Improving the Structural Control of Graft Copolymers by Combining ATRP with the Macromonomer Method

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Received November 14, 2000

ABSTRACT: The reactivity ratios of methyl methacrylate (MMA) and methacryloyl-terminated poly(dimethylsiloxane) macromonomer (PDMS-MA) were determined in four different systems, using either conventional radical copolymerization or atom transfer radical copolymerization (ATRP) and using low molecular weight initiators or poly(dimethylsiloxane) macroinitiators. While the relative reactivity of PDMS-MA ($1/r_{MMA}$) decreased to 0.3−0.4 in the conventional radical polymerization, the reactivity ratio was higher in ATRP systems (ca. 0.8). The use of macroinitiator in the ATRP system increased $1/r_{MMA}$ at high concentration and helped regularly incorporate PDMS-MA into the copolymer. However, in the conventional radical polymerization or redox systems, macro(azo)initiator did not as significantly improve the reactivity ratio of PDMS-MA. Graft copolymers obtained by ATRP (in both solution and semibulk) have much lower polydispersities than obtained in conventional radical systems.

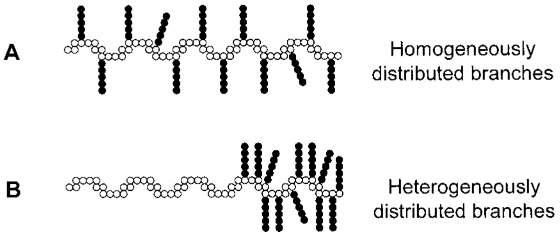
Introduction

Since the possibilities for producing new monomers at low cost have been diminishing, many scientists and engineers are striving to create specialized high-performance materials from existing monomers by making copolymers of various compositions and/or architectures. One such set of copolymers that is gaining interest is organic/inorganic hybrid polymers because inorganic polymers generally have unique and specific properties that organic polymers do not.[1]

From all of the possible architectures or topologies for the organic/inorganic hybrid polymers, we focus here on graft copolymers. Graft copolymers exhibit good phase separation[2] and are used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers, compatibilizers, and polymeric emulsifiers. Moreover, they generally have lower melt viscosities because of their branched structure, which is advantageous for processing. Since graft copolymers have many structural variables (composition, backbone length, branch length, branch spacing, etc.), they have great potential to realize new properties.

To make graft copolymers with specific properties, the structures must be controlled. For this reason, the macromonomer method[3,4] is one of the most useful ways to design and get well-defined graft copolymers. The macromonomer method copolymerizes macromonomers, which have a polymerizable end group, with low molecular weight comonomers. Well-defined side chains with predetermined molecular weights and low polydispersities can be obtained by preparing the macromonomer by a living polymerization. The backbone chain length can be controlled by copolymerizing the macromonomer and the comonomer by a living method. The average number of the side chains or the overall copolymer composition is determined by the molar ratio of macromonomer to comonomer in the feed and their reactivity ratios.

Scheme 1



However, the macromonomer method is still deficient in controlling the spacing of the side chains. For example, in Scheme 1, polymers A and B have the same backbone length, the same branch length, and the same number of branches but clearly a different distribution of the branches. Polymer A has homogeneously distributed branch spacing, while polymer B has heterogeneously distributed branch spacing structures.

The spacing distribution is determined by the reactivity ratios of the macromonomer and the low molecular weight comonomer. The reactivity ratios are influenced by many factors, especially (1) the inherent reactivity of the macromonomer and the comonomer based on their chemical structure, (2) the diffusion or kinetic excluded volume associated with the large size of the macromonomer, and (3) the potential incompatibility of the macromonomer and propagating comonomer chain due to thermodynamic repulsive interactions.[5−7]

Radke and Müller[8] clearly demonstrated the diffusion control effect by performing the copolymerization of methacryloyl-terminated PMMA macromonomer with MMA at 60 °C in toluene using AIBN as the initiator. In this case, factors 1 and 3 described above can be ignored. Nevertheless, they found that a lower rate of diffusion decreased the relative reactivity of the macromonomer with increasing macromonomer concentration. They concluded that, under conditions with a sufficiently low molar ratio of macromonomer to comonomer and with a low macromonomer concentration in the reaction mixture, the macromonomer chain length had no effect on its reactivity. Müller et al.[9] found for a copolymerization of *n*-butyl acrylate and PMMA mac-

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10.1021/ma001943j CCC: $20.00

romonomer that this diffusion control effect was reduced by using atom transfer radical polymerization (ATRP)[10−14] in which the time scale of the monomer addition is much slower than in a conventional radical polymerization.

The incompatibility effect becomes important with graft copolymers, such as organic/inorganic hybrid graft copolymers, when they contain dramatically different backbones and branches. Phase separation may be reduced by using a solvent that is a good solvent for both the macromonomer and the comonomer, although this may not be effective when the macromonomer and the comonomer segment are highly incompatible. Also, for economic or environmental reasons, the solvent concentration may need to be reduced and the reaction carried out at or close to bulk conditions. In these cases, the reactivity of the macromonomer decreases significantly, and graft copolymers may form with heterogeneously distributed branch spacing.

This incompatibility effect is a major obstacle to making well-defined graft copolymers but can be reduced by using a macromolecular initiator (macroinitiator) that has the same segment structure as the macromonomer. The reactivity of the macromonomer should be improved because the chain is already a block copolymer with both components present.

This paper reports the synthesis of organic/inorganic hybrid copolymers with homogeneously spaced branches. The organic backbone polymer is poly(methyl methacrylate) (PMMA), and the inorganic branches are poly(dimethylsiloxane) (PDMS). Although the preparation of PMMA-*g*-PDMS copolymers by copolymerizing a methacrylate-terminated PDMS macromonomer with MMA has been reported,[5,15−18] none of them discussed improved branch spacing distributions. The copolymerizations of methacrylate-functionalized PDMS macromonomer (PDMS-MA) and MMA were performed in four different systems using either conventional radical polymerization or ATRP, with either a low molecular weight initiator or macroinitiator. To clarify the effect of the macroinitiator in conventional polymerization, redox polymerizations with low molecular weight initiator or macroinitiator were also carried out. The relative reactivity of the macromonomer in each polymerization method was compared.

