cross-propagation efficiency.[30] Efficient cross-propagation depends on the propagation rate constants and the activation/deactivation equilibrium constants of both macroinitiator and growing chains. When well-matched,[31] the molecular weights of the polymers will be predictable with low polydispersity indices. Low molecular weight tBMA blocks were targeted, since ionomers with a large fraction of ionic groups are difficult to process due to strong ionic interactions.[2] Table 2 summarizes the results of copolymerization of *tert*-butyl methacrylate with PMMA macroinitiators. Block copolymers with a wide range of molecular weights and compositions were synthesized.

Low Molecular Weight Diblocks. The CuBr/PMDETA heterogeneous catalyst system in conjunction with a polar solvent methyl ethyl ketone was used in the block copolymerization of tBMA with low molecular weight PMMA−Cl macroinitiators (M1 to M4, Table 2) to obtain the corresponding diblock copolymers (DB1 to DB4, Table 2). A 1:1 ratio of CuBr to PMDETA and macroinitiator to solvent weight ratio of 1:2 were sufficient to achieve short reaction times (≈3−5 h) and low PDI polymers. The use of a highly active catalyst system (CuBr/PMDETA) and a polar solvent may result in a high cross-propagation efficiency. The use of copper bromide instead of copper chloride as catalyst in the block copolymerization results in lower polydispersity index values. This is due to the better efficiency of bromide in the deactivation step, as also observed by Bengouh[32] in a series of studies on the inhibition of MMA polymerization in DMF. Figure 1a and b shows the SEC traces of M1 (M_n = 4200, PDI = 1.22), diblock DB1 (M_n = 12 500, PDI = 1.30), M3 (M_n = 12 800, PDI = 1.15), and diblock DB3 (M_n = 21 500, PDI = 1.22). The SEC traces are unimodal and symmetrical, except for macroinitiator M3, and there is hardly any tail towards lower molecular weights in the block copolymer trace, which would have indicated for unreacted macroinitiator. The 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 (from monomer conversion, GC analysis) and the experimental molecular weight values as measured by SEC using the universal calibration curve for PMMA (Mark−Houwink−Sakurada constants[20] 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 (tBMA) to avoid side reactions, which could lead to higher PDI. The block copolymers were purified, dried, and analyzed by ^{1}H NMR to verify the incorporation of the tBMA monomer. The presence of a clear and distinct peak at 1.4 ppm in the NMR spectra of the block copolymer (not shown here) confirms the incorporation of the *tert*-butyl group in the block copolymers.

High Molecular Weight Diblocks. The CuBr/PMDETA catalyst system was also used for the polymerization of tBMA with high molecular weight PMMA macroinitiators (M5 to M7), resulting in corresponding high molecular weight block copolymers (DB5 to DB7). The ratio of the catalyst to initiator was 1:1. The macroinitiator to solvent weight ratio was 1:2 as in the case of the low molecular weight diblock synthesis. The viscosity of the M5 macroinitiator solution (M5) was higher than the (M1−M4) macroinitiator solutions. The reaction was stopped after nearly 4 h because it was not possible to keep the reaction mixture homogeneous with the magnetic stirrer as a result of the high viscosity of the solution. The results of the high molecular weight block copolymers are also summarized in Table 2. Figure 2 shows the SEC traces of macroinitiator (M5) and the resulting diblock copolymer (DB5). The SEC trace of the block copolymer is symmetrical and unimodal and shifted toward a lower retention time compared to the macroinitiator, indicating the increase in molecular weight. However, because of the low targeted degree of polymerization (DP = 105) of the second block

