Use of an Immobilized/Soluble Hybrid ATRP Catalyst System for the Preparation of Block Copolymers, Random Copolymers, and Polymers with High Degree of Chain End Functionality

Sung Chul Hong,[†] Jean-François Lutz,[†] Yoshihisa Inoue,[†] Christine Strissel,[†] Oskar Nuyken,[‡] and Krzysztof Matyjaszewski*,[†]

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, and Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

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ABSTRACT: An immobilized/soluble hybrid catalyst system (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) for atom transfer radical polymerization (ATRP) was applied to the preparation of polymers exhibiting various architectures. Polymers with high degree of halogen chain end functionality (~85%) were obtained using the hybrid catalyst system ensuring high efficiency of chain extension reactions through successive monomer addition, affording block (tapered) copolymers. Use of the immobilized catalyst also allowed the synthesis of block copolymers using macroinitiators synthesized by other mechanisms, such as poly(dimethylsiloxane). In the copolymerization of MMA and *n*-butyl acrylate, the molecular weight, molecular weight distribution, kinetics, and reactivity ratios were similar to those in a conventional homogeneous ATRP, indicating the chemical nature of the polymerization intermediates are similar for both systems. These examples demonstrate the broad applicability of the hybrid catalyst system to various ATRP processes.

Introduction

Controlled/"living" radical polymerization (CRP)[1−3] has been developed as an efficient synthetic tool for the nanostructured materials such as block or graft copolymers. Atom transfer radical polymerization (ATRP)[4−7] is one of the most robust CRP methods since it can be applied to polymerization of a wide variety of monomers and provides well-defined polymers.[6,8−11] The foundation of ATRP is the reversible transfer of a radically transferable atom, typically a halogen, from a monomeric or polymeric alkyl (pseudo)halide to a transition metal complex in a lower oxidation state, forming an organic radical and a transition metal complex in a higher oxidation state. The transition metal complexes therefore play a key role in ATRP and have been the subject of many studies, including development of catalyst systems based on various metals[12−16] and ligands.[17−23] However, one of the limitations of ATRP is the presence of a relatively large amount of transition metal catalyst in the polymerization system, which may cause process and environmental issues that commercial manufacturers will have to address.

We have previously reported that a "hybrid" catalyst system can overcome this difficulty. The hybrid catalyst is composed of an immobilized catalyst [24,25] acting in conjunction with a small amount of very active soluble catalyst that accelerates the rate of deactivation of the growing radical.[26,27] The major fraction of the active transition metal complex was immobilized on solid carriers, and the catalyst was successfully removed by simple filtration after the polymerization, resulting in low concentration of residual metal (<20 ppm) in the polymer.

To demonstrate the full utility of this hybrid catalyst system, we prepared polymers with more complex polymeric architectures, including block and gradient copolymers. Several experiments were conducted to clarify the scope of the hybrid catalyst systems, including a study on polymer chain end functionality, the preparation of block copolymers through successive monomer addition, the preparation of block copolymers using macroinitiators, and the preparation of gradient copolymers through copolymerization. Chain end functionality was measured by high-resolution 600 MHz ^{1}H NMR. The efficiency of preparation of block copolymers through successive monomer addition is another way to evaluate the chain end functionality. Block copolymers were prepared either by two subsequent ATRP polymerizations or by switching between two different mechanisms in the presence of the hybrid ATRP catalyst. In the latter case, poly(dimethylsiloxane) (pDMS) macroinitiator was prepared by anionic ring-opening polymerization of hexamethylcyclotrisiloxane (D$_3$) and subsequently functionalized to initiate ATRP.[28−30] Simultaneous copolymerization of MMA and *n*-butyl acrylate (nBA) yielded gradient copolymers, and the kinetic results were compared with those using conventional homogeneous ATRP catalyst systems.[31−33]

Experimental Part

Chemicals. CuBr/4,4′-dimethyl-2,2′-bipyridine (dMbpy) catalysts immobilized on cross-linked polystyrene (CuBr/PS8-dMbpy, 8 μm size, 1.028 × 10^{-3} mol of Cu/g of cat.),[26] tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN),[34] and 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy)[18] were synthesized following previously reported procedures. Methyl methacrylate (MMA, 99%, Aldrich), methyl acrylate (MA, 99%, Aldrich), and *n*-butyl acrylate (nBA, 99%, Acros) were passed through a column filled with neutral alumina to remove inhibitors, dried over CaH$_2$, distilled under reduced pressure, and stored in a freezer under nitrogen. Methyl 2-bromopropionate (98%, Aldrich) was distilled under vacuum prior to use. Allyl 2-bromoisobutyrate

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[†] Carnegie Mellon University.

[‡] Technische Universität München.

* To whom correspondence should be addressed: e-mail: km3b@andrew.cmu.edu.

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and allyl 2-bromopropionate were synthesized according to a published procedure.[29] Hexamethylcyclotrisiloxane (D_3) (98%, Aldrich) was dissolved in benzene and dried over calcium hydride at reflux overnight under nitrogen. After removing the solvent under reduced pressure, the D_3 was sublimed into a Schlenk flask and stored in a drybox at room temperature. *n*-Butyllithium (2.5 M solution in hexanes) and 2-methyl-1,4-naphthoquinone (MeNQ), from Aldrich, were used without further purification. Chlorodimethylsilane (DMSCl, Aldrich) was distilled from calcium hydride and stored in a drybox. The bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)platinum(0) complex in xylene (Karstedt's catalyst, 9.6×10^{-2} mol/L from Gelest) was used as received. Tetrahydrofuran (THF, HPLC grade, Fisher) and toluene (certified grade, Fisher) were freshly distilled from Na/K alloy with benzophenone (99%, Aldrich) and stored under nitrogen. Benzene (99%, Aldrich) was distilled over potassium. Anisole (99%, Aldrich) was distilled from calcium hydride. 1-Phenylethyl bromide (PEBr, 97%, Aldrich), CuBr (99+%, Aldrich), $CuBr_2$ (98%, Aldrich), and all other solvents were used without further purification.

