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A Thermodynamic Polymer Cross-Linking System Based on Radically Exchangeable Covalent Bonds

Yuji Higaki, Hideyuki Otsuka,* and Atsushi Takahara*

Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku,
Fukuoka 812-8581, Japan

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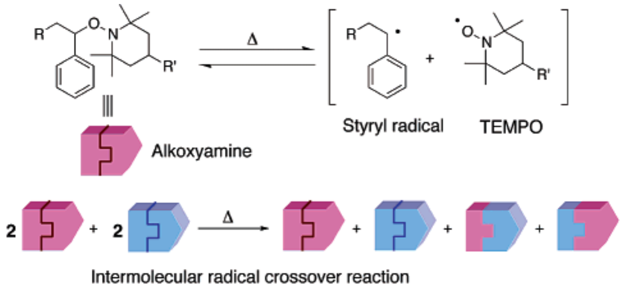
ABSTRACT: A thermodynamic covalent cross-linking system utilizing alkoxyamine units as thermally reversible covalent bonds was demonstrated. By heating the poly(methacrylic ester)s containing alkoxyamine units on the side chain, the cross-linking reaction was achieved as a result of a radical exchange reaction of alkoxyamine moieties. Kinetic studies have revealed that the cross-linking behavior depends remarkably on concentration and reaches equilibrium at a given reaction time, and characteristic reaction behaviors for thermodynamic reactions have been observed. The de-cross-linking reaction was carried out by heating the cross-linked polymer in the presence of an excess amount of alkoxyamine. It was found that the cross-linked points thermally dissociate and that the reaction system is reversible under stoichiometric control.

Introduction

Recent synergy between polymer synthesis and advanced organic chemistry allows the preparation of well-defined polymeric materials with excellent properties.[1−5] Over the past years, the field of noncovalent (supramolecular) cross-linking systems utilizing multiple hydrogen bonds[2,6] and metal complexation[3,7] has attracted considerable interest due to a desire to develop cross-linked polymers with reorganization properties. These materials exhibit reversible sol−gel transitions upon heating because of the temperature dependence of the K_a value of noncovalent association. Although the “virtual” molecular weight and lifetime of supramolecular networks based on strong noncovalent association is sufficiently high, extremely low creep resistance derived from fast dynamics of the scission−recombination process is an intrinsic property of these materials that may limit future applications.[6] Consequently, it is obvious that a large number of important properties of polymers require covalent (nonequilibrium) connections; for example, materials cross-linked with chemically stable covalent bonds possess high creep resistance, high modulus, high fracture strength, and high solvent resistance, and they are normally inert.

Materials cross-linked by reversible covalent bonds can be expected to possess the same stability as static materials due to covalent connections as well as the reorganizability as with dynamic materials. We have recently developed a dynamic covalent polymer whose structure is stable under normal conditions and is changeable by the crossover reaction of covalent bonds upon heating.[8,9] The 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)-based alkoxyamine unit has been employed as a fundamental unit of the reorganizable polymer. Although the alkoxyamine unit behaves as a typical covalent bond at room temperature, it homolytically cleaves upon heating and reaches an equilibrium state between dissociation/association. According to the model reaction results, radicals generated by the alkoxyamine dissociation can exchange, leading to an equilibrium state without side reactions and/or deactivation (Scheme 1).[8−12] On the basis of its stability at room temperature and its exchange property upon heating, the C−O bond in an alkoxyamine is regarded as a dynamic covalent bond.[13] Several reversible polymer reaction systems based on reversible covalent bonds such as imine metathesis,[14] thermoreversible Diels−Alder reaction,[15] addition−fragmentation chain transfer of allyl sulfide,[16] thiol-catalyzed reversible cleavage of disulfide,[17] exchange reaction of acylhydrazone,[18] and dynamic polymerization of cyclic monomers[19] have been reported and utilized for reversible covalent cross-linking systems with remendability and stimuli-induced plasticity. Among these dynamic covalent bonds, the alkoxyamine unit is characterized by thermodynamic stability as well as facile control of the dissociation temperature through its structure.[10,20] In addition, because the exchange reaction occurs in a radical process, it is tolerant to many functional groups and it can be applied to a wide range of polymers.

