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Dynamic Transformation of Polymer Structure by Radical Crossover Reaction

Yuji Higaki[1], Hideyuki Otsuka[1,2]* and Atsushi Takahara[1,2]*
[1]Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, JAPAN
[2]Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki, Higashi-ku,
Fukuoka 812-8581, JAPAN,
Tel: 81-92-642-2318, Fax: 81-92-642-2715, e-mail: otsuka@ms.ifoc.kyushu-u.ac.jp

A novel dynamic polymer reaction system using radical exchange of alkoxyamine units has been demonstrated. Polymethacrylic ester containing 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO)-based alkoxyamine units in the side chain and alkoxyamine-terminated polystyrene were prepared by atom transfer radical polymerization (ATRP) and nitroxide-mediated free radical polymerization (NMP), respectively. Radical crossover reaction of alkoxyamine units between the side chain and chain end of each polymer afforded the graft copolymers that polystyrene chains are connected to the polymethacrylic ester backbone. The structure of the graft copolymers is supported by size exclusion chromatography (SEC) and spectral data. Radical crossover reaction of alkoxyamine units among the side chains caused cross-linking to form gel like structure. The obtained graft polymers and cross-linked polymers were successfully transformed reversibly to the starting materials by heating with excess amount of alkoxyamine derivative.

Key words: Dynamic covalent bonds, Living radical polymerization, Polymer reaction, Graft copolymers

INTRODUCTION

Quite a few polymer reactions have been developed because of the desire to prepare advanced materials from limited palette. These techniques can also facilitate a novel polymer synthetic method. 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 reformed from it or for it to be converted into another product.

2,2,6,6-Tetramethylpiperidine-1-oxy (TEMPO)-based alkoxyamine derivatives have been used as unimolecular initiators for nitroxide-mediated living free radical polymerization (NMP)[1-3]. A number of reversible activation-deactivation cycles caused by dissociation and association of alkoxyamine unit allow all the chains to have an almost equal opportunity to grow and minimize side reactions which permanently deactivate the polymer chains, resulting in the formation of low molecular weight distribution polymers[4]. The thermally induced reversible dissociation/association nature of polystyrene-nitroxide system has been confirmed by ESR and exchange[5-7] studies. Recently, the authors have developed 'dynamic covalent polymer' which is capable of reorganization by the exchange of covalent bonds in the main chain[8-11]. The 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 many functional groups. The system can be responsive to external stimulation, and change its architecture depending on environmental conditions. 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. Furthermore, the system also allows access to more complex, thermodynamically stable polymeric architectures. The authors report herein the dynamic formation of graft copolymer and dynamic cross-linking reaction with thermally reversible covalent bonds.

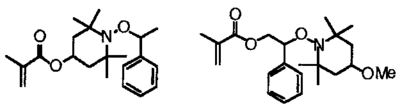
2. EXPERIMENTAL

2.1 Measurements

Monomer conversion was determined by ^{1}H NMR measurement (JEOL JNM-EX400) of the crude reaction mixtures in $CDCl_3$. Molecular weights as well as polydispersity 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)] at a flow rate of 0.8 $mL \cdot min^{-1}$. 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 $mL \cdot min^{-1}$. High performance liquid chromatography (HPLC) analyses were performed on a Shimadzu system equipped with a column (JASCO Crestpak C18S).

2.2 Materials

4-Hydroxy-TEMPO[12], 4-methoxy-TEMPO[13], and alkoxyamine derivatives[5] (**1**, **6**, **7**) were prepared and purified as previously reported. Ethyl 2-bromoisobutylate (2-(EiB)Br), (-)-sparteine (Sp), and methacryloyl chloride were used without further purification. Methyl methacrylate (MMA), styrene, and anisole were purified by distillation under reduced pressure over calcium hydride. All other reagents were purchased from commercial sources and used as received. The alkoxyamine derivative **2** and **8** were prepared by condensation reaction between **1** and methacryloyl chloride, and between **7** and methacryloyl chloride, respectively. TEMPO-terminated polystyrene **4** was synthesized through the conventional NMP procedure with **6** as initiator.



2 **8**

Fig.1. Chemical structure of **2** and **8**

2.3 Synthesis

General procedure for preparation of poly(methacrylic ester)s containing alkoxyamine units at the side chain.