$CuBr_2$/Me_6TREN Stock Solution. A stock solution of $CuBr_2$/Me_6TREN in acetone was freshly prepared prior to use. $CuBr_2$ (5.32 mg, 2.38×10^{-5} mol) was added to a 20 mL glass vial with a rubber septum. The vial was evacuated and backfilled with nitrogen three times. Me_6TREN (6.28 μL, 2.38×10^{-5} mol) and degassed acetone (10 mL) were added to the vial, and the resulting solution was placed in an ultrasonic bath for 5 min to dissolve the complex completely. The light green clear solution (Cu(II): 2.38×10^{-3} mol/L) was obtained and used as a stock solution.

Preparation of Poly(methyl acrylate) for ^{1}H NMR Analysis. The immobilized ATRP catalyst (CuBr/PS8-dMBpy, 150 mg, 1.55×10^{-4} mol of Cu) or the conventional homogeneous ATRP catalyst (CuBr, 22.2 mg, 1.55×10^{-4} mol; dNbpy, 126.6 mg, 3.1×10^{-4} mol) was added to a dry glass tube purged with nitrogen. In the reaction with the supported CuBr/PS8-dMbpy catalyst system, $CuBr_2$/Me_6TREN (0.650 mL, 1.55×10^{-6} mol of Cu in stock solution) was introduced via a degassed syringe. A solution of 1-phenylethyl bromide (PEBr, 28.6 mg, 1.55×10^{-4} mol) in methyl acrylate (1 g, 1.16×10^{-2} mol) was added, and the mixture was heated with stirring to 70 °C. The polymerization was stopped when the copolymerization mixture became viscous. The final polymer was dissolved in THF and filtered through alumina in order to remove catalyst, followed by nearly complete removal of residual monomer under vacuum.

Preparation of Poly(methyl acrylate)-*block*-poly(*n*-butyl acrylate) with a Tapered Structure through Successive Monomer Addition. CuBr/PS8-dMbpy (0.125 g, 9.23×10^{-5} mol of Cu/g of cat.) was placed in a 50 mL Schlenk flask followed by degassing under vacuum and backfilling three times with N_2. A measured amount of degassed monomer (methyl acrylate, MA, 0.80 g, 0.84 mL, 9.23×10^{-3} mol), toluene (0.64 mL), anisole (0.2 mL), and $CuBr_2$/Me_6TREN (9.23×10^{-7} mol, 0.39 mL of the stock solution) was then added to the Schlenk flask. Initiator (2-bromopropionitrile, 12.4×10^{-3} g, 8.02×10^{-3} mL, 9.23×10^{-5} mol) was added, yielding the following molar ratio of reagents: [MA]:[2-bromopropionitrile]:[CuBr/PS8-dMbpy]:[$CuBr_2$/Me_6TREN] = 100:1:1:0.01. The flask was immersed in an oil bath that was preset to a specific reaction temperature (70 °C). After a controlled polymerization time, *n*-butyl acrylate (nBA, 2.15 mL, 1.50×10^{-2} mol; [nBA]:[CuBr/PS8-dMbpy]:[$CuBr_2$/Me_6TREN] = 200:1:0.01) and toluene (2.15 mL) were added to the Schlenk flask, followed by increasing the reaction temperature to 100 °C. Samples were taken from the flask via syringe at timed intervals for kinetic measurements. The samples were diluted with THF and filtered through a Gelman Acrodisc PTFE filter (0.2 μm) for analyses by gas chromatography (GC) and gel permeation chromatography (GPC). The polymerization was terminated by removing the flask from the oil bath and cooling the reaction mixture to room temperature.

Monofunctional Poly(dimethylsiloxane) with Terminal Hydrosilyl Functionality (pDMS−SiH). In a drybox, hexamethylcyclotrisiloxane (D_3, 14.25 g, 63.7×10^{-3} mol), THF (5.3 mL), and toluene (5.3 mL) were introduced to a 50 mL round-bottom flask. The mixture was stirred until a clear, colorless solution was obtained. *n*-Butyllithium (0.28 mL, 7.0×10^{-4} mol) was then added followed by stirring at room temperature for 6 h. The polymerization solution was added dropwise to a solution of chlorodimethylsilane (DMSCl, 0.77 g, 7.0×10^{-3} mol) in 1.0 mL of THF. The heterogeneous white mixture was stirred in the drybox overnight at room temperature. All volatiles, including unreacted D_3, were separated from the polymer by vacuum transfer at 1 mmHg at room temperature. Finally, the salt was removed from the polymer by filtration through a Gelman Acrodisc PTFE syringe filter (0.2 μm). 11.5 g (80%) of a clear, colorless polymer was obtained. ^{1}H NMR ($CDCl_3$) δ (ppm) : 4.73 (s, 1H, Si−**H**), 1.33 (m, 4H, $CH_3-C\mathbf{H}_2-C\mathbf{H}_2$), 0.92 (t, 3H, $C\mathbf{H}_3-CH_2$), 0.58 (m, 2H, $C\mathbf{H}_2-Si$), 0.11 (s, 6H, $Si-C\mathbf{H}_3$). Integration of *n*-butyllithium methyl group (0.92 ppm) and the hydrosilyl proton (4.73 ppm) indicated that functionality was 97%.