Scheme 1. Radical Exchange Reaction of Alkoxyamine Derivatives



In this paper, we report a novel thermodynamic covalent cross-linking system based on the exchange reaction of alkoxyamine units, as represented in Scheme 2. The reaction system is characterized by the following points. First, the cross-linked polymer possesses the same high performance as conventional covalently cross-linked polymers, and once the system is heated above a given temperature, cross-linked points become an equilibrium state between dissociation/association and reorganize via radical exchange reactions. Second, because the reaction proceeds through reversible reactions, the most thermodynamically favorable structure reflecting the equilibrium and stoichiometric conditions is produced.

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* Corresponding author: Tel +81-92-642-2318; Fax +81-92-642-2715; e-mail otsuka@ms.ifoc.kyushu-u.ac.jp, takahara@cstf.kyushu-u.ac.jp.

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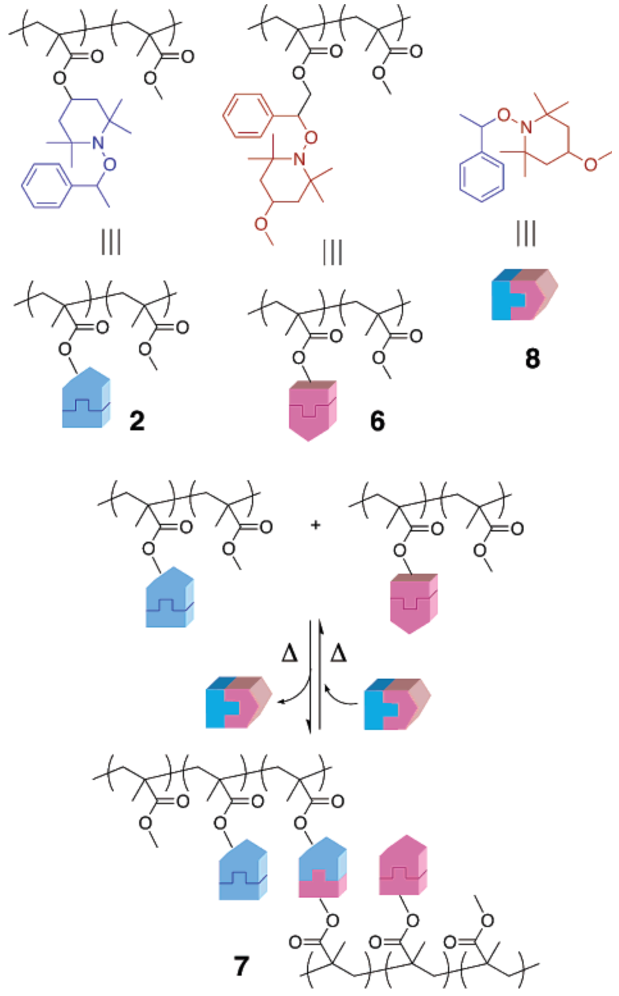
Scheme 2. Schematic Representation of the Thermodynamic Formation of Cross-Linked Polymers via Radical Exchange Reaction of Alkoxyamines



Experimental Section

Materials. 4-Hydroxy-TEMPO,[21] 4-methoxy-TEMPO,[22] 4-methacryloyloxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (**1**),[9] and 4-methoxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (**8**)[9] were prepared and purified as previously reported. Poly(methacrylic ester) (**2**) were prepared by random copolymerization of methyl methacrylate (MMA) and **1** with the atom transfer radical polymerization (ATRP) technique.[9] Ethyl 2-bromoisobutylate (2-(EiB)Br, 98%), (−)-sparteine (Sp, 99%), and methacryloyl chloride (98%) were purchased from Aldrich and used without further purification. 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* ($CDCl_3$). Monomer conversion was determined by ^{1}H NMR spectroscopy of the crude reaction mixtures. IR spectra were obtained with a Perkin-Elmer Spectrum One infrared spectrometer as thin films on NaCl or neat. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by gel permeation chromatographic (GPC) analysis. GPC was carried out at 40 °C on a JASCO high performance liquid chromatography (HPLC) system equipped with a guard column (TOSOH TSKguardcolumn SuperH-L), three mixed columns (TOSOH TSKgel SuperH6000, 4000, and 2500), and a differential refractometer. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL min^{-1}. Polystyrene (PS) standards (M_n = 800−152 000; M_w/M_n = 1.03−1.10) were used to calibrate the GPC system. HPLC measurement was carried out by a Shimazu LC-10AT equipped with a Shimazu SPD-10AV UV−vis detector and a JASCO CrestPak C18S column. A mixed solvent (CH_3CN/H_2O = 3/1) was used as the eluent at 1.0 mL min^{-1}. Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel (0.25 mm thick).

