Articles

Dynamic Formation of Graft Polymers via Radical Crossover Reaction of Alkoxyamines

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ABSTRACT: A novel dynamic polymer reaction system using radical exchange of alkoxyamine units has been demonstrated. Poly(methacrylic ester) having 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO)-based alkoxyamine units in the side chain and TEMPO-based alkoxyamine-terminated polystyrene were prepared by atom transfer radical polymerization (ATRP) and nitroxide-mediated free radical polymerization (NMP), respectively. By the use of living radical polymerization techniques, the molecular weights of each polymer were accurately controlled. Radical crossover reaction of alkoxyamine units between the side chain and chain end of each polymer afforded the graft polymer which polystyrene chains are connected to the poly(methacrylic ester) backbone. Equilibrium M_n apparently depends on the feed ratio of polymers. The structure of the graft polymers is supported by size exclusion chromatography (SEC) and spectral data. The obtained graft polymer could be transformed reversibly to the starting materials by heating with excess amount of alkoxyamine derivative.

Introduction

Quite a variety of polymer reactions have been developed because of the desire to prepare advanced materials from a limited palette.[1] These techniques can also facilitate a novel polymer synthetic method, in particular, a method that is effective for the preparation of polymers with complicated macromolecular architecture.[2] While polymer reactions are useful for the preparation of hybrid materials, most of them are irreversible; therefore, once the particular product is formed, it is not possible either for the starting materials to be transformed from it or for it to be converted into another product.

During the past decades the field on "living" free radical polymerizations has attracted considerable interest from the desire to develop a simple and versatile method for the preparation of wide variety of polymers with complex and controlled architectures.[3] One of the most widely studied approaches to "living" free radical polymerizations involves nitroxide-mediated free radical polymerization (NMP).[4] The genesis of this field can be traced back to the pioneering works of Moad and Rizzardo in the early 1980s and seminal report of Georges.[5,6] Subsequently, a large number of publications appeared, confirming the "living" nature of this procedure and demonstrating the usefulness of this approach to the preparation of a variety of well-defined and complex architectures, a number of which cannot be prepared using traditional methods. Particularly, the development of unimolecular initiators as well as 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO)-based alkoxyamine derivatives has induced the accurate control of macromolecular architecture.[7] Recent development of NMP has permitted the polymerization of a wide variety of monomer families, with a level of structural control approaching traditional anionic procedures. Reversible capping of growing polymer chains by the nitroxide radical limits the concentration of propagating radicals to levels where radical termination is inhibited to give polymers with a narrow molecular weight distribution. The reversible dissociation/association nature of polystyrene−nitroxide system has been established by electron spin resonance (ESR)[8] and exchange[9,10] studies. From the thermally induced hemolytic cleavage and exchange properties, the alkoxyamine moiety is regarded as one of the "dynamic covalent bond", which has the ability to be transformed upon heating.[11] Recently, the authors have developed "dynamic covalent polymer" which is capable of reorganization by the exchange of covalent bonds in the main chain.[12,13] The exchange reaction among different dynamic covalent polymers permits the hybridization of polymers at the main chain level. Exchange in alkoxyamine-based dynamic covalent polymer occurs in a radical process that is tolerant to many functional groups and does not require very high temperature. Consequently, the exchange process can be applicable to polymers with a variety of functional groups.

In this report, our studies on dynamic formation of graft polymer with thermally reversible covalent bonds are presented. The exchange reaction among polymers, which have alkoxyamine units, is considered as a novel reversible polymer reaction system, and the constitution of product depends on equilibrium control. This adapt-

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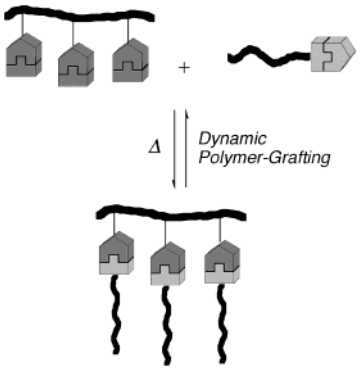


Figure 1. Schematic representation for the dynamic formation of graft polymer via radical crossover reaction of alkoxyamine.

ability potentially offers the development of "smart" materials that can respond to external stimulation through the use of reversible covalent bonds. Schematic representation of the system is illustrated in Figure 1.