Preparation of Poly(dimethylsiloxane) (pDMS) Macroinitiators. The pDMS macroinitiators were synthesized by conducting a hydrosilylation reaction in the presence of 2-methyl-1,4-naphthoquinone (MeNQ).[35] Monofunctional hydrosilyl terminal pDMS (6.0 g, 1.0×10^{-3} mol, $M_n = 5800$ g/mol, $M_w/M_n = 1.16$), allyl 2-bromoisobutyrate (1.16 g, 6.0×10^{-3} mol), and 10 mL of degassed toluene were placed in a 50 mL round-bottom flask sealed with a septum. The solution was deoxygenated by purging with argon for 15 min at room temperature. MeNQ (1.9 mg, 1.1×10^{-5} mol) and degassed toluene (1 mL) were placed into a scintillation vial and stirred until a homogeneous yellow solution is formed. After bubbling with nitrogen for 30 min, Karstedt's catalyst (5.6 μL, 5.4×10^{-6} mol) was added, and the solution was transferred to the reaction mixture via cannula. The flask was placed in an oil bath set at 70 °C, and the reaction mixture was stirred under argon overnight. The polymer was precipitated by adding the yellowish solution to 200 mL of methanol, and the slurry was stirred vigorously for 20 min. The stirring was stopped, allowing the pDMS to settle to the bottom of the beaker. The liquid was then decanted from the pDMS, which was stirred with 200 mL of fresh methanol for an additional 20 min. The pDMS was allowed to settle, and the methanol was again decanted. The product was dissolved in 10 mL of hexanes and transferred to a vial followed by removal of the solvents using rotary evaporator. The resulting colorless liquid was dried under vacuum (1 mmHg) at 60 °C for 12 h. Yield = 5.8 g (92%) (colorless liquid). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.06 (t, 2H, $O-C\mathbf{H}_2$), 1.86 (s, 6H, $C(Br)-(C\mathbf{H}_3)_2$), 1.61 (m, 2H, $C\mathbf{H}_2-CH_2-O$), 1.23 (m, 4H, $CH_3-(C\mathbf{H}_2)_2-$), 0.89 (t, 3H, $C\mathbf{H}_3-(CH_2)_2-$) 0.55 (m, 4H, $Si-C\mathbf{H}_2$), 0.08 (6H, s, $Si-C\mathbf{H}_3$). The functionality was determined to be 85% by the integrations of *n*-butyllithium methyl group (0.89 ppm) and the methyl group of the 2-bromoisobutyrate (1.86 ppm).

A similar reaction was used to synthesize allyl 2-bromopropionate functionalized macroinitiator using allyl 2-bromopropionate instead of allyl 2-bromoisobutyrate. A higher molecular weight pDMS was used for this reaction ($M_n = 8800$ g/mol, $M_w/M_n = 1.14$). Yield = 4.7 g (93%). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.34 (1H, q, $C\mathbf{H}-(CH_3)$), 4.10 (t, 2H, $O-C\mathbf{H}_2$), 1.80 (s, 3H, $CH(Br)-(C\mathbf{H}_3)$), 1.66 (m, 2H, $C\mathbf{H}_2-CH_2-O$), 1.30 (m, 4H, $CH_3-(C\mathbf{H}_2)_2$), 0.89 (t, 3H, $C\mathbf{H}_3-(CH_2)_2$) 0.56 (m, 4H, $Si-C\mathbf{H}_2$), 0.08 ppm (6H, s, $Si-C\mathbf{H}_3$). The functionality was determined to be 90% by the integration of *n*-butyllithium methyl group (0.89 ppm) and the methyl group of the 2-bromopropionate (1.80 ppm).

Polymerization of Methyl Methacrylate Using a pDMS Macroinitiator. The pDMS macroinitiator (0.33 g, 5.0×10^{-5} mol, $M_n = 6600$ g/mol) and $CuBr_2$/Me_6TREN (5.0×10^{-7} mol of Cu, 0.21 mL of the stock solution in acetone) were introduced to a Schlenk flask equipped with a magnetic stirring bar under nitrogen. The flask was degassed three times by freeze/pump/thaw cycles. Separately, monomer and toluene were deoxygenated by purging with nitrogen for 1 h. The immobilized catalyst (CuBr/PS8-dMbpy, 0.049 g, 5.0×10^{-5} mol of Cu) was added to a vial in a drybox and suspended in 1.06 mL of degassed toluene. The catalyst was transferred to the reaction flask via cannula. 1.06 mL of MMA was added to the flask by syringe to start the polymerization. Samples were taken periodically via a syringe and filtered through 0.2 μm Gelman Acrodisc PTFE filter for kinetic and molecular weight analysis.

Methyl Methacrylate and *n*-Butyl Acrylate Random Copolymerization. CuBr/PS8-dMbpy (32.8 mg, 3.37×10^{-5} mol of Cu) was added to 25 mL Schlenk flask equipped with a stirring bar under nitrogen. A mixture of MMA (0.541 mL, 5.06×10^{-3} mol), nBA (0.725 mL, 5.06×10^{-3} mol), toluene (1.17 mL), and anisole (0.10 mL) were added to this flask after deoxygenating by bubbling with nitrogen for 30 min. The volume ratio of (MMA + nBA)/(toluene + anisole) was kept 1/1 for all experiments. $CuBr_2/Me_6TREN$ (5.24×10^{-7} mol of Cu) and methyl 2-bromopropionate (3.37×10^{-5} mol) were then added to the flask. The resulting mixture was heated to 90 °C and stirred for 6 h. During the polymerization, samples for kinetic analysis were taken from the flask via a syringe at timed intervals. The samples were diluted with THF followed by filtration through a Gelman Acrodisc 0.2 μm PTFE filter for the analysis by gas chromatography (GC) and gel permeation chromatography (GPC).

Characterization. The ^{1}H NMR spectra used to determine chain end functionality were measured in deuterated acetone at 28 °C using a 600 MHz Bruker Avance DRX 600. The functionality of the pDMS macroinitiator was determined in deuterated chloroform ($CDCl_3$) as a solvent using Bruker 300 MHz ^{1}H NMR. A Shimadzu GC 14-A gas chromatograph equipped with a FID detector and J&W Scientific 30 m DB WAX Megabore column was used to determine conversions of monomers by measuring the decrease of the monomer peak area relative to the peak area of an added internal standard. Injector and detector temperatures were kept constant at 250 °C. Analysis was run isothermally at 40 °C for 5 min followed by an increase of temperature to 120 °C at the heating rate of 40 °C/min and holding at 120 °C for 3 min. The molecular weight and molecular weight distribution of polymers were determined by GPC equipped with Waters 515 liquid chromatograph pump and Waters 2410 differential refractometer using PSS column (Styrogel, 10^5, 10^3, and 10^2 Å). GPC was performed using THF as an eluent at the flow rate of 1 mL/min. Linear polystyrene and poly(methyl methacrylate) standards were used for calibration. Theoretical molecular weights were calculated using eq 1.

$$M_{n,th} = ([\text{monomer}]_0/[\text{initiator}]_0) \times \text{conversion} \times \text{MW(monomer)} \quad (1)$$

GPC measurements of the pDMS macroinitiator were conducted using toluene equipped with a Waters 510 liquid chromatograph pump (1 mL/min) and a Waters 2410 differential refractometer using PSS columns (guard, 10^5 and 10^2 Å) in series. Diphenyl ether was used as an internal standard.