4-Methoxy-1-((2′-benzoyloxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (3). Briefly, distilled styrene (300 mL, 2.62 mol), benzoyl peroxide (BPO, 7.27 g, 30 mmol), and 4-methoxy-TEMPO (13.04 g, 70 mmol) were charged into a round-bottom flask. The mixture was incubated at 85 °C under nitrogen for 18 h. After cooling, the solution was evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:10 ethyl acetate/hexane (v/v) and dried in vacuo to give the modified benzyl ester **3** as a waxy solid (10.64 g, 43% yield). ^{1}H NMR: δ/ppm 0.75 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 0.90−2.00 (m, 4H, CH_2), 3.30 (s, 3H, OCH_3), 3.43 (m, 1H, CH), 4.52 (dd, J = 11 Hz, 6 Hz, 1H, CH_2), 4.82 (dd, J = 11 Hz, 5 Hz, 1H, CH_2), 5.06 (t, J = 6 Hz, 1H, CH), 7.20−7.60 (m, 8H, aromatic), 7.92 (d, J = 5 Hz, 2H, aromatic). ^{13}C NMR: δ/ppm 21.33, 34.14, 34.24, 45.12, 45.24, 55.72, 60.31, 60.46, 66.63, 71.54, 84.07, 127.54, 127.57, 127.66, 128.00, 128.18, 129.44, 130.00, 132.75, 140.27, 166.12. FT-IR (neat, cm^{-1}): 3100−2800, 1723 (C═O), 1098 (C−O), 760, 712, 701. HRMS exact mass calculated for $[M + 1]^+$ $C_{25}H_{34}NO_4$ 412.2488; found 412.2443.

4-Methoxy-1-((2′-hydroxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (4). An aqueous solution of sodium hydroxide (1 M, 30 mL) was added to a solution of benzyl ester **3** (4.12 g, 10 mmol) in ethanol (300 mL), and the solution was stirred at room temperature under nitrogen for 18 h. The solution was evaporated to dryness and partitioned between water and dichloromethane. Then the aqueous layer was washed with dichloromethane, and the combined organic layers were dried with magnesium sulfate and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:6 ethyl acetate/hexane (v/v) and dried in vacuo to give the alcohol **4** as a waxy solid (2.61 g, 85% yield). ^{1}H NMR: δ/ppm 1.18 (s, 3H, CH_3), 1.26 (s, 6H, CH_3), 1.52 (s, 3H, CH_3), 1.30−1.60 (m, 2H, CH_2), 1.80−2.10 (m, 2H, CH_2), 3.31 (s, 3H, OCH_3), 3.47 (m, 1H, CH), 3.72 (m, 1H, CH), 4.18 (t, J = 9 Hz, 1H, OH), 5.03 (d, J = 9 Hz, 1H, CH_2), 5.21 (dd, J = 3 Hz, 9 Hz, 1H, CH_2), 7.20−7.40 (m, 5H, aromatic). ^{13}C NMR: δ/ppm 21.23, 21.50, 33.07, 34.64, 44.97, 45.11, 55.63, 60.47, 61.43, 68.70, 71.23, 84.09, 126.69, 127.70, 128.09, 138.71. FT-IR (neat, cm^{-1}): 3439 (OH), 3100−2850, 1098 (C−O), 758, 699. HRMS exact mass calculated for $[M + 1]^+$ $C_{18}H_{29}NO_3$ 308.2226; found 308.2228.