Experimental Section

General. 4-Hydroxy-TEMPO,[14] 4-methoxy-TEMPO,[15] and 4-hydroxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine[9] (**1**) were prepared and purified as previously reported. Ethyl 2-bromoisobutylate (2-(EiB)Br, 98%), (−)-sparteine (Sp, 99%), and methacryloyl chloride (98%) were purchased from Aldrich and used without further purification. Methyl methacrylate (MMA, 98%), styrene (99+%), and anisole (99+%) were obtained from Wako Pure Chemical Industries and purified by distillation under reduced pressure over calcium hydride. Cu(I)Br (99+%) was purchased from Wako Pure Chemical Industries and purified by stirring in acetic acid (Wako Pure Chemical Industries, 99+%), washing with ethanol (Wako Pure Chemical Industries, 99%), and then drying in vacuo. All other reagents were purchased from commercial sources and used as received.

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectroscopic measurements were carried out at 25 °C with a JEOL JNM-EX400 spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$). IR spectra were obtained with a Perkin-Elmer Spectrum One infrared spectrometer as thin films on NaCl or neat. Monomer conversion was determined by ^{1}H NMR spectroscopy of the crude reaction mixtures. Number- and weight-average molecular weights (M_n and M_w, respectively) as well as polydispersity (M_w/M_n) were estimated by size exclusion chromatography (SEC) in THF at 40 °C on a polystyrene gel column [Shodex GPC KF-804L (300 × 8.0 mm)] that was connected to a TOSOH HLC-8120GPC high-performance liquid chromatography (HPLC) system equipped with a refractive index (RI) detector at a flow rate of 0.8 mL min^{-1}. The columns were calibrated against six standard polystyrene samples (M_n = 800−152 000; M_w/M_n = 1.03−1.10). Fractionation was conducted on a JAI LC-908 HPLC system equipped with two mixed polystyrene gel columns [JAIGEL-2H, JAIGEL-3H (600 × 20 mm)]. Chloroform was used as an eluent at a flow rate of 3.8 mL min^{-1}. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel (0.25 mm thick).

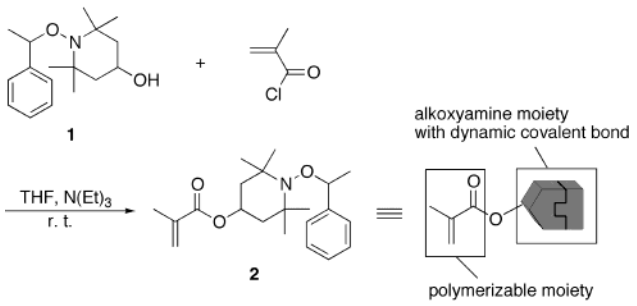
4-Methacryloyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (2). Methacryloyl chloride (440 μL, 4.5 mmol) was added to the solution of the alcohol **1** (832 mg, 3 mmol) and triethylamine (627 μL, 4.5 mmol) in anhydrous tetrahydrofuran (10 mL), and the solution was stirred at room temperature under nitrogen for 4 h and then evaporated to dryness. The residue was partitioned between water and dichloromethane. The organic layers was dried with magnesium sulfate and evaporated to dryness and purified by flash chromatography eluting with 1:10 ethyl acetate/ hexane (v/v). The isolated oil was dried in vacuo to give the methacrylic ester **2** as a white powder (883 mg, 85% yield). ^{1}H NMR: δ/ppm 0.67 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.49 (d, J = 7 Hz, 3H, CH_3), 1.40−2.00 (m, 4H, CH_2), 1.91 (s, 3H, CH_3), 4.77 (q, J = 7 Hz, 13 Hz, 1H, CH), 5.05 (m, 1H, CH), 5.52 (s, 1H, vinyl proton), 6.05 (s, 1H, vinyl proton), 7.10−7.40 (m, 5H, aromatic proton). ^{13}C NMR: δ/ppm 18.23, 21.15, 23.33, 34.09, 34.41, 44.57, 44.63, 59.96, 60.21, 67.04, 83.32, 125.05, 126.56, 126.89, 127.96, 136.53, 145.19, 166.86 (C═O). FT-IR (neat, cm^{-1}): 3100−2850, 1717 (C═O), 1639, 1327, 1165 (C−O), 762 (C−H), 699 (C−H). HRMS exact mass calculated for $[M + 1]^+$ $C_{25}H_{35}NO_5$ 346.2382; found 346.2381.