Results and Discussion

Determination of Chain End Functionality by ^{1}H NMR Analysis. Chain end functionality of poly(methyl acrylate) (pMA) prepared by using the conventional homogeneous ATRP catalyst and (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system was determined directly using high-resolution 600 MHz ^{1}H NMR. The polymers were isolated at the same conversion (~85%, Table 1) to eliminate or reduce any errors that may originate from different concentration of chain ends. The polymers had same molecular weight ($M_n \sim$ 6000 g/mol, Table 1) and exhibited a monomodal molecular weight distribution. However, the molecular weight distribution for the pMA sample prepared with the hybrid catalyst system ($M_w/M_n \sim 1.1$, Table 1) was more narrow than that for the sample prepared using the homogeneous ATRP catalyst ($M_w/M_n \sim 1.2$, Table 1), suggesting an efficient deactivation process in the hybrid system.

Table 1. Analytical Results of the Poly(methyl acrylate) Homopolymers

catalyst system	CuBr/2 dNbpy	(CuBr/PS8-dMbpy)/ ($CuBr_2/Me_6TREN$)
conversion	0.86	0.85
M_n (g/mol)	6000	6100
M_w/M_n	1.2	1.1
5[CH−Br]/[C_6H_5][a]	86 ± 3%	83 ± 3%
bromine terminated chains (%)[b]	93 ± 3%	92 ± 3%

[a] Determined by 600 MHz ^{1}H NMR. [b] Assuming termination by coupling.

Figure 1 shows a typical ^{1}H NMR spectra obtained from the pMA. The inset in Figure 1 presents an expansion of the region from 4 to 7.5 ppm. The signal from 7.1 to 7.4 ppm is representative of the five aromatic protons from the initiating moiety, 1-phenylethyl bromide, while the multiplet at 4.4−4.5 ppm is representative of the CH−Br from the other end group of the polymer chain. Signals around 6 ppm are due to the small amount of residual monomer. The percentage of bromine terminated polymer chains was calculated from the ratio of the integration of the CH−Br protons to the integration of the aromatic protons in the initiator residue, assuming termination by coupling. For both catalyst systems, the fraction of living chains was found to be around 92% (Table 1). These results confirm the similar efficiency of the hybrid and homogeneous ATRP catalyst systems. The results also suggest that irreversible termination reaction may not be the reason for the slower polymerization kinetics observed at higher conversion with the hybrid catalyst system.[26]

Block Copolymerization by Subsequent Comonomer Addition. A first method to evaluate the potential of the hybrid catalyst system for the preparation of controlled polymeric architectures was the preparation of a pMA-*block*-pnBA (Figure 2). The pMA segment was prepared using the hybrid catalyst system with a targeted DP = 100. After conversion reached 79%, nBA was added to prepare an A−B type tapered block copolymer.[36] As shown in Figure 2, the GPC traces exhibited a clear shift of molecular weight as the polymer chain extended from pMA to pnBA. The monomodal molecular weight distribution of the resulting block copolymer and good agreement between experimental and theoretical molecular weights demonstrate an efficient chain extension reaction and the “living” character of the polymerization system. However, an increase of polydispersity was observed ($M_w/M_n \sim 1.18-1.39$), which is a consequence of the low molecular weight tail, observable in the molecular weight distribution of the diblock copolymer (Figure 2). This tailing is mainly due to the pMA dead chains, which are unable to initiate nBA polymerization (the halogen chain end functionality of the pMA macroinitiator was around 90%; see previous paragraph).

Block Copolymerization Using Poly(dimethylsiloxane) (pDMS) Macroinitiators. Block copolymers have also been prepared through chain extension techniques using macroinitiators synthesized by other polymerization mechanisms. The preparation of block copolymers with a poly(dimethylsiloxane) (pDMS) segment was conducted by sequential combination of anionic polymerization and ATRP using the (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system (Scheme 1).[29] The macroinitiators were synthesized via anionic polymerization, which had narrower molecular