Experimental Section

Measurements. Gel permeation chromatography measurements in tetrahydrofuran (THF-GPC) were conducted using a Waters 515 liquid chromatograph pump (1 mL/min) equipped with four columns (guard, 10^5 Å, 10^3 Å, 100 Å; Polymer Standards Service) in series with a Waters 2410 differential refractometer with diphenyl ether as an internal standard. GPC measurements in toluene (toluene-GPC) were conducted using a Waters 510 liquid chromatograph pump equipped with columns (guard, 10^5 Å, 10^2 Å; Polymer Standards Service) in series with a Waters 2410 differential refractometer. The molecular weights were determined on the basis of low-polydispersity poly(methyl methacrylate) (PMMA) standards for THF-GPC and polystyrene standards for toluene-GPC.[19] The conversion of MMA was measured on a Shimadzu GC-14A gas chromatograph (GC) equipped with a wide-bore capillary column (30 m, DB-Wax, J&W Sci.). Injection temperature: 250 °C; column temperature: 40 °C, 2 min, then 40 °C/min until 160 °C. The functionality of the macromonomer and the macroinitiator was calculated from ^{1}H NMR spectra in deuteratred chloroform ($CDCl_3$) on a 300 MHz Bruker spectrometer using Tecmag data acquisition software.

Materials. Tetrahydrofuran (THF) and toluene were distilled from purple sodium benzophenone ketyl solutions. Hexamethylcyclotrisiloxane (D_3) (98%, Aldrich) was dissolved in benzene and refluxed over calcium hydride overnight under nitrogen. The solvent was removed by trap-to-trap distillation (10 mmHg, room temperature). The D_3 monomer was then sublimed (3 mmHg, 30−60 °C) into another flask and stored at room temperature in the glovebox. Methyl methacrylate (MMA) (99%, Acros) was washed three times with 5% aqueous sodium hydroxide and once with water. After drying with magnesium sulfate, MMA was distilled from calcium chloride. The purified MMA was stored in a freezer. MMA and *p*-xylene were deoxygenated by bubbling nitrogen gas through them for more than 1 h just before the polymerization. Copper chloride (CuCl) (98%, Aldrich) and copper bromide (CuBr) (98%, Aldrich) were both stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and ethyl ether under nitrogen. The solid was dried under vacuum at room temperature overnight. 4,4′-Di-*n*-nonyl-2,2′-bipyridine (dnNbpy) was synthesized by a modified literature procedure.[20] 3-Methacryloxypropyldimethylchlorosilane (98%, Gelest) was used as received. The PDMS macroazoinitiator having thermally labile azo groups between the main chains of poly(dimethylsiloxane) (VPS-1001, $M_n = 40\,000$) was provided by Wako Pure Chemical Industries, Ltd. 2,2′-Azobis(isobutyronitrile) (AIBN) (98%), ethyl 2-bromoisobutyrate (EBiB) (98%), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam) (98%), and all other reagents from Aldrich were used as received.

Syntheses. *Methacrylate Terminal PDMS Macromonomer (PDMS-MA).* In the drybox, D_3 (24.5 g, 0.11 mol) was placed into a 100 mL round-bottom flask and dissolved in a mixture of THF (8 mL) and toluene (8 mL). *n*-Butyllithium in hexane (4 mL, 10 mmol) was added to this clear colorless solution. The solution was stirred for 2 h at room temperature, and then 3-methacryloxypropyldimethylchlorosilane (2.65 g, 12 mmol) dissolved in hexanes (1.5 mL) was added to the solution. The heterogeneous white mixture was stirred at room temperature overnight. Room-temperature vacuum (1 mmHg) was applied for 5 h to remove all of the volatile materials, and the mixture was stored in a freezer overnight. The mixture was diluted with 20 mL of hexanes and filtered to remove all salts. The solvent was removed from the filtrate by rotary evaporation, and residual 3-methacryloxypropyldimethylchlorosilane was removed under 1×10^{-7} mmHg vacuum at 60 °C for 4 h. The clear liquid was then stored in a freezer. Yield = 17.6 g (72%). ^{1}H NMR δ (ppm): 6.1 (s, 1H, vinyl), 5.5 (s, 1H, vinyl), 4.1 (t, 2H, $-CH_2-O-$), 1.9 (s, 3H, $-CH_3$ in methacrylate), 1.7 (m, 2H, $-CH_2-C-O$), 1.3 (m, 4H, $-CH_2-CH_2-C-Si$), 0.9 (t, 3H, $-CH_3$ in butyl), 0.6 (m, 2H, $-CH_2-Si$), 0.1 (s, $-CH_3$ in siloxane). The functionality (F) of methacrylate terminal group calculated from the relative peak intensity in the ^{1}H NMR spectrum at 1.9 ppm (methyl 3H in methacrylate group) and 0.9 ppm (methyl 3H in butyl group) was 1.0. $M_n = 2200$; PDI $= M_w/M_n = 1.18$ (determined by GPC in toluene, polystyrene calibration).

PDMS Macroinitiator Containing 2-Bromoisobutyrate Terminal Group (PDMS-Br). A PDMS-Br was synthesized by the anionic polymerization of D_3 and terminated by chlorodimethylsilane, followed by reaction with 3-butenyl 2-bromoisobutyrate.[21] Yield, 78%. ^{1}H NMR δ (ppm): 4.2 (t, 2H, $-CH_2-O-$), 1.9 (s, 6H, $C(Br)-(CH_3)_2$), 1.7 (m, 2H, $-CH_2-C-O$), 1.5 (m, 2H, $Si-C-CH_2-$), 1.3 (m, 4H, $-CH_2-CH_2-C-Si$), 0.9 (t, 3H, $-CH_3$ in butyl), 0.6 (m, 4H, $-CH_2-Si$), 0.1 (s, $-CH_3$ in siloxane). The functionality ($F = 0.95$) was calculated by comparison of the integrations of the methyl protons in bromoisobutyrate group at 1.9 ppm with the methyl protons in *n*-butyl group at 0.9 ppm in the ^{1}H NMR spectrum. $M_n = 15\,600$; $M_w/M_n = 1.10$ (determined by GPC in toluene, polystyrene calibration).

Polymerizations. *Conventional Radical Copolymerization Initiated by AIBN.* A 25 mL Schlenk flask equipped with a stir bar containing a PDMS-MA ($M_n = 2200$, PDI = 1.18, $F = 1.0$, 0.98 g, 0.44 mmol) was evacuated overnight (<3 mmHg). The flask was filled with nitrogen and evacuated again (10 min). The degassing/back-filling procedure was repeated three times, and then the flask was filled with nitrogen. AIBN (3.6

mg, 0.022 mmol) was added to a separate 25 mL round-bottom flask equipped with a rubber septa and a stir bar. This flask was purged with a nitrogen gas flow for more than half an hour. Deoxygenated *p*-xylene (0.97 mL) and deoxygenated MMA (0.84 g, 8.36 mmol) were added via syringes. After the AIBN dissolved, the clear solution was cannula-transferred to the Schlenk flask under a nitrogen flow. A 0.1 mL aliquot of the reaction mixture was removed, and the flask was placed into a 75 °C oil bath under nitrogen. Periodically, 0.1 mL aliquots of the reaction mixture were removed and diluted with toluene to 30 wt % for kinetic and molecular weight analysis.