4-Methoxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (6). Ethylbenzene (200 mL, 1.63 mol), di-*tert*-butyl peroxide (24.7 mL, 134 mmol), and 4-methoxy-TEMPO (24.8 g, 134 mmol) were charged into a round-bottom flask. The mixture was refluxed at 125 °C under nitrogen for 24 h. After cooling, the solution was evaporated to dryness and purified by flash chromatography eluting with 1:14 ethyl acetate/hexane (v/v). The isolated oil was dried in vacuo to give the alkoxyamine derivative **6** as pale yellow oil (28.5 g, 73% yield). ^{1}H NMR: δ/ppm 0.68 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.48 (d, J = 7 Hz, 3H, CH_3), 1.20−2.00 (m, 4H, CH_2), 3.30 (s, 3H, OCH_3), 3.42 (m, 1H, CH), 4.77 (q, J = 7 Hz, 1H, CH), 7.20−7.40 (m, 5H, aromatic proton). ^{13}C NMR: δ/ppm 21.37, 23.48, 34.28, 34.59, 45.16, 55.71, 59.87, 60.06, 71.79, 83.24, 126.54, 126.81, 127.95, 145.40. FT-IR (neat, cm^{-1}): 3100−2800, 1454, 1376, 1362, 1100, 762 (C−H), 699 (C−H). Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.04; H, 9.93; N, 4.75. HRMS exact mass calculated for $[M + 1]^+$ $C_{18}H_{29}NO_2$ 292.2277; found 292.2277.

Copolymer of MMA and 2 (3). Cu(I)Br (12.9 mg, 0.09 mmol) and **2** (1.036 g, 3 mmol) were charged into a round-bottom flask containing a magnetic stirring bar, and the air was removed by evacuation and back-filled with argon three times. Then, MMA (1.60 mL, 15 mmol), anisole (2.55 mL, 23.5 mmol), and Sp (41.4 μL, 0.18 mmol) were added via syringes. The mixture was stirred until the formation of an essentially homogeneous yellow solution and degassed by three freeze−pump−thaw cycles. The flask was then immersed in an oil bath thermostated at 50 °C under argon, and 2-(EiB)Br (13.2 μL, 0.09 mmol) was added. After 22 h, the reaction mixture was quenched to room temperature and diluted with THF and the solution filtered through an Al_2O_3 column. The filtrate was concentrated in the rotary evaporator, diluted with chloroform, and then poured into excess hexane. The precipitation was then collected by vacuum filtration and dried in vacuo to give the purified polymer **3** as a white powder (651 mg, 25.7% yield). M_n = 11 800, M_w/M_n = 1.18. ^{1}H NMR: δ/ppm 0.66 (s, CH_3), 0.6−1.3 (br, α-CH_3), 1.10 (s, CH_3), 1.25 (s, CH_3), 1.34 (s, CH_3), 1.49 (d, J = 6 Hz, CH_3), 1.6−2.1 (s, CH_2), 1.88 (s, CH_3), 3.59 (s, OCH_3), 4.76 (br, CH), 4.84 (br, CH), 7.24 (s, aromatic proton), 7.30 (s, aromatic proton). ^{13}C NMR: δ/ppm 16.57 (br), 21.12, 23.22, 34.07, 34.40, 44.13, 44.56, 44.87, 51.77, 54.41 (br), 59.82, 60.01, 67.91, 83.29, 126.58, 126.93, 127.96, 145.06, 176.79 (C═O), 177.60 (C═O), 177.88 (C═O). FT-IR (neat, cm^{-1}): 2993, 2950, 1732 (C═O), 1150 (C−O), 755 (C−H), 700 (C−H).

TEMPO-Based Alkoxyamine-Terminated Polystyrene (4). A mixture of alkoxyamine **6** (1.75 g, 6.0 mmol) and styrene (34.37 mL, 300 mmol) was charged into a round-bottom flask containing a magnetic stirring bar and degassed by three freeze−pump−thaw cycles. The mixture was incubated at 125 °C under argon for 3 h. After the reaction mixture was quenched to room temperature, the mixture was diluted with chloroform and the solution was poured into methanol. The precipitation was then collected by vacuum filtration and dried in vacuo to give the purified polymer **4** as white powder (8.25 g, 25% yield). M_n = 1700, M_w/M_n = 1.15. ^{1}H NMR: δ/ppm 0.23 (br, CH_3), 0.41 (br, CH_3), 0.95 (s, CH_3), 0.80−2.50 (br, aliphatic proton), 3.23 (m, OCH_3), 3.97 (br, CH), 4.46 (br, CH), 6.20−7.30 (br, aromatic proton). ^{13}C NMR: δ/ppm 21.28, 34.11, 40.42 (br), 43.94 (br), 55.63, 59.23, 71.68, 85.62, 125.57 (br), 127.70 (br), 145.19 (br). FT-IR (NaCl, cm^{-1}): 3100−2850, 1601 (C═C), 1493, 1453, 1098, 1028, 907, 757 (C−H), 698 (C−H).