4-Methoxy-1-((2′-methacryloyloxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (5). Methacryloyl chloride (293 μL, 3 mmol) was added to a solution of alcohol **4** (769 mg, 2.5 mmol) and triethylamine (446 μL, 3.2 mmol) in dry 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. Then the aqueous layer was washed with dichloromethane, and the combined organic layers were dried with magnesium sulfate and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:8 ethyl acetate/hexane (v/v) and dried in vacuo to give the methacrylic ester **5** as a waxy solid (771 mg, 82% yield). ^{1}H NMR: δ/ppm 0.72 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.20−2.00 (m, 4H, CH_2), 1.85 (s, 3H, CH_3), 3.30 (s, 3H, OCH_3), 3.42 (m, 1H, CH), 4.34 (dd, J = 6 Hz, 11 Hz, 1H, CH_2), 4.63 (dd, J = 5 Hz, 11 Hz, 1H, CH), 4.97 (t, J = 5 Hz, 1H, CH_2), 5.48 (s, 1H, vinyl), 5.99 (s, 1H, vinyl), 7.20−7.40 (m, 5H, aromatic). ^{13}C NMR: δ/ppm 18.22, 21.25, 34.07, 45.07, 45.20, 55.60, 60.17, 60.37, 66.28, 71.46, 83.95, 125.38, 127.47, 127.54, 127.84, 135.93, 140.17, 166.80. FT-IR (neat, cm^{-1}): 3100−2850, 1722 (C═O), 1168 (C−O), 1099 (C−O), 760, 701. HRMS exact mass calculated for $[M + 1]^+$ $C_{22}H_{33}NO_4$ 376.2488; found 376.2490.

Poly(MMA-*ran*-5) (6). Cu(I)Br (15.1 mg, 0.105 mmol) and methacrylic ester **5** (376 mg, 1 mmol) were charged into a round-bottom flask containing a magnetic stirring bar, and the air was removed by evacuation and backfilled with argon three times. Then, MMA (2.14 mL, 20 mmol), anisole (2.39 mL), and Sp (48.3 μL, 0.21 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 then 2-(EiB)Br (15.4 μL, 0.105 mmol) was added. After 22 h, the reaction mixture was quenched to room temperature and diluted with THF, and the solution was 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 **6** as a white powder (877 mg, 37% yield). $M_n = 15\,500$, $M_w/M_n = 1.12$. ^{1}H NMR: δ/ppm 0.66 (s), 0.6−1.3 (br, α-CH_3), 1.09 (s), 1.25 (s), 1.36 (s), 1.6−2.1 (s, CH_2), 3.32 (s, OCH_3), 3.42 (s, CH), 3.60 (s, OCH_3), 4.10 (br, CH_2), 4.40 (br, CH_2), 4.88 (br, CH), 7.34 (br, aromatic proton). ^{13}C NMR: δ/ppm 16.36, 18.60, 21.19, 34.22, 44.41, 44.75, 44.99, 51.72, 54.22, 55.65, 60.39, 71.38, 127.56, 127.91, 176.70 (C═O), 177.53 (C═O), 177.83 (C═O). FT-IR (neat, cm^{-1}): 3100−2850, 1731 (C═O), 1149 (C−O), 752, 702.

Cross-Linking Reaction (Polymer Reaction of 2 with 6). In a typical run, a 5.0 wt % anisole solution of the mixture of **2** ($M_n = 16\,200$, $M_w/M_n = 1.19$, MMA/**1** = 19/1) and **6** ($M_n = 15\,500$, $M_w/M_n = 1.12$, MMA/**5** = 19/1) was charged into a glass tube, degassed by freeze−pump−thaw cycles, and sealed off under vacuum. The solution was incubated at 100 °C for 24 h. The alkoxyamine **8** generated as a result of radical exchange reaction was recovered by immersing reaction product in chloroform for 24 h and then in hexane for 24 h. The cycle was alternatively repeated several times until there was no detectable amount of **8**. The relative ratio of **8** in supernatant was evaluated by HPLC measurement.

De-Cross-Linking Reaction (Polymer Reaction of 7 with 8). The cross-linked polymer **7** (40 mg) was swelled in anisole solution (5.0 wt %) with an excess amount of alkoxyamine **8** (50 mg, 0.17 mmol, 20 equiv/alkoxyamine) and charged into a glass tube. The swelled gel was degassed by freeze−pump−thaw cycles, sealed off under vacuum, and incubated at 100 °C for 48 h. The solution was evaporated to dryness, and molecular weight and its distribution were evaluated by GPC measurement without any purification. $M_n = 17\,200$, $M_w/M_n = 1.24$.