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.

Dynamic grafting reaction

In a typical run, a 1.0 wt% anisole solution of polymer **3** (M_n = 11800, M_w/M_n = 1.18, 92 mg, MMA/**2** = 4.8/1) 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 = 24000, M_w/M_n = 1.16 (Molecular weight increased with time)

Dynamic cross-linking reaction

In a typical run, **3** (M_n = 15500, M_w/M_n = 1.12, MMA/**2** = 19/1, 10mg) and **9** (M_n = 16200, M_w/M_n = 1.19, MMA/**8** = 19/1, 10 mg) were dissolved in anisole (10 wt% of total polymer concentration) and the solution was degassed by three freeze-pump-thaw cycles and sealed off under vacuum. The solution was incubated at 100 °C under argon for 24 h. The reaction product was alternatively immersed in chloroform and hexane for 24 hours to recover eliminated **6**, and the weight of **6** was measured by HPLC measurement.

3.RESULTS AND DISCUSSION

3.1 Synthesis of polymers containing alkoxyamine units.

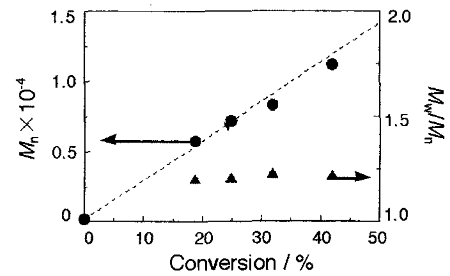
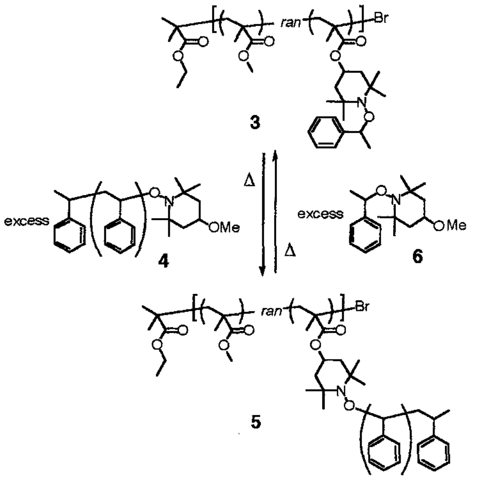


Fig.2. The evolution of M_n and M_w/M_n of the polymers as a function of monomer conversion for solution polymerization of MMA and **2** in anisole.

Methacrylic ester containing TEMPO-based alkoxyamine unit **2** was prepared by condensation reaction of TEMPO-based alcohol derivative **1** and methacryloyl chloride. The reaction proceeded smoothly at room temperature to give the desired monomer **2** in 85% yield after purification. To control the molecular weight as well as macromolecular architecture with facile procedure, we have examined the use of "living" free radical polymerizations for the preparation of reactive polymers. As detailed previously, TEMPO-based alkoxyamine unit does not exchange under 60 °C[8]. Accordingly, the atom transfer radical polymerization (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 M_n and M_w/M_n of resulting polymers are plotted as a function of conversion in Fig.2. M_ns increase linearly with conversion and are in good agreement with those calculated, which is fully consistent with a "living" free radical polymerization. The ^{1}H NMR spectrum of resulting polymer **3** revealed the signals assigned to alkoxyamine units and methyl esters, and confirmed from the integration of each peak that the composition of copolymer approximately corresponds to feed ratio of monomers (copolymer composition; MMA/**2** = 4.8/1).

A TEMPO-terminated polystyrene **4** with controlled molecular weight (M_n = 1700, M_w/M_n = 1.15) was synthesized through the conventional NMP procedure with **6** as initiator. The ^{1}H NMR spectrum of **4** shows the signals between 0.1 and 0.5 ppm that have been previously assigned to the chain-capping TEMPO moiety. 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

Scheme 1. Schematic representation of dynamic grafting reaction



molecular weight similar to those obtained from the GPC measurement, indicating approximately no loss of alkoxyamine chain end.