Scheme 1



Polymer Reaction of 3 with 4. In a typical run, a 1.0 wt % anisole solution of polymer **3** (M_n = 11 800, M_w/M_n = 1.18, 92 mg) and alkoxyamine-terminated polystyrene **4** (M_n = 1700, M_w/M_n = 1.15, 918 mg) was charged into a round-bottom flask containing a magnetic stirring bar and degassed by three freeze−pump−thaw cycles. The mixture was incubated at 100 °C under argon for 24 h. The solution was evaporated to dryness, diluted with chloroform, and fractionated by HPLC with SEC column to give the polymer **5** as colorless oil (158 mg). M_n = 24 000, M_w/M_n = 1.16 (molecular weight increases with time). ^{1}H NMR: δ/ppm 0.21 (br, CH_3), 0.50−2.50 (br, aliphatic proton), 3.59 (s, OCH_3), 4.77 (br, CH), 6.20−7.40 (br, aromatic proton), 7.30 (s, aromatic proton assigned to unreacted alkoxyamine units). ^{13}C NMR: δ/ppm 16.70, 21.09, 40.55, 44.55, 51.75, 125.42, 127.75, 145.18. FT-IR (NaCl, cm^{-1}): 3100−2800, 1731 (C=O), 1602 (C=C), 1493, 1453, 1150 (C−O), 910, 757 (C−H), 699 (C−H).

Polymer Reaction of 5 with 6. A 1.0 wt % anisole solution of polymer **5** (M_n = 24 000, M_w/M_n = 1.16, 50.2 mg) and alkoxyamine **6** (73 mg, 0.25 mmol) was charged into a round-bottom flask containing a magnetic stirring bar and degassed by three freeze−pump−thaw cycles. The mixture was incubated at 100 °C under argon for 30 h. The solution was evaporated to dryness, diluted with chloroform, and fractionated by HPLC with SEC column to give the polymer as colorless oil (21 mg). M_n = 12 300, M_w/M_n = 1.13 (molecular weight decreases with time). ^{1}H NMR: δ/ppm 0.66 (s, CH_3), 0.6−1.3 (br, α-CH_3), 1.10 (s, CH_3), 1.25 (s, CH_3), 1.34 (s, CH_3), 1.49 (d, J = 6 Hz, CH_3), 1.6−2.1 (s, CH_2), 1.88 (s, CH_3), 3.59 (s, OCH_3), 4.76 (br, CH), 4.84 (br, CH), 7.24 (s, aromatic proton), 7.30 (s, aromatic proton). ^{13}C NMR: δ/ppm 16.57 (br), 21.12, 23.22, 34.07, 34.40, 44.13, 44.56, 44.87, 51.77, 54.41 (br), 59.82, 60.01, 67.91, 83.29, 126.58, 126.93, 127.96, 145.06, 176.79 (C=O), 177.60 (C=O), 177.88 (C=O). FT-IR (neat, cm^{-1}): 2993, 2950, 1731 (C=O), 1149 (C−O), 754 (C−H), 700 (C−H).

Results and Discussion

The methacrylic ester-containing TEMPO-based alkoxyamine unit **2** was prepared by condensation reaction of TEMPO-based alcohol derivative **1** and methacryloyl chloride (Scheme 1). The reaction proceeded smoothly at room temperature to give the desired monomer **2** in 85% yield after purification. Although there have been some reports of the polymerization of monomers containing TEMPO-based alkoxyamine unit, all of them were polymerized by conventional free radical polymerization, and the structures have not been controlled.[16] The C−O bond of the alkoxyamine is thermally unstable and dissociates on heating to give an initiating radical as well as a nitroxide radical. In the case of the radical polymerization of monomer-containing alkoxyamine moiety, initiation and termination caused by generated radicals result in poor polymerization control. To control the molecular weight as well as macromolecular architecture with a facile procedure, we have examined the use of atom transfer radical polymerization (ATRP)[3,17] for the preparation of polymer