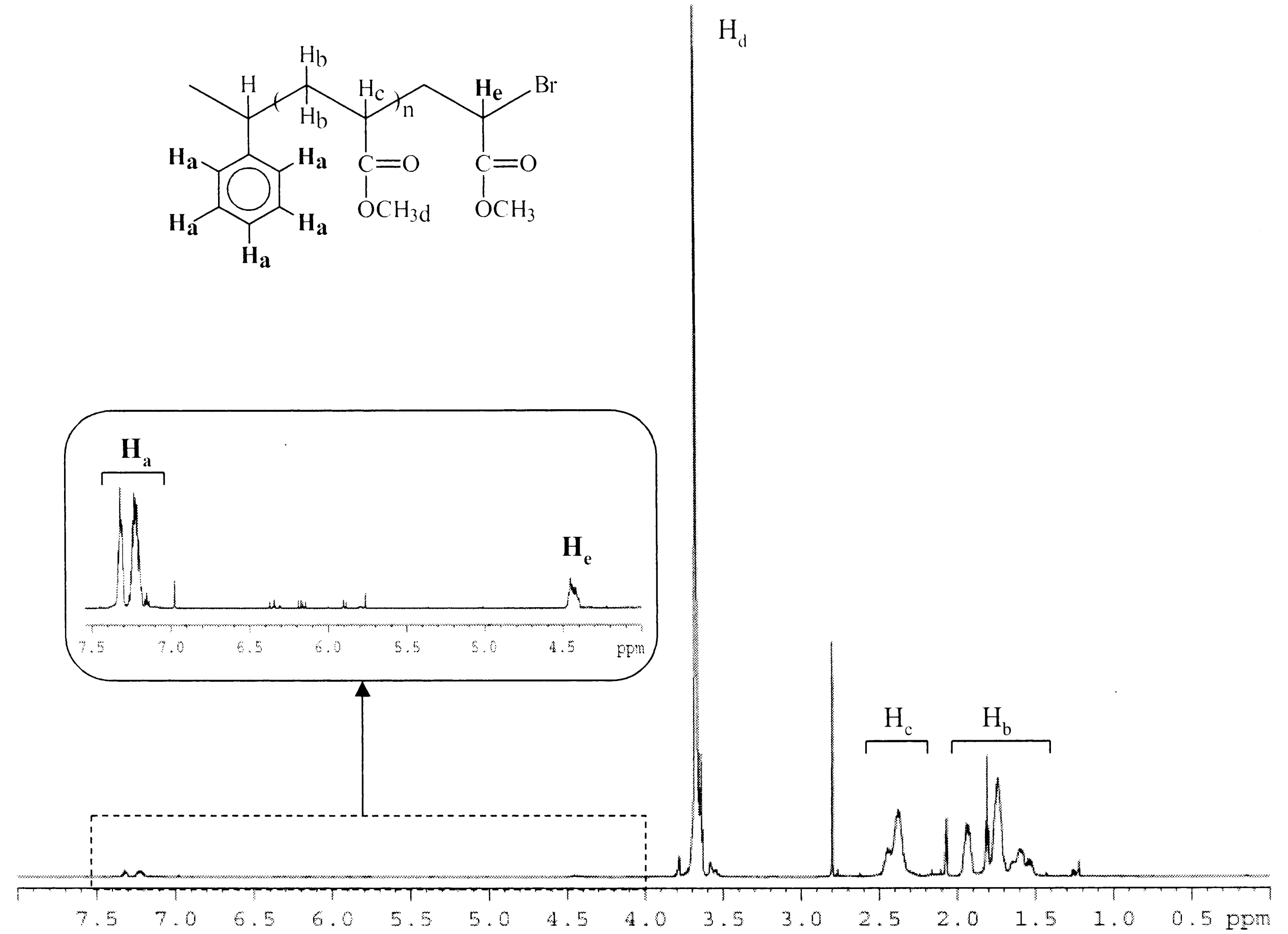


Figure 1. The 600 MHz ^{1}H NMR spectrum of poly(methyl methacrylate) homopolymer synthesized by ATRP, in deuterated acetone at 28 °C. Polymerization conditions: $[\mathrm{MA}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuBr/PS8\text{-}dMbpy}]_0$:$[\mathrm{CuBr_2/Me_6TREN}]_0 = 75{:}1{:}1{:}0.01$, $[\mathrm{MA}]_0 = 8.6$ mol/L, temperature = 70 °C.

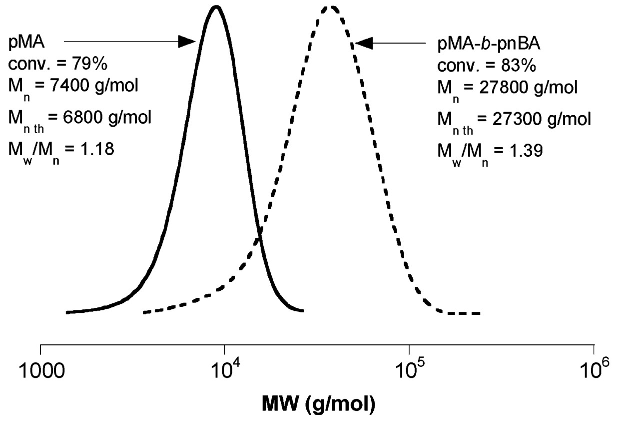
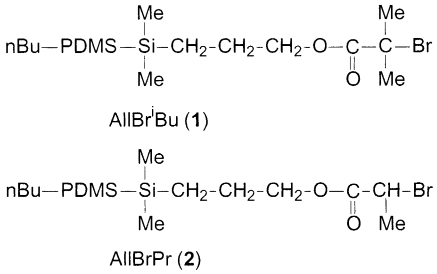


Figure 2. GPC traces for the preparation of poly(methyl acrylate)-*block*-poly(*n*-butyl acrylate) through successive addition of monomers.

weight distribution (M_w/M_n < 1.2) than the telechelic pDMS macroinitiators used previously[28,29] synthesized via a step growth process. An electron-deficient ligand, 2-methyl-1,4-naphthoquinone (MeNQ),[35] was added, and the concentration of platinum catalyst was reduced to reach higher macroinitiator functionality (>0.85).[29] The functionality *f* was quantified by integrations of the methyl protons of the isobutyrate (1.86 ppm) or the propionate group (1.80 ppm), with the methyl group of the *n*-butyl initiating group (0.89 ppm) in the ^{1}H NMR spectrum.

Scheme 1. Structure of the Synthesized PDMS Macroinitiators



$$\mathrm{nBu{-}PDMS{-}Si(Me)_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}C(=O){-}C(Me)_2{-}Br}$$

AllBr^{i}Bu (**1**)

$$\mathrm{nBu{-}PDMS{-}Si(Me)_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}C(=O){-}CH(Me){-}Br}$$

AllBrPr (**2**)

ATRP of MMA from pDMS macroinitiators with 2-bromoisobutyrate ($M_n = 9000$ g mol^{-1}, $M_w/M_n = 1.15$, $f = 0.85$) (**1**) and 2-bromopropionate groups ($M_n = 6600$ g mol^{-1}, $M_w/M_n = 1.16$, $f = 0.90$) (**2**) was conducted using the (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system. The kinetic plots of conversion of MMA vs time are shown in Figure 3. The rate of polymerization with **1** as macroinitiator was slower than that with **2** at the later stages. This was not expected because the 2-bromoisobutyrate group is a better initiator for MMA than 2-bromopropionate.[37] It is possible that the more efficient initiation produced more radicals which terminated more efficiently, yielding a larger amount of the deactivator, Cu(II) species, which retarded polymerization at the later stage.

The evolution of M_n and M_w/M_n with conversion is shown in Figure 4. Molecular weight exhibits a continuous increase with conversion. However, a discrepancy

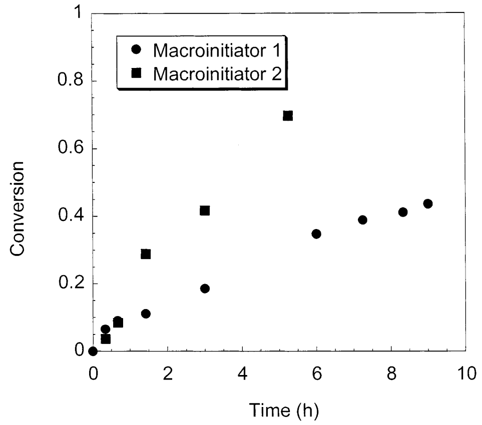


Figure 3. Kinetic plots for the ATRP of MMA using AllBr^{i}Bu (1) and AllBrPr (2) functionalized pDMS macroinitiators and (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system: $[\text{MMA}]_0$:$[\text{I}]_0$:$[\text{CuBr/PS8-dMbpy}]_0$:$[\text{CuBr}_2/\text{Me}_6\text{TREN}]_0$ = 200:1:1:0.01, $[\text{MMA}]_0$ = 4.29 mol/L, MMA/toluene/acetone = 1/1/0.22 v/v/v, temperature = 90 °C.