Table 2. Summary of ATR Block (DB*x*) Copolymerizations of TBMA Initiated by PMMA (M*x*) Macroinitiators, and Catalyzed by CuBr in Methyl Ethyl Ketone[a]

expt	macro-initiator	mol wt (PDI)	DP[c] of second block [reaction time (h), conv (%)]	[MEK]/[macroinitiator]	theor M_n[d] of block PtBMA	MW's from GPC[e] M_n	MW's from GPC[e] PDI	mol % of tBMA from FTIR
DB1[b]	M1	4 200 (1.22)	50 [2, 85]	72	10 200	12 500	1.30	38
DB2	M2	11 600 (1.14)	70 [3.5, 82]	160	19 800	19 450	1.23	24
DB3	M3	12 800 (1.15)	70 [3, 86]	180	21 500	21 400	1.22	23
DB4	M4	16 700 (1.14)	70 [5, 73]	280	24 000	24 100	1.20	16
DB5	M5	38 600 (1.20)	105 [5, 31]	1050	NA	45 500	1.28	8
DB6	M6	53 200 (1.17)	105 [3.5, 42]	1500	58 300	59 600	1.25	9
DB7	M6	53 200 (1.17)	176 [3.5, NA]	1500	NA	62 700	1.27	9
DB7-1	M7	60 900 (1.18)	245 [10, NA]	5300	NA	69 700	1.32	<1
DB7-2[f]	M7	60 900 (1.18)	245 [20, NA]	5100	NA	66 700	1.18	<1

[a] Temperature of the reaction = 90 °C. [b] DB1 to DB7 with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) ligand, [MI]:[CuBr]:[PMDETA] = 1:1:1. [c] DP is targeted degree of polymerization of the second block PtBMA. [d] MI + (monomer MW)($[M]_0/[I]_0$ × conversion). [e] From SEC analysis in THF using universal calibration for PMMA with PS standards. [f] Dinonylbipyridine (dNbpy) as ligand, [MI]:[CuBr]:[dNbpy] = 1:3:9.

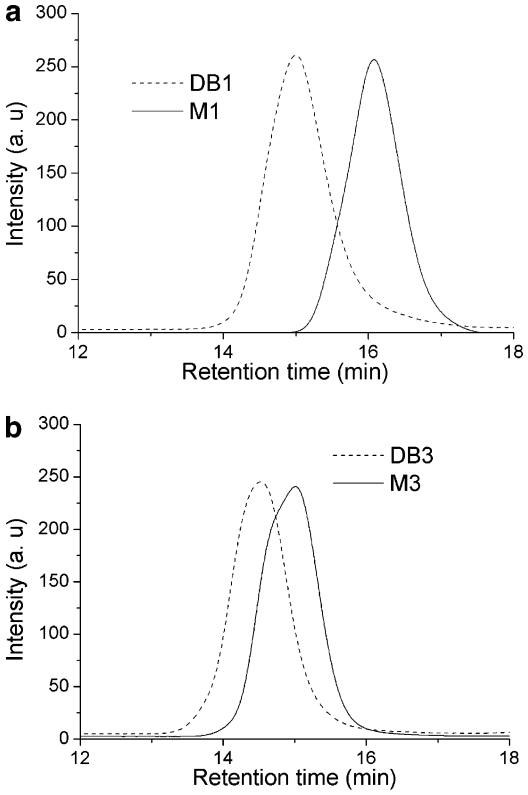


Figure 1. (a) SEC traces of macroinitiator M1 (chlorine functional PMMA macroinitiator; M_n = 4200, PDI = 1.22) and DB1 (diblock copolymer of tBMA using M1 as macroinitiator; M_n = 12 500, PDI = 1.30). $[PMMA-Cl]_0 = [CuBr]_0 = [PMDETA]_0 = 6.85 \times 10^{-2}$ mol/L; $[tBMA]_0 = 3.38$ mol/L. (b) SEC traces of macroinitiator M3 (chlorine functional PMMA macroinitiator; M_n = 12 800, PDI = 1.15), and DB3 (diblock copolymer of tBMA using M3 as macroinitiator; M_n = 21 500, PDI = 1.22). $[PMMA-Cl]_0 = [CuBr]_0 = [PMDETA]_0 = 3.64 \times 10^{-2}$ mol/L; $[tBMA]_0 = 2.57$ mol/L.