Conventional Radical Copolymerization Initiated by PDMS Macroazoinitiator. A 25 mL Schlenk flask with a stir bar, containing a PDMS-MA ($M_n = 2200$, PDI = 1.18, $F = 1.0$, 1.00 g, 0.45 mmol), was evacuated overnight. A PDMS macroazoinitiator (PDMS-azo) (0.23 g, 0.023 mmol of azo group) was placed in a separate 25 mL round-bottom flask, equipped with a stir bar, and sealed with a rubber septa. The flask was also evacuated overnight. Both flasks were filled with nitrogen and evacuated again. After this degassing/back-filling procedure was repeated three times, both flasks were filled with nitrogen. Deoxygenated *p*-xylene (1.41 mL) and deoxygenated MMA (0.87 g, 8.6 mmol) were added to the round-bottom flask via syringes. After the PDMS macroazoinitiator dissolved, the clear solution was cannula-transferred to the Schlenk flask under a nitrogen flow. The polymerization was performed at 75 °C and sampled periodically as in the case of the AIBN-initiated reaction described above.

ATRP Initiated by Ethyl 2-Bromoisobutyrate. In typical polymerization, a PDMS-MA ($M_n = 2200$, PDI = 1.18, $F = 1.0$, 0.95 g, 0.43 mmol) was added to a 25 mL Schlenk flask equipped with a stir bar and deoxygenated by degassing overnight and back-filling with nitrogen. CuCl (2.9 mg, 0.029 mmol) and dnNbpy (23.5 mg, 0.058 mmol) were placed in a 25 mL round-bottom flask equipped with a stir bar. This flask was capped with a rubber septum, purged with nitrogen gas for half an hour, and then charged with deoxygenated MMA (0.82 g, 8.2 mmol) and deoxygenated xylene (0.95 mL) via syringes. The mixture was stirred at room temperature under nitrogen for about half an hour until a homogeneous maroon solution formed. This solution was cannula-transferred to the Schlenk flask under a nitrogen flow. Ethyl 2-bromoisobutyrate (EBiB) (4.2 μL, 0.029 mmol) was added to the flask through the capped arm on the flask. A 0.1 mL aliquot of the reaction mixture was removed, and the flask was placed into a 90 °C oil bath under nitrogen. Periodically, 0.1 mL aliquots of the reaction mixture were removed and diluted with toluene to 30 wt % for kinetic and molecular weight analysis.

ATRP Initiated by PDMS Macroinitiator. In a typical polymerization, a 25 mL Schlenk flask equipped with a stir bar containing a PDMS-MA ($M_n = 2200$, PDI = 1.18, $F = 1.0$, 0.84 g, 0.38 mmol) and a PDMS-Br ($M_n = 15\,600$, PDI = 1.10, $F = 0.95$, 0.42 g, 0.025 mmol) was evacuated overnight and back-filled with nitrogen. A stir bar, CuCl (2.5 mg, 0.025 mmol), and dnNbpy (20.7 mg, 0.051 mmol) were placed in a 25 mL round-bottom flask. This flask was capped with a rubber septum and purged with nitrogen gas for half an hour; then deoxygenated MMA (0.72 g, 7.2 mmol) and deoxygenated xylene (1.62 mL) were added via syringes. The mixture was stirred at room temperature under nitrogen for about half an hour until a homogeneous maroon solution formed. This solution was cannula-transferred to the Schlenk flask under nitrogen. The polymerization was performed at 90 °C and sampled periodically as in the case of the EBiB-initiated reaction described above.

Redox Polymerization. In a typical polymerization, a 25 mL round-bottom flask equipped with a stir bar containing a PDMS-MA ($M_n = 2370$, PDI = 1.25, $F = 1.0$, 1.04 g, 0.44 mmol) was evacuated overnight and back-filled with nitrogen. A stir bar, CuBr (4.2 mg, 0.029 mmol), copper (Cu^0) powder (7.4 mg, 0.117 mmol), and Me_4-cyclam (7.5 mg, 0.029 mmol) were placed in a 25 mL Schlenk flask. After this Schlenk flask was purged with nitrogen gas for half an hour, deoxygenated MMA (0.83 g, 8.3 mmol) was added, and the solution was stirred under nitrogen for half an hour. Deoxygenated xylene (0.96 mL) was added into the round-bottom flask, and the PDMS macromonomer was dissolved. This macromonomer solution was cannula-transferred to the Schlenk flask under a nitrogen flow. EBiB (4.3 μL, 0.029 mmol) was added to the flask through the capped arm on the flask. The polymerization was performed at 75 °C, and periodic sampling and measurements were done in the same way as in the ATRP reaction described above.

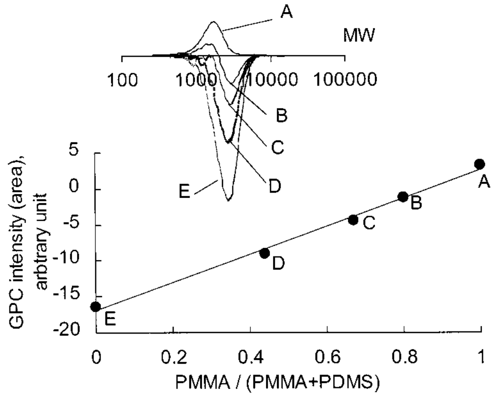


Figure 1. Toluene-GPC curves of polymer solution of PMMA and PDMS in various compositions and the linearity of intensities. The area was taken at the same injected concentration.

Results and Discussion

In the copolymerization of MMA and the PDMS macromonomer, GPC analysis of the reaction mixture samples showed that the amount of macromonomer decreased and the amount of copolymer increased with increasing conversion.

To measure the conversion of PDMS macromonomer, the relationship between the polymer concentrations and their relative intensities in the GPC was studied. Because the refractive index (RI) of PDMS ($n_D \approx 1.40$) is lower than that of toluene ($n_D \approx 1.49$), the RI signal of the PDMS macromonomer was negative in the toluene-GPC traces. A linear correlation between the concentration of the PDMS in the sample and the RI intensity in the GPC was found by measuring the peak areas of sample solutions at various concentrations of PDMS. On the other hand, since the refractive index of PMMA ($n_D \approx 1.49$) is very close to that of toluene, it appeared as a small peak in the toluene-GPC traces. The RI responses of the peak intensities of different compositions of PMMA/PDMS mixtures add linearly (Figure 1). The intensity (area) ratio of PMMA to PDMS at the same concentration was −0.2.