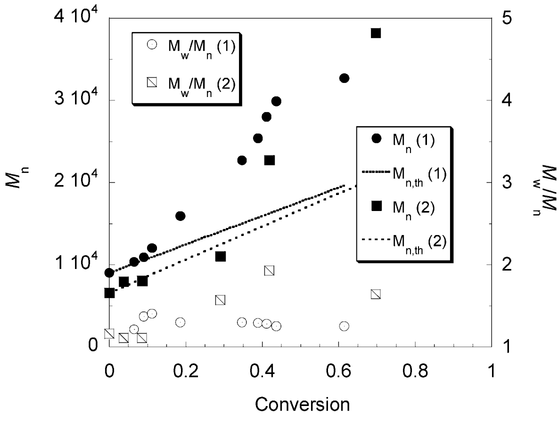


Figure 4. M_n and M_w/M_n vs conversion for the ATRP of MMA using AllBr^{i}Bu (1) and AllBrPr (2) functionalized pDMS macroinitiators and the (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system: $[\text{MMA}]_0$:$[\text{I}]_0$:$[\text{CuBr/PS8-dMbpy}]_0$:$[\text{CuBr}_2/\text{Me}_6\text{TREN}]_0$ = 200:1:1:0.01, $[\text{MMA}]_0$ = 4.29 mol/L, MMA/toluene/acetone = 1/1/0.22 v/v/v, temperature = 90 °C.

between theoretical and experimental molecular weight was observed. This could be ascribed not only to the differences in the hydrodynamic volumes of linear pMMA standards and the block copolymers but also to the efficiency of initiation of the pDMS macroinitiators. It is difficult to assess the initiator efficiency from the overall molecular weights when both macroinitiator and block copolymers are taken into account. However, GPC traces for block copolymer synthesized via ATRP from **2** exhibit a clear bimodality (Figure 6), which is less obvious when **1** is used as the macroinitiator (Figure 5). This bimodality cannot be ascribed to low macroinitiator functionalities (*f* was measured to be around 85%) but can be explained by the effect of the initiator structure on initiator efficiency in systems with homogeneous ATRP catalysts without halogen exchange.[29,37−39] As a consequence of the observed bimodality, the overall M_w/M_n values shown in Figure 4 reveal much higher values for 2-bromopropionate macroinitiator **2** than 2-bromoisobutyrate macroinitiator **1**.

Simultaneous Copolymerization of Methyl Methacrylate (MMA) and *n*-Butyl Acrylate (nBA) The simultaneous copolymerization of MMA and nBA was studied using the hybrid catalyst system. The initial monomer feed conditions were 85%, 50%, and 15% (mol) of nBA. Toluene was used as a solvent to prevent polymer/monomer phase separation. Detailed experimental conditions are given in Table 2.

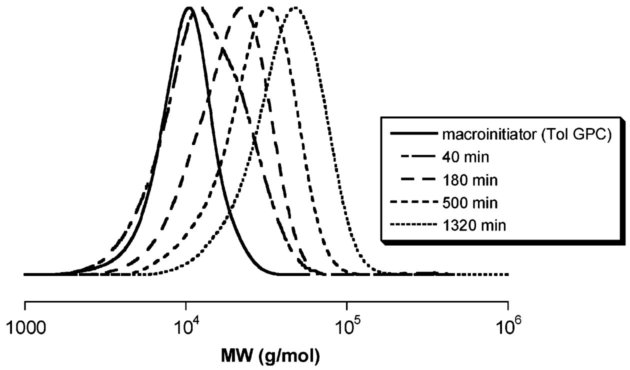


Figure 5. Molecular weight distribution of pDMS-*block*-pMMA synthesized from **1** (GPC measurements in THF except for macroinitiator). $[\text{MMA}]_0$:$[\text{I}]_0$:$[\text{CuBr/PS8-dMbpy}]_0$:$[\text{CuBr}_2/\text{Me}_6\text{TREN}]_0$ = 200:1:1:0.01, $[\text{MMA}]_0$ = 4.29 mol/L, MMA/toluene/acetone = 1/1/0.22 v/v/v, temperature = 90 °C.

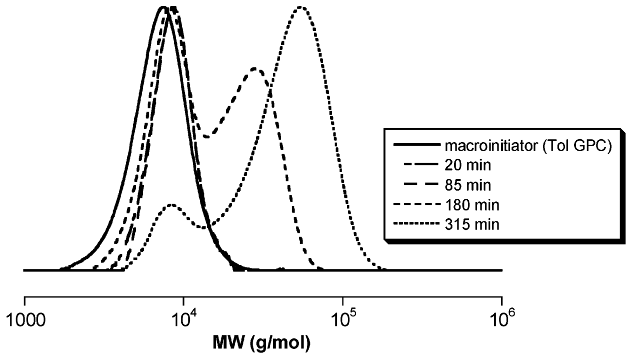


Figure 6. Molecular weight distribution of pDMS-*block*-pMMA synthesized from **2** (GPC measurements in THF except for macroinitiator). $[\text{MMA}]_0$:$[\text{I}]_0$:$[\text{CuBr/PS8-dMbpy}]_0$:$[\text{CuBr}_2/\text{Me}_6\text{TREN}]_0$ = 200:1:1:0.01, $[\text{MMA}]_0$ = 4.29 mol/L, MMA/toluene/acetone = 1/1/0.22 v/v/v, temperature = 90 °C.

The evolution of M_n and M_w/M_n with conversion for different initial monomer feed ratios is shown in Figure 7. For all conditions, molecular weight increased with conversion, although slight deviations from theoretical molecular weight were observed. Molecular weight distributions decreased with conversion and reached values of $M_w/M_n < 1.3$.