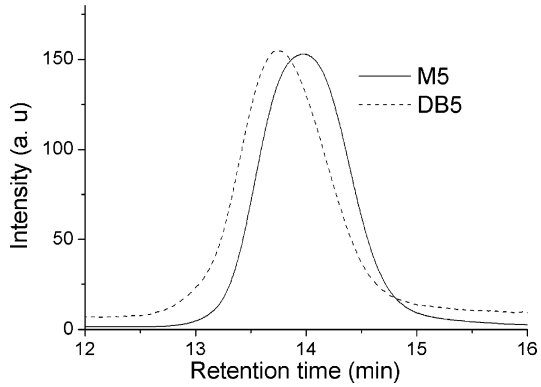


Figure 2. SEC traces of macroinitiator M5 (chlorine functional PMMA macroinitiator; M_n = 38 600, PDI = 1.20) and DB5 (diblock copolymer of tBMA using M5 as macroinitiator; M_n = 45 500, PDI = 1.28). $[PMMA-Cl]_0 = [CuBr]_0 = [PMDETA]_0 = 8.83 \times 10^{-3}$ mol/L; $[tBMA]_0 = 0.933$ mol/L.

(PtBMA), there is only a small increase in the molecular weight of the block copolymer (DB5, M_n = 45 500) compared to the macroinitiator (M5, M_n = 38 600). This leads to large overlap of the two peaks in SEC, providing no further information about the purity of the block copolymer. Similar SEC results were obtained with M6 and DB6. A low PDI was obtained in both cases. To further investigate the structure and purity of the block copolymers, gradient polymer elution chromatography was used.

GPEC Analysis of Block Copolymers. Characterization techniques such as NMR and IR can give information about the overall chemical composition of copolymers but can hardly distinguish between a polymer blend and a copolymer with the same overall chemical composition. In contrast, SEC can give an indication of the existence of a 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 of the block copolymer. Gradient polymer elution chromatography[33] is an established technique for selective separation and characterization of block and random copolymers. In GPEC, separation of polymers is based on differences in column interactions, as is the case of isocratic chromatography, but also on precipitation and redissolution mechanisms as the eluent composition changes gradually in time. Therefore, GPEC separates polymeric compounds according to molecular weight, chemical composition, and chain(-end) functionality. In the current study, we used normal phase GPEC with THF and *n*-heptane as eluents. The gradient used and the details of the GPEC method were explained in depth in a previous publication.[12] The two homopolymers PMMA and PtBMA are well separated with a retention time difference of 15 min at all molecular weights. PtBMA with its bulky nonpolar ester group elutes first compared to PMMA with the methyl ester group. 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.