Since the intensity ratio of PMMA/PDMS is low and the MMA/PDMS weight composition in the feed was 0.85, in the first approximation, the small contribution of the PMMA in the toluene-GPC peak of the generated copolymer, especially at lower MMA conversions, could be ignored. The macromonomer conversion was determined by calculating the decrease in peak area from that of the initial sample by assuming the total area of the GPC peaks (PDMS macromonomer + copolymer) stays constant throughout the copolymerization. However, for accuracy, the PMMA composition in the samples was calculated from the MMA conversion (estimated by GC), and the observed toluene-GPC peak areas were then corrected by taking the small contribution of the PMMA contained in the sample into account.

The THF-GPC was used to estimate the apparent molecular weight distributions of the copolymers since the toluene-GPC might not detect any homo-PMMA in

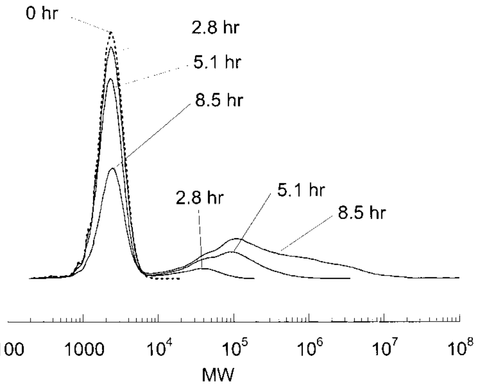


Figure 2. Toluene-GPC traces for the conventional radical polymerization of MMA and PDMS macromonomer (PDMS-MA) (M_n = 2200, F = 1.0) using AIBN as the initiator. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[AIBN]_0$ = 380/20/1, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$. Note: the observed negative curves were inverted for convenience.

the copolymer samples. Since the refractive index of the PDMS is close to that of THF ($n_D \approx 1.41$), PDMS chains are almost "invisible" in the THF-GPC, compared to the high intensity of PMMA. The intensity (area) ratio of PDMS to PMMA at the same weight concentration was 0.18. It should be noted that the molecular weights calculated from the THF-GPC are apparent because the calibration is based on linear PMMA, not on branched copolymers of respective compositions.

Conventional Radical Polymerization Initiated by AIBN. A PDMS macromonomer (PDMS-MA, in Scheme 2) with methacrylate end groups (F = 1.0) was prepared according to the method described by Schunk.[22] MMA and PDMS-MA were copolymerized in xylene using 2,2′-azobis(isobutyronitrile) (AIBN) at 75 °C. The weight ratio of xylene to MMA was 1:1. The reaction mixture was clear and homogeneous throughout the reaction. The toluene-GPC curves of the samples taken periodically from the reaction mixture showed that the concentration of macromonomer continuously decreased and the concentration of generated polymer increased (Figure 2). The macromonomer conversion was calculated from the decrease of the macromonomer peak area.

MMA was incorporated more quickly into the copolymer than the PDMS-MA (Figure 3). Since the PDMS-MA feed composition was low (5 mol %), we used the Jaacks method[23] to estimate the reactivity ratio of MMA ($r_{MMA} = k_{MMA^*/MMA}/k_{MMA^*/PDMS-MA}$).

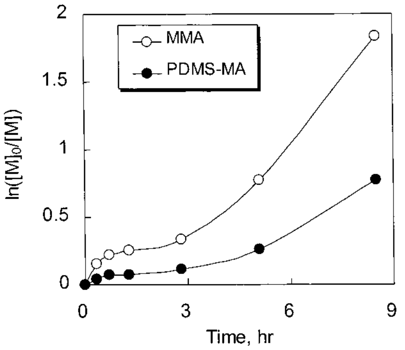


Figure 3. Kinetic plot for the conventional radical polymerization of MMA and PDMS macromonomer (PDMS-MA) (M_n = 2200, F = 1.0) using AIBN as the initiator. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[AIBN]_0$ = 380/20/1, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$.

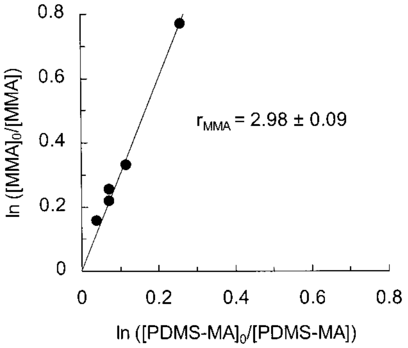
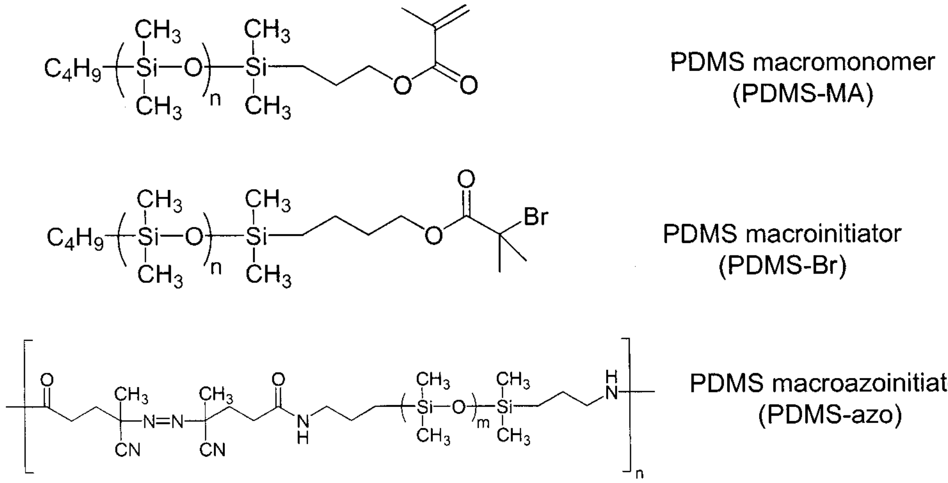


Figure 4. Jaacks plot[23] for the conventional radical copolymerization of MMA and PDMS macromonomer (PDMS-MA) (M_n = 2200, F = 1.0) using AIBN as the initiator. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[AIBN]_0$ = 380/20/1, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$.

$$r_{MMA} = \ln([MMA]_0/[MMA])/\ln([PDMS\text{-}MA]_0/[PDMS\text{-}MA])$$

The r_{MMA} for this system calculated from Figure 4 was 2.98 ± 0.09. This value means that the methyl methacrylate radical at the growing chain end reacts about 3 times faster with MMA than with PDMS-MA. When comonomer M_1 is copolymerized with a much smaller