The semilogarithmic kinetic plots for the copolymerization reaction with three different initial monomer feed ratio are represented in Figure 8. All exhibit linear first-order kinetic plots. After 5 h, monomer conversion reached ∼70% regardless of initial monomer feed ratios. Polymerization rates for all three runs starting with different initial monomer feed ratios were similar, although in a homogeneous ATRP catalyst system (CuBr/dNbpy), the higher polymerization rates were observed at higher initial nBA concentration.[31]

A representative conversion graph for both MMA and nBA (initial monomer ratio of 50%) is shown in Figure 9. As in conventional radical copolymerization, MMA was consumed faster than nBA using the hybrid ATRP catalyst system, indicating propagation with similar radical intermediate. After 6 h, MMA conversion reached 87%, while nBA conversion was 60%. Copolymerizations conducted with different initial monomer feed ratios exhibited similar behavior.

Table 2. Conditions and Results for the Copolymerization of MMA and nBA Using the (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) Hybrid Catalyst System

entry	$[MMA]_0/[n\text{-}BA]_0$	t (h)	conv (MMA, %)	conv (nBA, %)	conv (total, %)	M_n ($\times10^{-4}$)	$M_{n,th}$ ($\times10^{-4}$)	M_w/M_n
1	0.15/0.85	5	95.8	71.2	74.9	2.16	2.76	1.30
2	0.50/0.50	6	86.7	59.8	73.3	2.17	2.45	1.36
3	0.85/0.15	6	80.1	51.5	75.8	2.24	2.34	1.42

[a] Polymerization conditions: initiator = methyl 2-bromopropionate; ($[MMA]_0 + [nBA]_0)/[I]_0/[CuBr/PS8\text{-}dMbpy]_0/[CuBr_2/Me_6TREN]_0 = 300/1/1/0.03$; $[M_{total}]_0 = 3.16$ mol/L (entry 1), $[M_{total}]_0 = 3.41$ mol/L (entry 2), $[M_{total}]_0 = 3.75$ mol/L (entry 3); monomer/(toluene + anisole)/acetone = 1/1/0.30 (v/v/v) (entry 1), monomer/(toluene + anisole)/acetone = 1/1/0.33 (v/v/v) (entry 2), monomer/(toluene + anisole)/acetone = 1/1/0.37 (v/v/v) (entry 3); temperature = 90 °C.

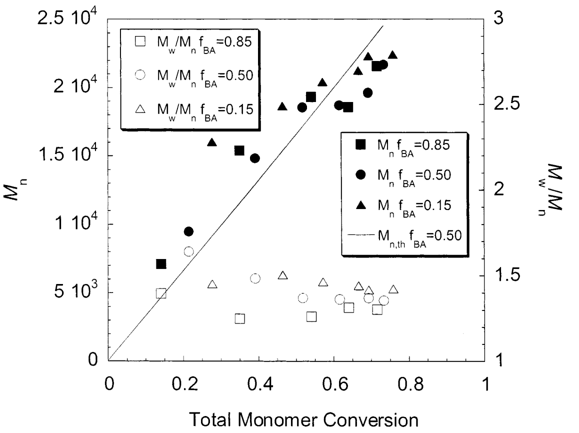


Figure 7. Evolution of M_n and M_w/M_n vs conversion for copolymerization of MMA and nBA using (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system: $[MMA + nBA]_0$:$[I]_0$:$[CuBr/PS8\text{-}dMbpy]_0$:$[CuBr_2/Me_6TREN]_0 = 300:1:1:0.03$, temperature = 90 °C; see Table 2 for other polymerization conditions.

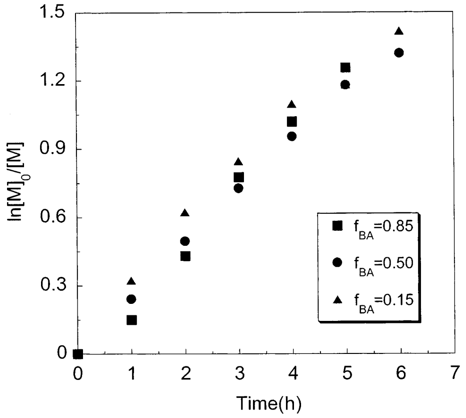


Figure 8. Kinetic plot for the copolymerization of MMA and nBA using (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system: $[MMA + nBA]_0$:$[I]_0$:$[CuBr/PS8\text{-}dMbpy]_0$:$[CuBr_2/Me_6TREN]_0 = 300:1:1:0.03$, temperature = 90 °C; see Table 2 for other polymerization conditions.

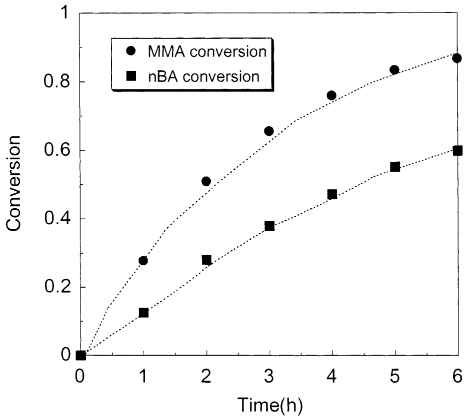


Figure 9. Individual monomer conversion plots for the copolymerization of MMA and nBA catalyzed by (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst. The initial monomer feed in this copolymerization consists of 50 mol % of nBA: $[MMA + nBA]_0$:$[I]_0$:$[CuBr/PS8\text{-}dMbpy]_0$:$[CuBr_2/Me_6TREN]_0 = 300:1:1:0.03$, $[M_{total}] = 3.41$ mol/L, (MMA + nBA)/(toluene + anisole)/acetone = 1/1/0.33 v/v/v, temperature = 90 °C.