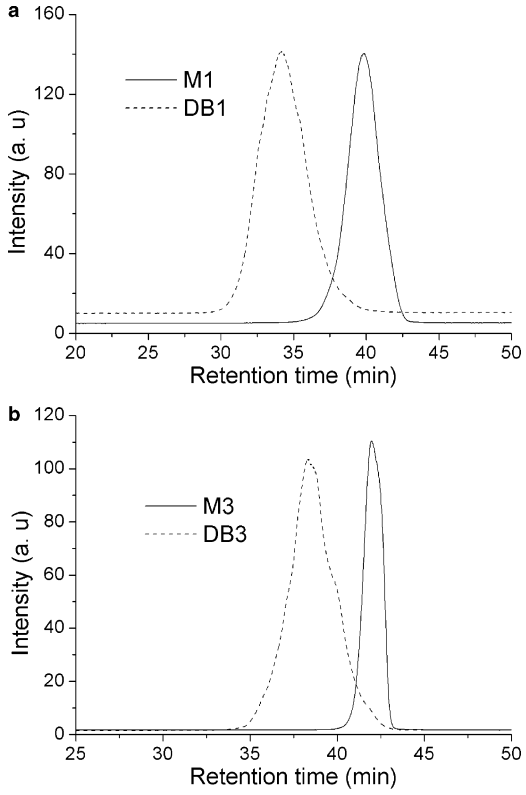


Figure 3. (a) GPEC traces of macroinitiator M1 (chlorine functional PMMA macroinitiator; $M_n = 4200$, PDI = 1.22) and DB1 (diblock copolymer of tBMA using M1 as macroinitiator; $M_n = 12\,500$, PDI = 1.30) using heptane−THF gradient (2%/min) on silica column. (b) GPEC traces of macroinitiator M3 (chlorine functional PMMA macroinitiator; $M_n = 12\,800$, PDI = 1.15) and DB3 (diblock copolymer of tBMA using M3 as macroinitiator; $M_n = 21\,500$, PDI = 1.22) using heptane−THF gradient (2%/min) on silica column.

The GPEC traces of M1, DB1 and M3, DB3 are shown in parts a and b of Figure 3, respectively. The retention time of DB1 is lower than that of the macroinitiator M1 and shifted clearly toward the PtBMA homopolymer. This shift in the peak position is a clear evidence for the block copolymer structure. The absence of tailing in the block copolymer peak clearly indicates the high efficiency of the PMMA macroinitiator in the polymerization of the tBMA. GPEC traces of the high molecular weight macroinitiator (M5) and block copolymer (DB5) are shown in Figure 4. The retention time of the block copolymer is lower than that of M5 even though the molecular weight of the block copolymer is higher. The difference in elution behavior is a direct indication of the chemical composition difference between the macroinitiator and block copolymer. The sensitivity of GPEC compared to that of SEC is evident from the elution behavior of M5 and DB5 in SEC and GPEC, respectively (Figures 2 and 4). In GPEC, the peaks from the block copolymer and the macroinitiator are well-resolved. However, the block copolymer peak in GPEC has two distinct features. The first feature is that part of the peak for the diblock copolymer falls under the macroinitiator peak, which may indicate the presence of a small fraction of dead polymer chains. The second feature is the asymmetric nature of the peak due to the broad chemical composition distribution of the PtBMA in the block copolymer as demonstrated in our earlier studies.[12] This shows that the block polymerization was poorly controlled. Note that a low PDI (1.20) of the

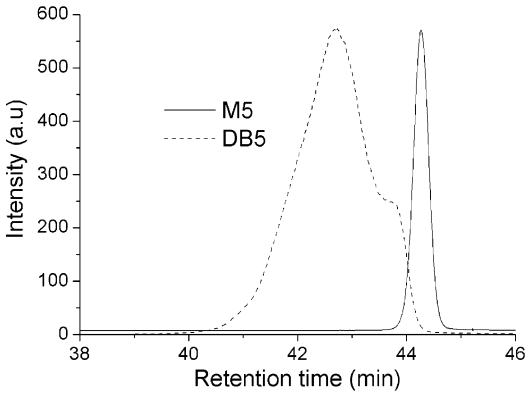


Figure 4. GPEC traces of macroinitiator M5 (chlorine functional PMMA macroinitiator; $M_n = 38\,600$, PDI = 1.20) and DB5 (diblock copolymer of tBMA using M5 as macroinitiator; $M_n = 45\,500$, PDI = 1.28) using heptane−THF gradient (2%/min) on silica column.

block copolymer is obtained by SEC analysis. The origin of the dead material can be due to the following two reasons. The first may be due to termination reactions during the block copolymerization. The second may be due to the presence of a small fraction of nonfunctional (without chlorine end group) macroinitiator in the high molecular weight macroinitiator synthesis (from the macroinitiator step, Scheme 1).