Scheme 2



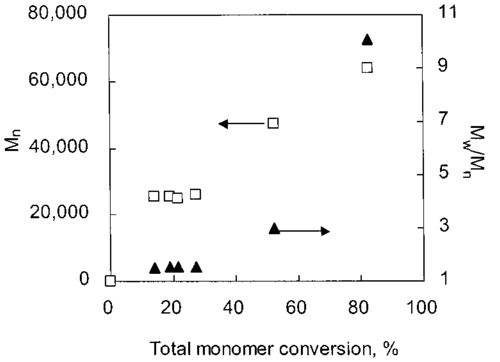


Figure 5. Molecular weight plot for the conventional radical polymerization of MMA and PDMS macromonomer (PDMS-MA) using AIBN as the initiator. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[AIBN]_0 = 380/20/1$, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$. M_n and M_w/M_n were determined by THF-GPC.

molar ratio of macromonomer M_2, the relative copolymerization reactivity of the macromonomer is usually evaluated by $1/r_1$, which represents the preference of addition of M_2 over that of M_1 toward the same growing polymer chain end radical ($-M_1^{\bullet}$).[6] For this system, $1/r_{MMA}$ was 0.33. Since the macromonomer used in this study had a methacrylate group at the chain end and was copolymerized with MMA, the deviation of $1/r_{MMA}$ from 1.0 can be attributed to the effect of both diffusion control and incompatibility, both of which seem to be significant in this system.

The apparent change in the molecular weight of the copolymer was examined using the THF-GPC (Figure 5). The molecular weight increased relatively quickly at the early stages of the polymerization, stayed constant until about 40% total monomer conversion, and then increased as the incorporation of the macromonomer increased. The formation of high molecular weight polymer at the beginning of the reaction is typical for a conventional radical polymerization. The polydispersity of the final polymer was quite high ($M_w/M_n > 10$).

ATRP Initiated by Ethyl 2-Bromoisobutyrate. The atom transfer radical copolymerization of MMA with PDMS-MA using ethyl 2-bromoisobutyrate (EBiB) as a low molecular weight initiator and CuCl/dnNbpy as the catalyst was conducted in xylene solution. The total monomer (MMA + PDMS-MA) ratio to initiator was 300 to 1. The concentrations of MMA and PDMS-MA in the initial reaction mixture were the same as in the conventional radical polymerization. The solution was homogeneous and maroon throughout the reaction. Toluene-GPC curves of the kinetic samples from the reaction mixture show that the macromonomer was continuously incorporated into the polymer backbone (Figure 6). The copolymer peaks were bimodal at higher conversions, due to either chain coupling or transfer to polymer.

The kinetic plot of this reaction (Figure 7) demonstrates that both MMA and PDMS-MA were consumed almost simultaneously. The reactivity ratio of MMA (r_{MMA}) obtained by the Jaacks method was 1.24 ± 0.01 (Figure 8). The reduction of the reactivity of macromonomer by the diffusion control effect was much lower ($1/r_{MMA} = 0.81$) in this ATRP system than in the conventional radical system described above ($1/r_{MMA} = 0.33$). As Müller[9] pointed out, the frequency of the monomer addition to a polymer chain is small enough in ATRP systems that the diffusion control effect becomes less important.

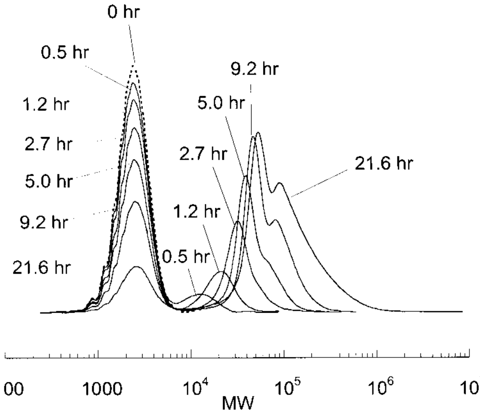


Figure 6. Toluene-GPC traces for the ATRP of MMA and PDMS macromonomer (PDMS-MA) ($M_n = 2200$, $F = 1.0$) using a small molecule weight initiator (EBiB). Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0 = 285/15/1/1/2$, weight ratio of xylene to MMA = 1, 90 °C, $N_2(g)$. Note: the observed negative curves were inverted for convenience.

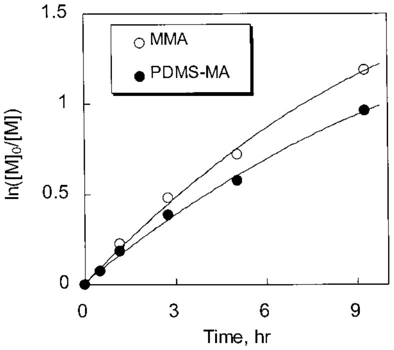


Figure 7. Kinetic plot for the ATRP of MMA and PDMS macromonomer (PDMS-MA) ($M_n = 2200$, $F = 1.0$) using a small molecule initiator (EBiB). Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0 = 285/15/1/1/2$, weight ratio of xylene to MMA = 1, 90 °C, $N_2(g)$.

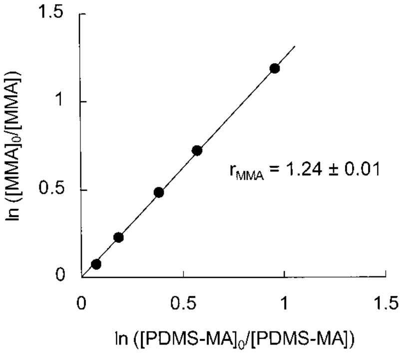


Figure 8. Jaacks plot[23] for the ATRP of MMA and PDMS macromonomer (PDMS-MA) ($M_n = 2200$, $F = 1.0$) using a small molecule initiator (EBiB). Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0 = 285/15/1/1/2$, weight ratio of xylene to MMA = 1, 90 °C, $N_2(g)$.

The molecular weight of the graft polymer (by THF-GPC) increased almost proportionally to monomer conversion (Figure 9). The polydispersity remained low ($M_w/M_n < 1.45$) until the conversion reached 70%.