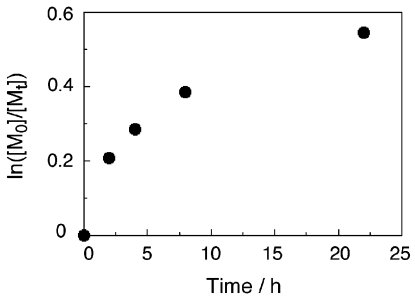


Figure 2. The ln([M]$_0$/[M]$_t$) vs time plots for solution polymerization of MMA and **2** in anisole (50 wt %) at 50 °C: [MMA]$_0$/[**2**]$_0$/[2-(EiB)Br]$_0$/[Cu(I)Br]$_0$/[Sp]$_0$ = 167/33/1/1/2.

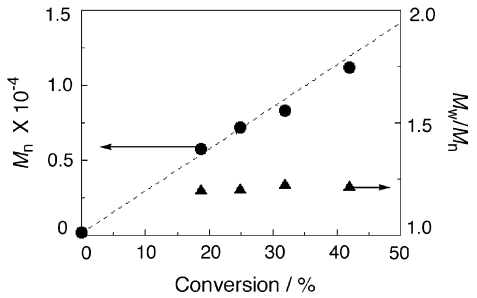


Figure 3. Evolution of M_n and M_w/M_n of the polymers as a function of monomer conversion for solution polymerization of MMA and **2** in anisole (50 wt %) at 50 °C: [MMA]$_0$/[**2**]$_0$/[2-(EiB)Br]$_0$/[Cu(I)Br]$_0$/[Sp]$_0$ = 167/33/1/1/2. The calculated molecular weights are shown as a dashed line.

that has alkoxyamine units in the side chain. In comparison with other living polymerization techniques, the unique features of living free radical polymerizations are their compatibility with a wide range of functional groups, coupled with their ability to prepare well-defined random copolymers.[4,18] As reported in our previous report, the TEMPO-based alkoxyamine unit does not dissociate below 60 °C.[12] Therefore, the ATRP of MMA and **2** was presumed to proceed without dissociation of alkoxyamine unit by conducting polymerization below 60 °C, affording linear polymer incorporating alkoxyamine units in the side chain with high degree of molecular weight control. Accordingly, the ATRP of 5:1 mixture of MMA and **2** was conducted in anisole at 50 °C using 2-(EiB)Br as the initiator and Cu(I)Br/Sp as the catalyst complex. The number-average molecular weight and polydispersity of the resulting polymers were determined by SEC calibrated with polystyrene standards. The ln([M]$_0$/[M]$_t$) vs time plot is shown in Figure 2. The saturation effect was observed at high conversion on the first-order kinetic plot, indicating that the concentration of active species gradually decreased. This result presumably derived from inactivation of metal complex catalyst due to the long reaction time. M_n and M_w/M_n of the obtained polymers before purification are plotted as a function of conversion in Figure 3. The dashed line in Figure 3 shows the theoretical M_ns. The observed M_ns increase linearly with conversion and are in good agreement with those calculated, while polydispersities were relatively low (M_w/M_n < 1.23). From these results it is concluded that some inactivation was observed in the first-order kinetic plot; however, the molecular weights and polydispersities could be controlled to afford well-defined linear polymer. Figure 4A shows the ^{1}H NMR spectrum of resulting polymer **3** (M_n = 11 800, M_w/M_n = 1.18). The signals assigned to alkoxyamine units (0.5−2.1, 4.76, 4.84, 7.24, 7.30 ppm) and methyl esters (3.59 ppm)