To improve the control of the polymerization and to understand the origin of the observed dead material in GPEC, polymerizations were also done under homogeneous catalyst conditions. Two approaches were considered to obtain homogeneous polymerization conditions. The first approach was to use an excess of polar solvent MEK, which increases the solubility of the CuBr/PMDETA catalyst in the polymerization. The weight ratio of macroinitiator to solvent was increased from the earlier used ratio of 1:2 to 1:6. The result of this experiment is listed in Table 2 (entry 8). The macroinitiator used was M7 ($M_n = 60\,900$), and the corresponding block copolymer was DB7-1. The SEC and GPEC results of M7 and DB7-1 are shown in parts a and b of Figure 5, respectively. Once again, SEC peaks of the macroinitiator and block copolymer are highly overlapping, giving no information about the purity and the chemical composition of the block copolymer. In contrast to SEC analysis, GPEC analysis of the M7 and DB7-1 shows two well-separated peaks, indicating the block copolymer formation. Moreover, the block copolymer peak DB7-1 is unimodal without any shoulder that is present under the macroinitiator peak, in contrast to the GPEC trace of block copolymer DB5 (Figure 4). The improved control over the polymerization is attributed to the nearly homogeneous polymerization conditions obtained using an excess of MEK. The increased solubility of Cu^{II} species under homogeneous conditions effectively deactivates the growing polymer radicals and regulates the polymerization in a better fashion. Note that SEC analysis gives a low PDI of the block copolymer. The second approach of using a completely homogeneous catalyst, namely CuBr/dNbpy, in the polymerization was also carried out with macroinitiator M7. The weight ratio of macroinitiator to solvent was 1:6 as in the case of the DB7-1. A 3 times excess of catalyst was used compared to the concentration of the macroinitiator to counterbalance the low activity of the dNbpy catalyst system. The activity of the ATRP catalyst system is related to its redox potential, which can be

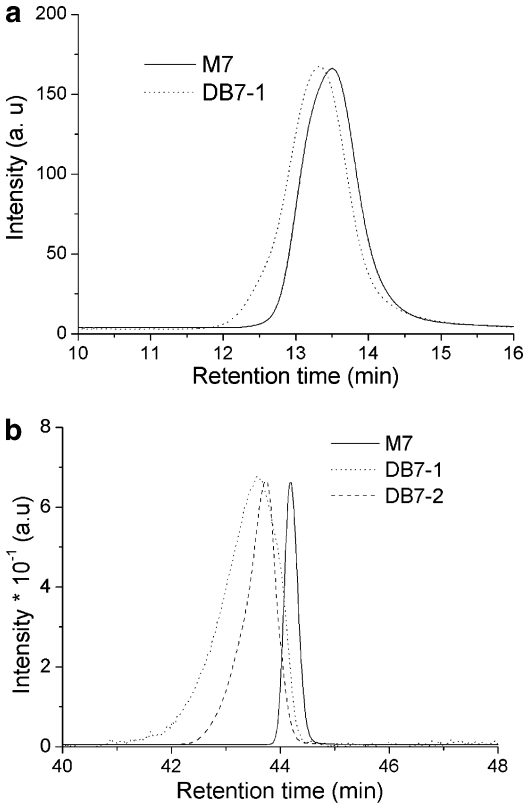


Figure 5. (a) SEC traces of macroinitiator M7 (chlorine functional PMMA macroinitiator; M_n = 60 900, PDI = 1.18) and DM7-1 (diblock copolymer of tBMA using M7 as macroinitiator; M_n = 69 700, PDI = 1.32). $[PMMA-Cl]_0 = [CuBr]_0 = [PMDETA]_0 = 1.95 \times 10^{-3}$ mol/L; $[tBMA]_0 = 0.481$ mol/L. (b) GPEC traces of macroinitiator M7 (chlorine functional PMMA macroinitiator; M_n = 60 900, PDI = 1.18), DM7-1 (diblock copolymer of tBMA using M7 as macroinitiator; M_n = 69 700, PDI = 1.32), and DM7-2 (diblock copolymer of tBMA using M7 as macroinitiator; M_n = 66 700, PDI = 1.18 using heptane−THF gradient (2%/min) on silica column.