For a reference, MMA was polymerized by ATRP in the presence of a nonpolymerizable hydrosilyl-terminal PDMS under the same reaction conditions. This PDMS ($M_n = 3020$, $M_w/M_n = 1.34$) was synthesized by anionic polymerization of D_3 and terminated by chlorodimethylsilane. As the reaction progressed, the homogeneous

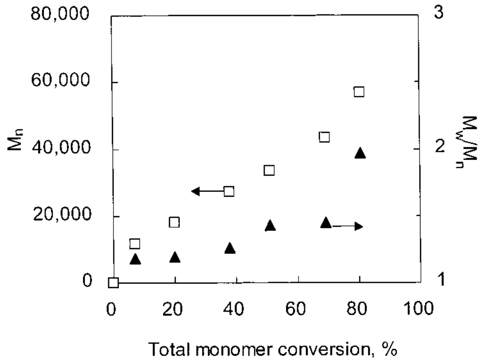


Figure 9. Molecular weight plot for the ATRP of MMA and PDMS macromonomer (PDMS-MA) using a small molecule initiator (EBiB). Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0 = 285/15/1/1/2$, weight ratio of xylene to MMA = 1, 90 °C, $N_2(g)$. M_n and M_w/M_n were determined by THF-GPC.

clear solution became heterogeneous, and eventually a brown precipitate appeared. This is due to the poor miscibility of PMMA homopolymer with PDMS. After 3 h, the MMA conversion was 33%. In the toluene-GPC curve of the reaction mixture, a small positive peak (M_n around 10 000, probably due to PMMA) appeared, while the large negative PDMS peak was almost identical to that of PDMS before the reaction. This suggests that no significant side reactions (e.g., radical transfer) occurred with the PDMS chain during the MMA polymerization.

To investigate the effect of the amount of solvent, a copolymerization using the minimum amount of xylene to homogenize the reaction mixture (10 wt % of MMA, i.e., semibulk) was performed. Small brown particles appeared in the reaction mixture at the early stages (<1 h) and then disappeared at later stages. The mixture became a viscous brown homogeneous solution. The incorporation of PDMS-MA was slower than the MMA according to GPC. The r_{MMA} obtained by the Jaacks method was 2.05 ± 0.09, and $1/r_{MMA}$ was 0.49. This confirms that decreasing the amount of solvent may lead to microscopic phase separation and that the incompatibility effect becomes more significant.

ATRP Initiated with PDMS Macroinitiator. A PDMS macroinitiator containing a 2-bromoisobutyrate end group (PDMS-Br) (as shown in Scheme 2) was prepared by the process previously reported.[21] The molecular weight of the macroinitiator was high enough that its GPC peak was clearly distinguishable from that of macromonomer; macromonomer conversion could be calculated accurately. The polymerization using the PDMS-Br was conducted under the same conditions as the ATRP with EBiB in a semibulk (10 wt % xylene to MMA) system. The solution was homogeneous throughout the reaction and became very viscous at higher monomer conversions.

The toluene-GPC traces in Figure 10 show a continuous increase in the molecular weight of the copolymer starting from the PDMS-Br, along with a continuous decrease of the PDMS-MA peak. The low molecular weight shoulder found on the copolymer peak is most likely due to the 5% dead PDMS chains not properly functionalized in the hydrosilylation reaction.

The kinetic shows that both MMA and the macromonomer were incorporated into the copolymer almost simultaneously (Figure 11). From the Jaacks plot, r_{MMA} was 1.17 ± 0.05, and therefore, $1/r_{MMA}$ was 0.85. This suggests that the growing polymer (PDMS−PMMA block copolymer) chain is compatible enough with the PDMS-MA chain that the active center will have a better chance at approaching and reacting with the macromonomer than when the growing chain is PMMA homopolymer.

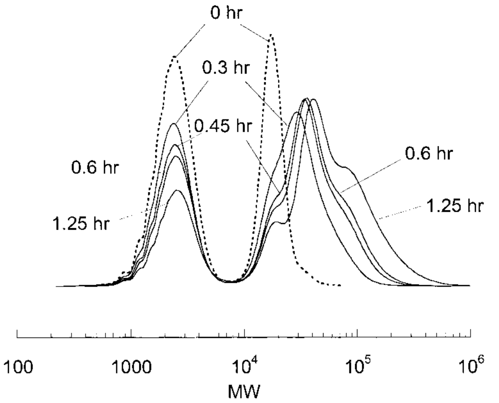


Figure 10. Toluene-GPC traces for the ATRP of MMA and PDMS macromonomer (PDMS-MA) (M_n = 2200, F = 1.0) initiated with PDMS macroinitiator (PDMS-Br) (M_n = 15 600, F = 0.95) in semibulk. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[PDMS\text{-}Br]_0/[CuCl]_0/[dnNbpy]_0 = 285/15/1/1/2$, weight ratio of xylene to MMA = 0.1, 90 °C, $N_2(g)$. Note: the observed negative curves were inverted for convenience.

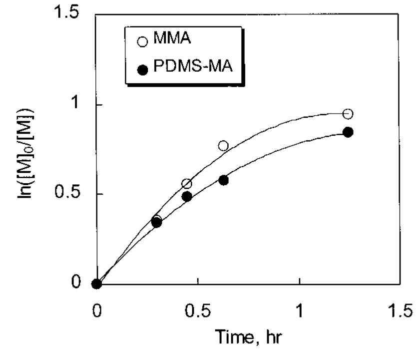


Figure 11. Kinetic plot for the ATRP of MMA and PDMS macromonomer (PDMS-MA) (M_n = 2200, F = 1.0) initiated with PDMS macroinitiator (PDMS-Br) (M_n = 15 600, F = 0.95) in semibulk. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[PDMS\text{-}Br]_0/[CuCl]_0/[dnNbpy]_0 = 285/15/1/1/2$, weight ratio of xylene to MMA = 0.1, 90 °C, $N_2(g)$.

The apparent molecular weight measured by THF-GPC increased linearly with the total monomer conversion. (Figure 12). The polydispersity of the copolymer remained low despite the fact that it was overestimated because of the contamination of the unreacted macroinitiator on the low molecular weight side of the GPC peak.

Conventional Radical Polymerization Initiated with PDMS Macroazoinitiator. The macroazoinitiator (PDMS-azo, as shown in Scheme 1) used for the conventional radical polymerization was a silicone having thermally labile azo groups between the main chains of PDMS. The molecular weight of this PDMS-azo was about 40 000 with molecular weights of the PDMS segments between the azo groups around 10 000.

MMA and PDMS-MA were copolymerized at 75 °C in xylene solution using an amount of the MAI such that the molar ratio of azo groups to the monomers was the same as in the AIBN-initiated reaction discussed above. The reaction mixture became viscous and, after 6 h, was insoluble in toluene.

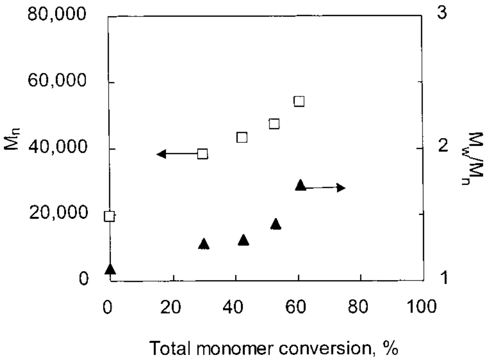


Figure 12. Molecular weight plot for the ATRP of MMA and PDMS macromonomer (PDMS-MA) initiated with PDMS macroinitiator (PDMS-Br) in semibulk. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[PDMS\text{-}Br]_0/[CuCl]_0/[dnNbpy]_0$ = 285/15/1/1/2, weight ratio of xylene to MMA = 0.1, 90 °C, $N_2(g)$. M_n and M_w/M_n were determined by THF-GPC.