Results and Discussion

Synthesis of Reactive Polymers. Methacrylic esters **1** and **5** containing the TEMPO-based alkoxyamine unit were synthesized by a condensation reaction from an alkoxyamine alcohol and methacryloyl chloride. The reaction proceeds even at room temperature to give the desired monomer in over 80% yield without any byproducts derived from the dissociation and/or decomposition of the alkoxyamine unit. Although there have been some reports on polymerizations of monomers containing alkoxyamine unit, all of them were polymerized by conventional free radical polymerization techniques, and the synthesized polymers have been used as macroinitiators for further polymerization on the side chains of polymers.[23] It was previously demonstrated that the copolymerization of MMA and methacrylic ester **1** with alkoxyamine moiety can be accurately controlled through the atom transfer radical polymerization (ATRP) technique.[9,10] This control can be obtained because the TEMPO-based alkoxyamine units do not dissociate below 60 °C.[8a] Therefore, the ATRP of MMA and methacrylic ester **5** with the alkoxyamine moiety of opposite direction to **1** was performed in a similar manner (Scheme S3). The ATRP of the 20/1 mixture of MMA and **5** was carried out in anisole at 50 °C using 2-(EiB)Br as the initiator and Cu(I)Br/Sp as the catalyst complex. Although a slight saturation was observed at the initial stage of polymerization, the concentration of active species was almost constant throughout the polymerization (Figure S1). M_ns increased linearly with conversion and were in good agreement with those calculated, and the polydispersities were relatively low (Figure S2). The signals assigned to the alkoxyamine units (3.32, 3.42, 4.10, 4.40, 4.88, and 7.34 ppm) and the methyl esters (3.60 ppm) were clearly observed in the ^{1}H NMR spectrum of **6** and confirmed from the integration of each peak that the composition of copolymer approximately corresponds to the feed ratio of monomers (copolymer composition; MMA/**5** = 19/1). This also means that the alkoxyamine units are randomly distributed along the PMMA chain.

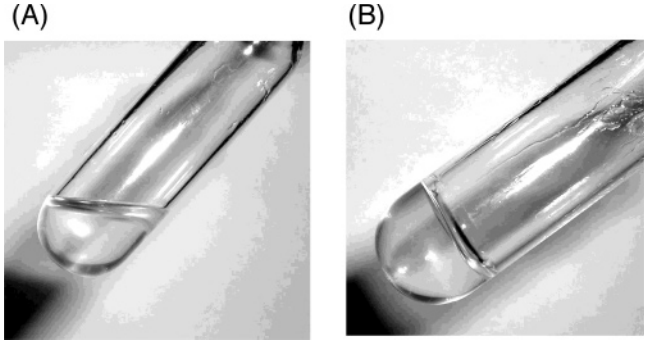


Figure 1. Pictures of the solution of the mixture of **2** ($M_n = 16\,200$, $M_w/M_n = 1.19$, MMA/**1** = 19/1) and **6** ($M_n = 15\,500$, $M_w/M_n = 1.12$, MMA/**5** = 19/1) in anisole (10 wt %) (A) before and (B) after heating at 100 °C for 24 h.

Dynamic Covalent Cross-Linking Reaction. Prior to the polymer reaction between **2** ($M_n = 16\,200$, $M_w/M_n = 1.19$, MMA/1 = 19/1) and **6** ($M_n = 15\,500$, $M_w/M_n = 1.12$, MMA/5 = 19/1), 10 wt % anisole solutions of each polymer were heated independently at 100 °C. In these cases, there was no change in the molecular weight or the molecular weight distribution. Although the alkoxyamine units on the side chain dissociated homolytically at 100 °C producing carbon and nitroxide radicals, no detectable intra- and intermolecular carbon−carbon coupling reactions occurred due to the rapid capping of carbon radicals by nitroxide radicals. This finding is also supported by the color observation of the solution. If the carbon−carbon coupling reaction occurs in the system, the solution turns from colorless to red due to the generation of nitroxide free radicals. In these cases, there was no change in color of the solutions, which demonstrates the absence of a carbon−carbon coupling reaction.