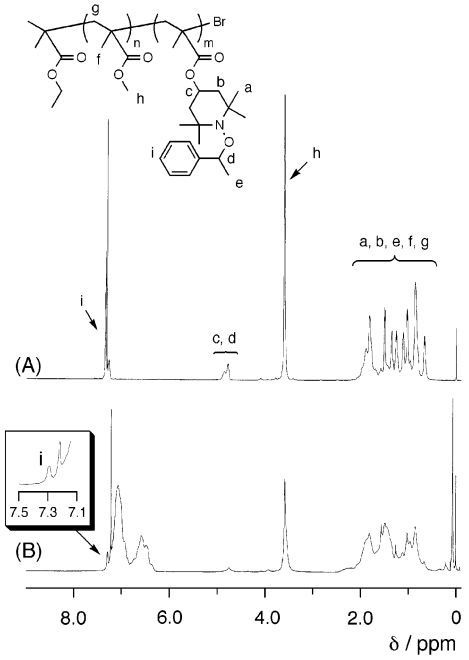
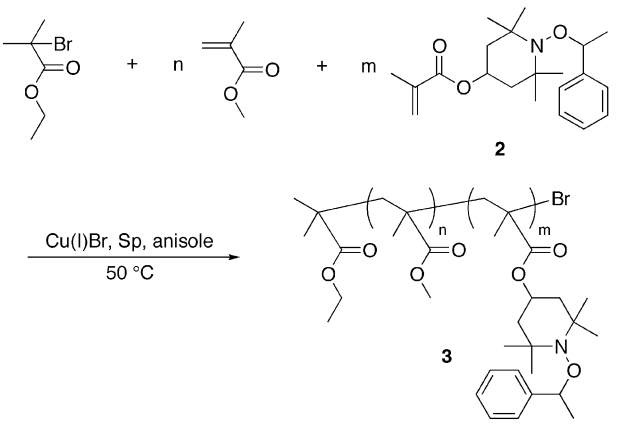


Figure 4. ^{1}H NMR spectra of (A) copolymer **3** (M_n = 11 800, M_w/M_n = 1.18) and (B) graft polymer **4** (M_n = 24 000, M_w/M_n = 1.16) fractionated by HPLC.

Scheme 2



were observed and confirmed from the integration of each peak that the composition of copolymer approximately corresponds to the feed ratio of monomers (copolymer composition; MMA/**2** = 4.6/1). This also means that the alkoxyamine units are randomly distributed along the PMMA chain.

The TEMPO-based alkoxyamine-terminated polystyrene **4** was prepared through the conventional NMP procedure. Polymerization of styrene was conducted in bulk with the unfunctionalized unimolecular initiator **6** at 125 °C under argon to give the polystyrene with predictable molecular weight and low polydispersity. The ^{1}H NMR spectrum of **4** (M_n = 1700, M_w/M_n = 1.15) shows the signals between 0.1 and 0.5 ppm that have been previously assigned to the chain-capping TEMPO moiety.[19] The signal that is assigned to methoxy protons was also observed. Comparison of the integration values for the end group with the main polystyrene chain gave molecular weight similar to those obtained from the SEC measurement, indicating approximately no loss of alkoxyamine chain end. It is considered that the isolated polymer may contain trace amounts of uncapped polymer chains arising from macroradical termination and

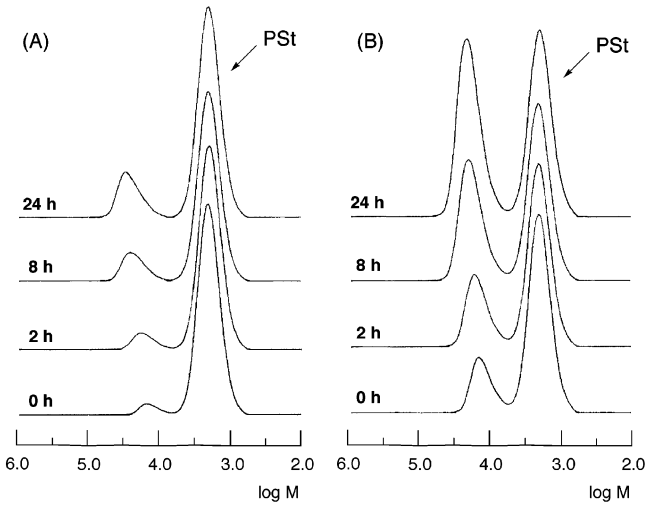
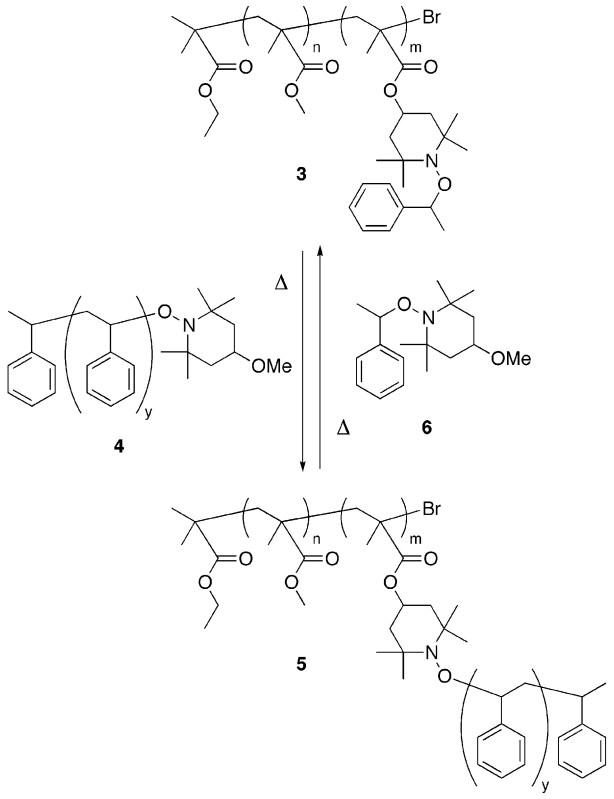