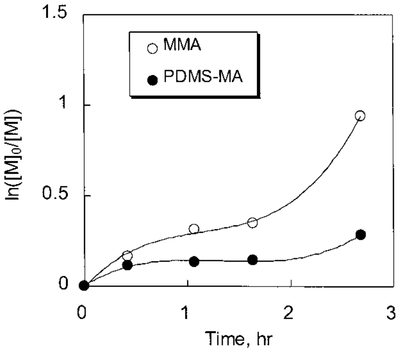


Figure 13. Kinetic plot for the conventional radical copolymerization of MMA and PDMS macromonomer (PDMS-MA) (M_n = 2200, F = 1.0) initiated with PDMS macroazoinitiator (PDMS-azo) (M_n = 40 000). Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/$[azo group in PDMS-azo]$_0$ = 380/20/1, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$.

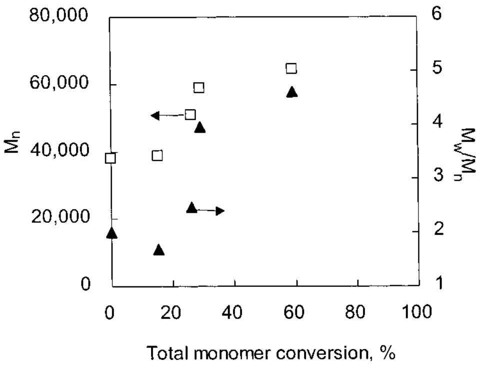


Figure 14. Molecular weight plot for the conventional radical polymerization of MMA and PDMS macromonomer (PDMS-MA) initiated with PDMS macroazoinitiator (PDMS-azo). Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/$[azo group in PDMS-azo]$_0$ = 380/20/1, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$. M_n and M_w/M_n were determined by THF-GPC.

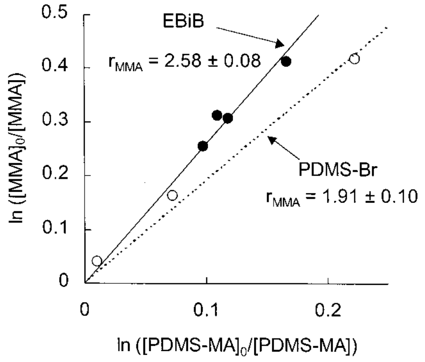


Figure 15. Jaacks plot[23] for the redox copolymerization MMA and PDMS-MA (M_n = 2200, F = 1.0) using EBiB or PDMS-Br (M_n = 15 600, F = 0.95) as the initiator. Conditions: $[MMA]_0/[PDMS\text{-}MA]_0/[initiator]_0/[CuBr]_0/[Me_4\text{-}cyclam]_0/[Cu^0]_0$ = 285/15/1/1/1/2, weight ratio of xylene to MMA = 1, 75 °C, $N_2(g)$.

The kinetic plot in Figure 13 shows that the incorporation of PDMS-MA into the copolymer was not significantly accelerated by using the PDMS-azo as compared to the conventional AIBN system. The r_{MMA} values from the Jaacks plot were scattered, and r_{MMA} was 2.84 ± 0.35. The rate of monomer addition in this system is so fast that the block copolymer (growing polymer chain) does not act as an efficient compatibilizer.

In the toluene-GPC traces, along with a decrease of the macromonomer peak, the polymer peak corresponding to the PDMS-azo increased in intensity and broadened to higher molecular weights without any significant shift in its peak molecular weight. The change of apparent molecular weight and polydispersity are shown in Figure 14.

Redox Polymerization. When an alkyl halide initiator is activated by a copper halide complex with Me_4-cyclam (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) ligand, a radical is generated that initiates the polymerization of vinyl monomers. In this catalytic system, the deactivation rate is very slow, such that the reaction proceeds via a mechanism similar to a conventional redox polymerization.[24] In a separate experiment, MMA in xylene (1:1 weight ratio) was heated at 75 °C in the presence of EBiB and a 1:1 complex of CuBr and Me_4-cyclam with additional copper (Cu^0) powder[25] in a molar ratio of MMA/EBiB/CuBr/Me_4-cyclam/Cu^0 = 300/1/1/1/2. The polymerization occurred rapidly and resulted in 69% MMA conversion in 2.5 h. The number-average molecular weight of the formed PMMA was M_n = 17 900, and the polydispersity was M_w/M_n = 2.23.

The copolymerization of MMA and PDMS-MA using either EBiB or PDMS-Br was conducted under the same conditions (molar ratio of MMA/PDMS-MA/initiator/CuBr/Me_4-cyclam/Cu^0 = 285/15/1/1/1/2, weight ratio of MMA/xylene = 1/1). When the small molecule initiator (EBiB) was used, the profile of the kinetics and the molecular weight change were similar to the conventional radical polymerization initiated with AIBN. The generated polymer had a high molecular weight from the early stages of the polymerization. M_n in THF-GPC was 45 200 (M_w/M_n = 1.78) at 22% MMA conversion, and M_n = 60 700 (M_w/M_n = 2.71) at 32% MMA conversion. After 9 h, the reaction mixture was gel-like and insoluble in either toluene or THF. Side reactions like radical transfer to the PDMS chain might occur, probably due to the large amount of radicals generated in such a short time.

When the macroinitiator (PDMS-Br) was used, the reaction mixture quickly became viscous. After 1 h, the viscosity was so high that stirring was impossible. After 45 min, the MMA conversion was about 15%; the M_n of the generated polymer in THF-GPC was already 50 100, and the polydispersity was 4.6.