Cross-linking reactions were carried out by heating an anisole solution of the mixture of **2** and **6** at 100 °C at various concentrations. After heating, the solution transformed into a gel at high concentrations (Figure 1). To follow the details of the thermodynamic covalent cross-linking reaction, the dependence on reaction time and concentration was investigated. The polymer molecular weight after the cross-linking reaction was evaluated by GPC. GPC profiles of the polymers after cross-linking reaction at 0.5 wt % condition are shown in Figure 2. Molecular weight increased with increasing reaction time and became constant after 24 h, indicating that the reaction reached equilibrium at 24 h under this concentration condition. Figure 3 represents the GPC profiles of the polymers after the cross-linking reaction at various concentrations for 6 h. The cross-linking behavior depended remarkably upon the concentration; the molecular weight increased rapidly with increasing concentration, and the gelation occurred above 5.0 wt %.

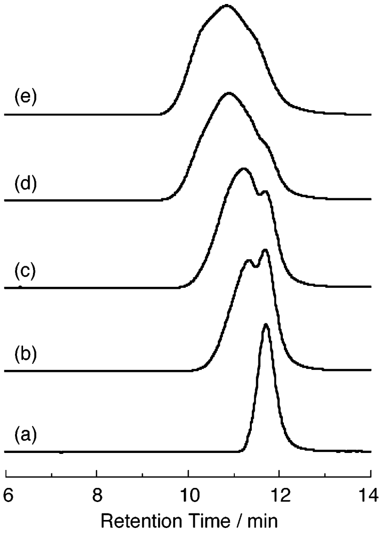


Figure 2. Comparison of GPC profiles of (a) the mixture of the starting polymers **2** (M_n = 16 200, M_w/M_n = 1.19, MMA/**1** = 19/1) and **6** (M_n = 15 500, M_w/M_n = 1.12, MMA/**5** = 19/1) and the reaction product after heating at 100 °C at the 0.5 wt % concentration condition for (b) 2, (c) 6, (d) 12, and (e) 24 h.

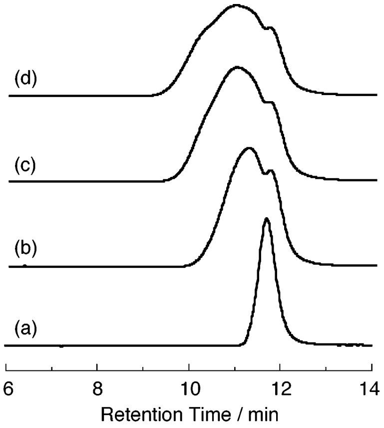


Figure 3. Comparison of GPC profiles of (a) the mixture of the starting polymers **2** (M_n = 16 200, M_w/M_n = 1.19, MMA/**1** = 19/1) and **6** (M_n = 15 500, M_w/M_n = 1.12, MMA/**5** = 19/1) and the reaction product after heating at 100 °C for 6 h at (b) 0.5, (c) 1.0, and (d) 2.0 wt % concentration conditions.

In the polymer cross-linking system, if cross-linking due to the radical exchange reaction among alkoxyamine units occurs, alkoxyamine **8** is formed. The nature can be applied to the determination of the number of cross-linked points. Generated **8** was recovered by immersing the reaction product in chloroform for 24 h and then in hexane for 24 h, and the amount of **8** in supernatant was evaluated by HPLC. The cycle was repeated several times until there was no detectable amount of **8**. Figure 4 shows the relationship between reaction time and the relative ratio of **8** recovered from the product. The relative ratio was normalized by setting the maximum value to 1. The amount of **8** increased with reaction time and maintained a constant value after the gelation. Because of the restricted molecular motion at the gel state, the radical exchange reaction became difficult and apparently reached equilibrium. Interestingly, at the same reaction times, the relative ratio of **8** was higher at low concentrations, indicating that the number of cross-linked points at low concentrations was larger than that at high concentrations. On the other hand, as shown in Figure 3, the molecular weight was higher at high concentrations at the same reaction times.