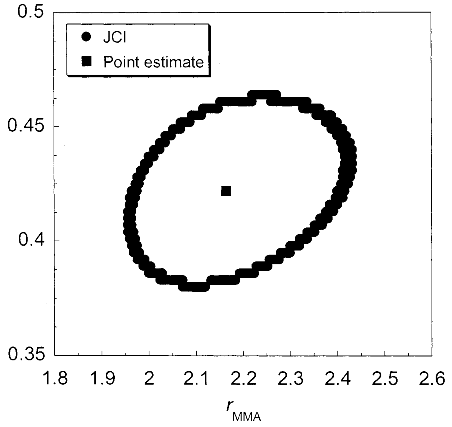


Figure 10. The 95% joint confidence intervals and point estimates for the copolymerization of MMA and nBA using (CuBr/PS8-dMbpy)/($CuBr_2/Me_6TREN$) hybrid catalyst system: $[MMA + nBA]_0$:$[I]_0$:$[CuBr/PS8\text{-}dMbpy]_0$:$[CuBr_2/Me_6TREN]_0 = 300:1:1:0.03$, temperature = 90 °C.

The reactivity ratios and 95% joint confidence intervals in MMA/nBA copolymerization were calculated using the nonlinear regression techniques reported previously.[31,32] Because the residual feed analysis at low and high monomer conversion might include large experimental error, the conversion data of 20−80% range were used to calculate the reactivity ratio. The joint confidence intervals (JCI) and point estimated for the hybrid catalyst system are shown in Figure 10. In this catalyst system, the reactivity ratio of MMA (r_{MMA}) and nBA (r_{BA}) was estimated to be 2.16 and 0.42, respectively. The reactivity ratios calculated from this experiment and those reported in several literature references[31,40−45] are summarized in Table 3. The reactivity ratio for the hybrid catalyst system fairly agrees with the literature values; however, the agreement is not perfect. There are several reasons for these discrepancies as discussed previously,[31,46,47] which include the differences in experimental conditions used in previous studies and in the present work.

Cumulative and instantaneous copolymer compositions were calculated by using eqs 2 and 3.

$$F_{cum,1} = (\%\ conv)_1[M_1]_0/((\%\ conv)_1[M_1]_0 + (\%\ conv)_2[M_2]_0) \quad (2)$$

$$F_{inst,1} = F_{cum,1} + (\%\ conv)(\Delta F_{cum,1}/\Delta(\%\ conv)) \quad (3)$$

Table 3. Reactivity Ratios of MMA and nBA from Various Studies[a]

source	r_{MMA}	r_{BA}	source	r_{MMA}	r_{BA}
this work	2.16	0.42	FRP[42]	1.88	0.31
CuBr/dNbpy[31]	2.52	0.265	FRP[43]	2.86	0.11
CuBr/PMDETA[31]	3.15	0.37	FRP[44]	1.79	0.30
CuBr/PMDETA[40]	2.07	0.36	FRP[45]	2.06	0.35
$NiBr_2/(PPh_3)_2$[41]	1.3	0.35	FRP[40]	2.15	0.26
FRP[41]	1.75	0.35			

[a] FRP = free radical polymerization.

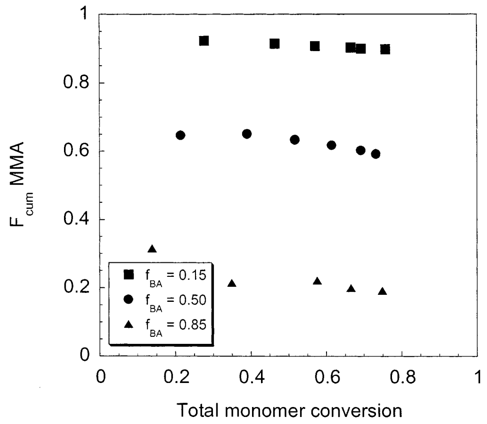


Figure 11. Cumulative copolymer composition vs total conversion of monomer for the copolymerization of MMA and nBA using (CuBr/PS8-dMbpy)/($CuBr_2$/Me_6TREN) hybrid catalyst system: $[MMA + nBA]_0:[I]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 300:1:1:0.03$, temperature = 90 °C; see Table 2 for other polymerization conditions.

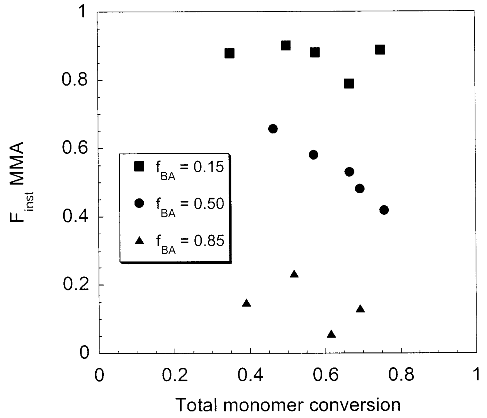


Figure 12. Instantaneous copolymer composition vs total conversion of monomer for the copolymerization of MMA and nBA with (CuBr/PS8-dMbpy)/($CuBr_2$/Me_6TREN) hybrid catalyst system: $[MMA + nBA]_0:[I]_0:[CuBr/PS8\text{-}dMbpy]_0:[CuBr_2/Me_6TREN]_0 = 300:1:1:0.03$, temperature = 90 °C; see Table 2 for other polymerization conditions.

The calculated cumulative, and instantaneous polymer compositions, are plotted against conversion in Figures 11 and 12. Copolymer compositions changed continuously with conversion, resulting in the formation of spontaneous gradient copolymers (Figure 12). Similar polymerization behavior had been reported for homogeneous catalyst systems, again indicating the similar reaction mechanism and chemical nature of active species in this biphasic hybrid polymerization medium.

Conclusions

A (CuBr/PS8-dMbpy)/($CuBr_2$/Me_6TREN) hybrid catalyst system was successfully applied to the preparation of polymers exhibiting various polymeric architectures. The degree of halogen chain end functionality was similar in hybrid and homogeneous systems ensuring efficient chain extension through sequential monomer addition, affording tapered block copolymers. The hybrid catalyst also allowed synthesis of pDMS-*block*-pMMA copolymers using pDMS macroinitiators. In the gradient copolymerization of MMA and nBA, molecular weight, molecular weight distribution, kinetic data, and reactivity ratios were similar to those determined for conventional homogeneous ATRP. These results indicate the similar chemical nature of polymerization intermediates to those of conventional homogeneous ATRP. Small differences and slightly higher polydispersities may be due to slower deactivation in hybrid catalyst system.

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