3.2 Dynamic grafting reaction

The mixture of **3** and excess amount (5.0 eq./alkoxyamine) of **4** was dissolved in anisole, and heated at 100 °C under argon (Scheme 1). As shown in Fig.3(A), as the reaction proceeded, the SEC profiles derived from **3** clearly shifted to a higher molecular weight region. In addition, integral ratio of the peak derived from **4** to that for **3** significantly decreased. After 24 h, M_n and the integral ratio became constant, which indicates that the equilibrium is reached in the system. By careful fractionation of the reaction mixture using preparative HPLC, the polymer at higher molecular weight region was successfully separated. ^{1}H NMR spectrum of isolated polymer **5** revealed significant signals assigned to polystyrene units appeared at 1.0-2.5 ppm and 6.2-7.4 ppm as well as the signals assigned to methacrylic ester backbone. The resonance derived from unreacted alkoxyamine units also appears at 7.3 ppm, and its integral ratio to methyl ester apparently decreased, compared with **3**. By comparing the integration value of the signals for the unreacted alkoxyamine units and that for methyl ester, degree of grafting was evaluated to be 58 % in 5.0 eq. system. On account of the bulkiness of the grafted polystyrene chains, the degree of grafting is limited to relatively low value. The molecular weight calculated from integration value of ^{1}H NMR spectrum was found to be 28200. On the other hand, the M_n estimated by SEC measurement was 24000, 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.

The reversibility of the reaction system was also investigated. The mixture of isolated graft polymer **5** (M_n = 24000, M_w/M_n = 1.16) and excess amount (8.3 eq./alkoxyamine) of alkoxyamine derivative **6** was dissolved in anisole, and heated at 100 °C under argon. As shown in Fig.3(B), as the reaction proceeded, SEC profile of **5** shifted to the lower molecular weight region. Significantly, SEC profile corresponding to eliminated polystyrene appeared, and integral ratio of the profile to the one of graft polymer increased with increasing reaction time. The dependence of M_n on reaction time is presented in Fig.4 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**. These results prove that the dynamic polymer grafting system is realized by the exchange reaction of alkoxyamine groups and that the reaction system is apparently reversible under equilibrium control[14].

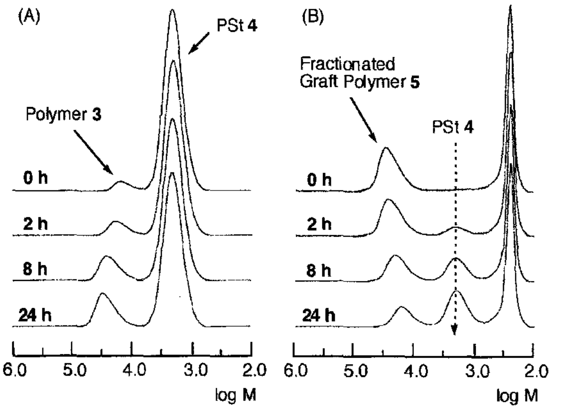


Fig.3. SEC profiles for (A) polymer reaction of **3** with **4** (5.0 eq. alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon and (B) polymer reaction of **5** with **6** (8.3 eq. alkoxyamine units) in anisole (1 wt % polymer solution) at 100 °C under argon.

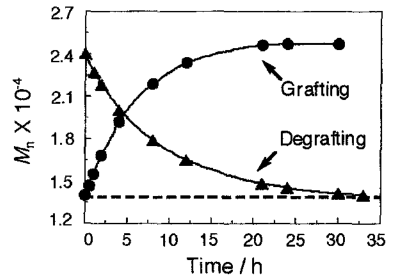


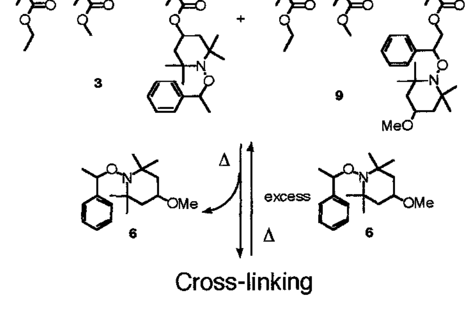
Fig.4. Dependence of M_n on reaction time for (circle) polymer reaction of **3** with **4** in anisole at 100 °C under argon and (triangle) polymer reaction of **5** with **6** in anisole at 100 °C under argon.