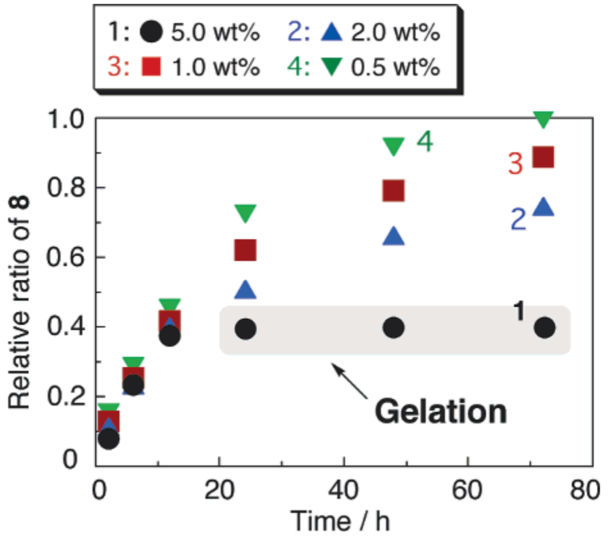


Figure 4. Dependence of the relative ratio of **8** on reaction time for the cross-linking reaction of **2** (M_n = 16 200, M_w/M_n = 1.19, MMA/**1** = 19/1) and **6** (M_n = 15 500, M_w/M_n = 1.12, MMA/**5** = 19/1) in anisole at 100 °C at 5.0, 2.0, 1.0, and 0.5 wt %. The relative ratio is normalized by setting the maximum value to 1.

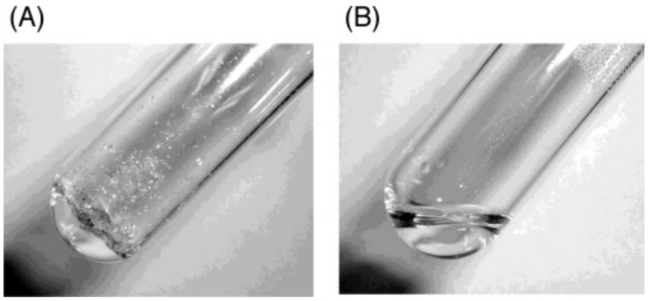


Figure 5. Pictures of the cross-linked polymer **7** swelled in anisole solution with an excess amount of alkoxyamine **8** (10 wt %, 20 equiv/alkoxyamine units) (A) before and (B) after heating at 100 °C for 24 h.

On the basis of the above observations, we have developed a reaction model for the thermodynamic covalent cross-linking system. As the reaction proceeds, the cross-linking reaction occurs by intermolecular and intramolecular cross-linking. It is considered that the restricted molecular motion of the polymer chains at high concentrations results in fewer cross-linked points. However, at high concentrations, intermolecular cross-linking precedes intramolecular cross-linking because collision with the surrounding macromolecules is a facile process, resulting in drastic molecular weight increases with fewer cross-linked points. On the other hand, at low concentrations, intramolecular cross-linking precedes intermolecular cross-linking because collision with the surrounding macromolecules is difficult. Thus, the reaction system gives cross-linked polymers with thermodynamically favorable molecular weights reflecting the concentration conditions in an equilibrium state. The reaction behavior is characteristic of thermodynamic reaction systems.

Dynamic Covalent De-Cross-Linking Reaction. In the thermodynamic polymer reaction, the product structure depends completely on the equilibrium and stoichiometric conditions. The reverse reaction, transformation from gel to solution, was examined through stoichiometric control. The cross-linked polymer **7** was swelled in anisole solution with an excess amount of alkoxyamine **8** (20 equiv/alkoxyamine unit) and heated at 100 °C for 48 h. After heating, the sample transformed from a gel state to a colorless solution (Figure 5). Interestingly, the polymer molecular weight after the de-cross-linking reaction

($M_n = 17\,200$, $M_w/M_n = 1.24$) almost corresponded to that of a mixture of the starting polymers ($M_n = 15\,800$, $M_w/M_n = 1.17$), and there were no remarkable shoulder peaks in the high molecular weight region. These results prove that the cross-linked points are thermally dissociable and that the reaction system is apparently reversible under stoichiometric control.

Conclusion

We have demonstrated that reversible covalent cross-linking is accomplished by the use of alkoxyamine-based dynamic covalent bonds as the cross-linking units. The poly(methacrylic ester)s containing alkoxyamine units on the side chains cause cross-linking via a radical exchange reaction of the alkoxyamines upon heating. The cross-linked structure is quantitatively de-cross-linked under stoichiometric control. The novel dynamic polymer cross-linking system would afford materials that can be reorganized in response to heating to form the proper macromolecular architecture reflecting the equilibrium and stoichiometric conditions. Future work will describe evaluations of true reversibility, rheological properties, and the structure of the gels.

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Supporting Information Available: Schemes representing the synthesis of label compounds **1**−**6** as well as figures showing the controlled atom transfer radical copolymerization of MMA and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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