Figure 5. SEC profiles for (A) polymer reaction of **3** (M_n = 11 800, M_w/M_n = 1.18, 92 mg) with **4** (M_n = 1700, M_w/M_n = 1.15, 918 mg, 5.0 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon and (B) polymer reaction of **3** (M_n = 11 800, M_w/M_n = 1.18, 168 mg) with **4** (M_n = 1700, M_w/M_n = 1.15, 337 mg, 1.0 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon.

Scheme 3



thermal initiation process;[20] however, almost all polymer chains have the alkoxyamine unit at the chain end.

The mixture of **3** and **4** (5.0 or 1.0 equiv/alkoxyamine units) was dissolved in anisole and heated at 100 °C under argon. As shown in Figure 5, the SEC profile derived from **3** clearly shifted to the higher molecular weight region with increasing reaction time. In addition, the integral ratio of the peak derived from **4** to that for **3** significantly decreased. The behavior is fully consistent with the attachment of **4** to **3**. Because there are no other reactive groups at chain ends of **4**, the increase of molecular weight was undoubtedly caused by the

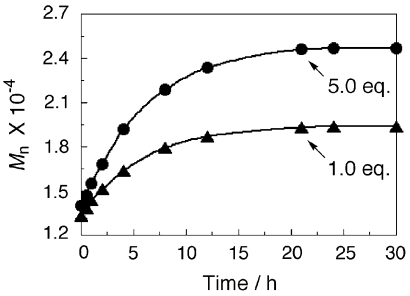


Figure 6. Dependence of M_n on reaction time for (circle) polymer reaction of **3** (M_n = 11 800, M_w/M_n = 1.18, 92 mg) with **4** (M_n = 1700, M_w/M_n = 1.15, 918 mg, 5.0 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon and (triangle) polymer reaction of **3** (M_n = 11 800, M_w/M_n = 1.18, 168 mg) with **4** (M_n = 1700, M_w/M_n = 1.15, 337 mg, 1.0 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon.

radical crossover reaction of alkoxyamine units. Significantly, no product derived from bimolecular termination of styryl radicals was observed, which provides further support for the absence of significant termination reaction in radical crossover reaction of alkoxyamine derivative. Furthermore, because the direction of alkoxyamine units in the side chain is identical, gelation and formation of high molecular weight polymer derived from coupling reaction among polymethacrylic ester were not observed. The dependence of M_n on reaction time is shown in Figure 6. After 24 h, M_n and the integral ratio of **4** to **3** became constant in both systems, which indicates that the equilibrium is reached in the system. Since equilibrium M_n depends on the feed ratio of polymers, it can be confirmed that **3** can be reorganized in response to heating to form the proper macromolecular architecture that reflects the equilibrium condition. By careful fractionation of the reaction mixture treated with **4** (5.0 equiv/alkoxyamine) using HPLC with a SEC column, the polymer at the higher molecular weight region was successfully separated. Confirmation of structure of the separated polymer **5** (M_n = 24 000, M_w/M_n = 1.16) was accomplished by ^{1}H NMR and IR measurements. The ^{1}H NMR spectrum of **5** is shown in Figure 4B. The significant signals of polystyrene chains were observed at 1.0−2.5 and 6.2−7.4 ppm as well as those of PMMA backbone and the methyl esters at 0.85, 1.02, and 3.59 ppm. The resonance derived from unreacted alkoxyamine units also appears at 7.3 ppm, and its integral ratio to methyl ester apparently decreased compared to the case of **3**. By comparing the integration value of the signal for the unreacted alkoxyamine units and that for methyl ester, the degree of grafting was evaluated to be 58% in the 5.0 equiv system. On account of the bulkiness of the grafted polystyrene chains, the degree of grafting is limited to a relatively low value. The molecular weight calculated from integration value of ^{1}H NMR spectrum was found to be 28 200. On the other hand, the M_n estimated by SEC measurement was 24 000, which was smaller than that estimated by ^{1}H NMR. This discrepancy in molecular weights is, however, fully consistent with the proposed structure since the hydrodynamic volume of a graft polymer is less than that of a comparable linear polymer.[16,21] The IR spectrum also revealed the significant signals of polystyrene chains at 699 and 1602 cm^{-1} as well as those of PMMA segments at 1150 and 1731 cm^{-1}. These findings demonstrate that the increase of molecular weight is caused by the grafting of polystyrene chains to **3**, and