3.3 Dynamic cross-linking reaction

Similarly to the preparation of **2**, methacrylic ester **8** containing TEMPO-based alkoxyamine unit was prepared by condensation reaction of TEMPO-based alcohol derivative **7** and methacryloyl chloride to give the desired monomer **8** in 82% yield after purification. Polymerization of 20:1 mixture of MMA and **8** was conducted in anisole at 50 °C using 2-(EiB)Br as the initiator and Cu(I)Br/Sp as the catalyst complex. The nearly linear relationships between ln([M]$_0$/[M]$_t$) and time were observed, indicating that the number of active species is almost constant throughout the polymerization. M_ns increase linearly with conversion and are in good agreement with those calculated, that is, the control of molecular weight is also accomplished on the copolymerization of MMA and **8** as well as the one of MMA and **2**.

In advance of polymer reaction between **3** and **9**, 10 wt% anisole solutions of each polymer were heated independently at 100 °C. In these cases, there were no

Scheme 2. Schematic representation of dynamic cross-linking reaction



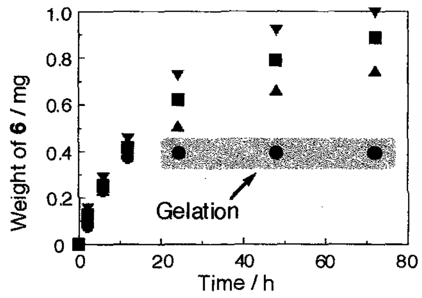


Fig. 5. Dependence of the amount of **4** on reaction time for polymer reaction of **3** with **9** in anisole at 100 °C under argon.

changes in molecular weight and molecular weight distribution. It can be concluded that there are no detectable intra- and intermolecular carbon-carbon coupling reactions at the side chains. This fact is also supported by the color observation of solution. If the carbon-carbon coupling reaction occurs in the system, the solution changes from colorless to red caused by generation of nitroxide free radicals. In these cases, there was no change in color of solution, which demonstrates the absence of carbon-carbon coupling reaction.

Cross-linking reactions were then performed by heating an anisole solution of the mixture of **3** and **9** at 100 °C at various concentration conditions (Scheme 2). Cross-linking behavior remarkably depends on the concentration condition and the gelation occurred above 5.0 wt%. Because this reaction is regarded as thermodynamic reaction, intramolecular crossover reaction would be preceded under dilution condition. Thus, the gelation accomplished only under high concentration condition enough to intermolecular crossover reaction is preceded. In this polymer reaction system, if the cross-linking reaction due to the radical crossover reaction among alkoxyamine units occurs, alkoxyamine derivative **6** is formed. The nature of this reaction system can be applied to the determination of cross-linking points. The generated **6** were recovered by immersing reaction product in chloroform for 24 hours and then in hexane for 24 hours. The cycle was alternatively repeated several times until there was no detectable amount of **6**. Fig.5 shows the relationship between reaction time and the weight of **6** recovered from the product. The amount of **6** increased with reaction time and maintained constant value after the formation of gel. On account of the restriction of molecular motion at the gel state, radical crossover reaction becomes difficult and apparently reaches to pseudo-equilibrium. In addition, molecular weight of polymers was determined by SEC measurement. Interestingly, although the weight of **6** recovered from the product was higher at low concentration condition, the molecular weight of the polymer at the same time was higher at high concentration condition. These phenomena are probably due to the intermolecular coupling reaction at low concentration condition.

The reverse reaction, transformation from gel to solution, was then examined. The cross-linked polymer formed by radical crossover reaction was swelled by the anisole solution of **4** (10 eq./alkoxyamine units). The gel was degassed by three freeze-pump-thaw cycles and sealed off under vacuum and heated at 100 °C for 24 h. After heating, the sample transformed from gel state to colorless solution. Molecular weight of the product was evaluated by SEC. Interestingly, the M_n of product almost corresponds to the initial M_n of the mixture of **3** and **9**, which indicating that the reaction system is apparently reversible under equilibrium control and the cross-linking state is thermodynamically unstable.

4. CONCLUSION

In summary, the authors have demonstrated that dynamic formation of graft copolymers and cross-linked polymers are accomplished by radical crossover reaction among the alkoxyamine units. The molecular weight of reactive polymers containing alkoxyamine units can be controlled by utilizing dual living free radical polymerization techniques. 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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