The Jaacks plots (Figure 15) showed that although the macroinitiator accelerated the incorporation rate of

Table 1. Copolymerizations of Methyl Methacrylate (MMA) and Poly(dimethylsiloxane) Macromonomer (MM)[a]

polymerization type[b]	initiator (I)[c]	catalyst	MMA/MM/I molar ratio	xylene, wt ratio to MMA	initial polymer concn, wt %[d]	temp, °C	r_1[e]	$1/r_1$
RP	AIBN		380/20/1	1.0	37	75	2.98 ± 0.09	0.34
ATRP	EBiB	CuCl, dnNbpy	285/15/1	1.0	37	90	1.24 ± 0.01	0.81
				1.0	38	75	1.37 ± 0.10	0.73
				0.1	51	90	2.05 ± 0.09	0.49
ATRP with MI	PDMS-Br	CuCl, dnNbpy	285/15/1	1.0	37	90	1.37 ± 0.01	0.73
				0.1	62	90	1.17 ± 0.05	0.85
RP with MAI	PDMS-azo		380/20/1	1.0	37	75	2.84 ± 0.35	0.35
redox	EBiB	CuBr, Cyclam, Cu^0	285/15/1	1.0	38	75	2.58 ± 0.08	0.39
redox with MI	PDMS-Br	CuBr, Cyclam, Cu^0	285/15/1	1.0	46	75	1.91 ± 0.10	0.52

[a] MMA/MM composition in feed: 95/5 (mol/mol), 46/54 (wt/wt). [b] RP = conventional radical polymerization, ATRP = atom transfer radical polymerization, redox = redox polymerization, MI = macroiniator, MAI = macroazoinitiator. [c] AIBN = 2,2′-azobis(isobutyronitrile), EBiB = ethyl 2-bromoisobutyrate, PDMS-Br = 2-bromoisobutyrate-terminal PDMS macroinitiator, PDMS-azo = PDMS macroinitiator containing azo groups inside the chain. [d] (MM + MI)/(MM + MI + MMA + xylene) × 100. [e] Reactivity ratio of MMA determined by Jaacks plot.

PDMS-MA into the copolymer slightly, it was not very significantly different from the EBiB-initiated reaction.

Copolymer Structures. The copolymerization conditions and the reactivity ratios in the various systems in this study are summarized in Table 1.

The relative reactivities of the PDMS-MA ($1/r_{\mathrm{MMA}}$) in the conventional AIBN-initiated radical polymerization and the redox polymerization were far lower than 1.0. In these "uncontrolled" polymerization systems, the appreciable decrease in the reactivity of macromonomer means that there are obvious differences in the copolymer composition between the copolymer chains. Thus, at the early stages of polymerization, "homo-PMMA-like" copolymers containing a small number of PDMS branches are probably generated. Then, at the later stages, when the macromonomer dominates the residual comonomer pool, the macromonomer incorporation rate increases, and densely branched copolymers might be produced. At high conversions, the polymers will be a mixture of these types of structures.

Unlike the conventional radical polymerization where the rate of initiation is much slower than propagation, in ATRP all of the chains are initiated within the first 10% monomer conversion. The number of polymer chains is predetermined by the amount of initiator, and the chain length is increased proportionally to the monomer conversion. Moreover, in the absence of significant termination or transfer reactions, most of the growing chains remain active throughout the course of the polymerization. Therefore, when the reactivity ratio of the macromonomer is close to that of comonomer, the branches will be constantly incorporated into all copolymer chains at a certain rate according to the macromonomer/comonomer composition in feed.

Figure 16 shows that in the ATRP systems, except for the semibulk system with EBiB, the cumulative composition of the PDMS chains was fairly close to the feed composition (0.05) regardless of the conversion. This suggests that the polymers obtained in these systems have branches incorporated at constant intervals.

The decrease in the reactivity of the macromonomer in the semibulk ATRP system may lead to a "toothbrush" or "palm tree" type copolymer. Even if the relative reactivity of macromonomer is lower than that of the comonomer, the copolymers obtained in the ATRP system are heterogeneously branched intramolecularly but intermolecularly are compositionally homogeneous. Each copolymer chain should have a similar gradient branch structure.

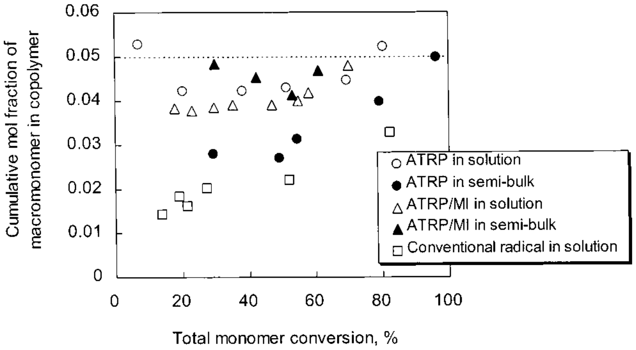


Figure 16. Change of cumulative copolymer composition for copolymerization of MMA and PDMS macromonomer (PDMS-MA). The cumulative compositions were calculated from the conversion of MMA and PDMS-MA. Initiator, ATRP: EBiB, ATRP/MI: PDMS-Br, conventional radical: AIBN.

Conclusions

In the atom transfer radical copolymerization of MMA and PDMS-MA in solution, the diffusion control effect became less important and the macromonomer incorporation rate was more regular compared to the conventional radical polymerization. When the ATRP was conducted with little or no cosolvent and when the repulsive interaction between the different polymers was significant, the use of a PDMS macroinitiator helped incorporate the macromonomer into the copolymer more regularly. In the conventional radical or redox systems, using a PDMS macroazoinitiator or end-functionalized macroinitiator also increased the reactivity ratio of the macromonomer, but to a smaller extent. The copolymers prepared using a conventional free radical method were heterogeneous in terms of copolymer composition, branching regularity, and molecular weights. Graft copolymers obtained by ATRP (in both solution and semibulk) have essentially predetermined molecular weights with much lower polydispersities than obtained in the conventional radical systems. In summary, the combination of ATRP and macroinitiator in the macromonomer method is the most beneficial and effective at controlling the graft copolymer structure in terms of main chain length/polydispersity and branch distribution/homogeneity.

Acknowledgment. Financial support from National Science Foundation (DMR-9871450) and Mitsui Chemicals (H.S.) is greatly acknowledged.

Supporting Information Available: Toluene-GPC traces for the ATRP of MMA in the presence of nonpolymerizable

PDMS, THF-GPC traces for the ATRP of MMA and PDMS-MA, Jaacks plot for the ATRP of MMA and PDMS-MA initiated with PDMS-Br, Jaacks plot for the conventional radical copolymerization of MMA and PDMS-MA initiated with PDMS-azo, and toluene-GPC traces for the conventional radical copolymerization of MMA and PDMS-MA initiated with PDMS-azo. This material is available free of charge via Internet at http://pubs.acs.org.

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(19) Note: since the refractive index of PMMA is close to that of toluene, polystyrene was used as the standard in the toluene-GPC.

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(25) Note: when Me_4-cyclam is used, a large concentration of radicals will be produced and efficiently cause termination. This leads to an excess of Cu(II) in the equilibrium process, and Cu(I) may be reduced to levels preventing the (re)-activation of alkyl halides. Cu(0) was used to maintain the sufficient concentration of Cu(I) throughout the polymerization by the redox reaction with Cu(II).

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