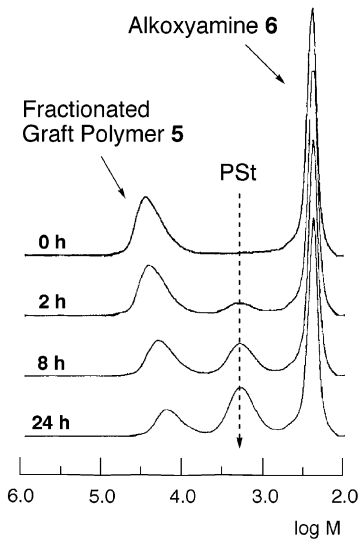


Figure 7. SEC profiles for polymer reaction of **5** (M_n = 24 000, M_w/M_n = 1.16, 50.2 mg) with **6** (73 mg, 8.3 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon.

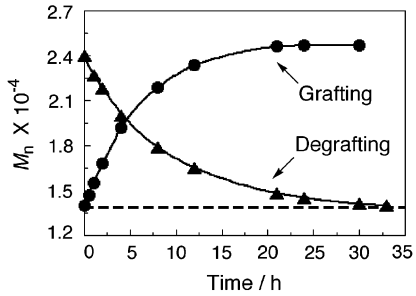


Figure 8. Dependence of M_n on reaction time for (circle) polymer reaction of **3** (M_n = 11 800, M_w/M_n = 1.18, 92 mg) with **4** (M_n = 1700, M_w/M_n = 1.15, 918 mg, 5.0 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon and (triangle) polymer reaction of **5** (M_n = 24 000, M_w/M_n = 1.16, 50.2 mg) with **6** (73 mg, 8.3 equiv/alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon.

the alkoxyamine units attached to the backbone of **3** and chain end of **4** are capable of dynamic exchanging via radical crossover reaction.

To demonstrate the consideration, the reversibility of the reaction system was also investigated. The mixture of **5** and excess amount (8.3 equiv/alkoxyamine unit) of unfunctionalized alkoxyamine derivative **6**, which is also used as the unimolecular initiator for the preparation of **4**, was dissolved in anisole and heated at 100 °C under argon. As shown in Figure 7, as the reaction proceeded, the SEC profile derived from **5** shifted to the lower molecular weight region. Significantly, the SEC profile corresponding to eliminated polystyrene (M_n = 1700, M_w/M_n = 1.15) appeared, and the integral ratio of the profile to graft polymer increased with increasing reaction time. The dependence of M_n on reaction time is presented in Figure 8 with grafting reaction data as the reference. The degrafting system reached the equilibrium after 30 h. Interestingly, equilibrium M_n almost corresponds to the initial M_n of **3**. The polymer at the higher molecular weight region was successfully separated by fractionation of reaction mixture by HPLC with a SEC column. The ^{1}H NMR spectrum of separated polymer revealed no significant peak assigned to polystyrene chains, and the spectrum was fully in accord

with the spectrum of **3**. A similar result was identified by IR measurement. These results prove that the graft system is produced by the exchange reaction of alkoxyamine groups and that the reaction system is apparently reversible under equilibrium control.

Conclusion

In summary, the authors have demonstrated that dynamic synthesis of graft polymer is accomplished by radical crossover reaction among the alkoxyamine units attached to the side chain and chain end. The molecular weight of backbone and graft chains can be controlled by utilizing dual living free radical polymerization techniques. The present system permits the use of various well-defined alkoxyamine-terminated polymers that can be readily prepared by NMP. The novel dynamic polymer reaction system affords the material that can be reorganized in response to heating to form the proper macromolecular architecture that reflects the equilibrium condition.

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