measured by cyclic voltametry. Matyjaszewski et al.[34] showed that the redox potential ($E_{1/2}$) of the CuBr/dNbpy complex ($E_{1/2} = -0.060$ V) is higher than the redox potential ($E_{1/2} = -0.075$ V) of the CuBr/PMDETA complex, reflecting the lower activity of the former catalyst complex. The result of this experiment is also listed in Table 2 (entry 9). Longer reaction times (20 h) were required in the dNbpy system compared to the PMDETA catalyst system (10 h), indicating the lower activity of the dNbpy complex, even when using 3 times excess of the catalyst compared to macroinitiator. SEC was again not useful in the analysis of the resulting block copolymer (DB7-2). The result of the GPEC analysis of M7 and DB7-2 is also shown in Figure 5b. Here again, the block copolymer peak is unimodal and shifted clearly toward the lower retention time, revealing the presence of the block copolymer structure. The absence of the shoulder further demonstrates the good control achieved in the polymerization. The difference in the activities of the dNbpy and PMDETA ligand is distinctively seen from the PDI of the resulting block copolymers. A lower PDI (1.18) was observed with dNbpy compared to that of PMDETA (PDI = 1.32) system, indicating the higher rate of deactivation with the dNbpy ligand. This difference clearly demonstrates that a lower number of monomers is inserted per activation−deactivation cycle in the case of the CuBr/dNbpy system compared to the CuBr/PMDETA system. These differences are also reflected in the GPEC traces of the DB7-1 and DB7-2 (see Figure 5b). A broader peak was seen with DB7-1 compared to DB7-2. It was shown in our previous work[12] that the broadness of the peak is related to the distribution of PtBMA block length. The results obtained in this study indicate that homogeneous catalyst conditions are needed in the initiation of high molecular weight PMMA macroinitiators to obtain the corresponding high molecular weight block copolymers with pure block copolymer structure. This is due to the increased solubility of the Cu^{II} species (deactivator in ATRP) during the polymerization. Furthermore, the shoulder observed in the GPEC traces of DB5 and DB6 may originate from possible termination reactions occurring under the observed heterogeneous polymerization conditions (due to the low amount of polar solvent MEK in conjunction with the CuBr/PMDETA catalyst, which results in the limited solubility of the Cu^{II} species). This shoulder is not originating from the nonfunctional macroinitiator from the high molecular weight PMMA macroinitiator synthesis.

Conclusions

The results of the atom transfer radical polymerization of methyl methacrylate using CuCl/*N*,*N*′,*N*″,*N*‴,*N*⁗-hexamethyltriethylenetetramine (HMTETA) catalyst system with 2,2,2-trichloroethanol (TCE) as initiator indicate that poly(methyl methacrylate) (PMMA) macroinitiators with well-defined molecular weight, low polydispersity index (PDI), and high end-group functionality can be obtained. PMMA macroinitiators successfully initiate the block copolymerization of *tert*-butyl methacrylate (tBMA), resulting in poly(MMA-*b*-tBMA) diblock copolymers with low PDI for a range of tBMA block lengths. Gradient polymer elution chromatography (GPEC) was used to confirm the block copolymer structure and was successfully used to demonstrate the effect of molecular weight of the macroinitiator, nature of catalyst system (heterogeneous vs homogeneous), and the amount of solvent on the degree of control achieved in the block copolymerization. In particular, the use of a homogeneous catalyst system, CuBr/4,4′-di-5-nonyl-2,2′-bypyridine (dNbpy), and an excess of methyl ethyl ketone (MEK) as solvent lead to the synthesis of well-controlled high molecular weight diblock copolymers with a short second block length. This can be explained by the complete solubility of the Cu^{II} complex, the deactivating species in the ATRP mechanism due to use of dNbpy ligand and the polar solvent (MEK). The homogeneous catalyst condition results in dynamic activation/deactivation exchange reactions between the growing polymer chains and dormant polymer chains, giving rise to well-controlled block copolymers. GPEC is a powerful complementary technique to SEC in the analysis of block copolymers, especially with a short second block length. The synthesized precursor materials can be selectively hydrolyzed and neutralized with metal salts to obtain well-defined block ionomers.

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