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Reorganizable Chemical Polymer Gels Based on Dynamic Covalent Exchange and Controlled Monomer Insertion

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ABSTRACT: Covalently networked polymer gels were developed with two notable functionalities: de-cross-linking by dynamic covalent exchange based on a radical crossover reaction and insertion of a monomer into the cross-linkers. The network polymer gels were synthesized by free-radical copolymerization of styrene and a bifunctional monomer with an alkoxyamine linker that has two capabilities to exchange with other alkoxyamine derivatives in the radical process and to polymerize styrene in a controlled manner. Three types of network polymers with different cross-linking densities were obtained by changing the ratio of the bifunctional monomer to styrene. The de-cross-linking reaction was carried out by heating the network polymers with excessive alkoxyamine compound in anisole, and it was made clear that the de-cross-linking behavior strongly depended on the cross-linking densities. The insertion of styrene into the alkoxyamine units at the cross-linking points was also performed by heating the network polymers swollen with styrene and anisole, and it was revealed that the mesh sizes grew larger by the insertion of styrene into their skeleton and that the cross-linking density decreased as the reaction proceeded. The variation of the network structures in these reactions was successfully evaluated by small-angle X-ray scattering and dynamic viscoelasticity measurements.

Introduction

Polymer gels have attracted much attention and have been widely applied in various fields due to their particular abilities such as intake of solvents[1] and/or substances[2] and functionalities.[3] When we focus on the basic science of these soft and wet materials, they are classified into two types, chemical gels and physical gels, which are networked by covalent bonds and noncovalent bonds, respectively. Because the cross-linking points of typical chemical gels such as poly(styrene-*co*-divinylbenzene)[4] consist of strong covalent bonds, it is difficult to change their structures after preparation. Therefore, the cross-linking density and composition of a network polymer should be controlled in the preparation step. Meanwhile, in the case of physical gels, the cross-linking states can be changed by external stimuli like temperature,[5] pressure,[6] and substance,[7] known as the so-gel transition, because their bonding states and/or structure depend on thermodynamic control.

Recently, covalent bonds with the ability to reach an equilibrium state between combination and dissociation under certain conditions have been studied, and the systematic method for controlling the structures of compounds and polymers based on these reversible covalent bonds has been spotlighted as dynamic covalent chemistry (DCC).[8] So far, by using such covalent bonds with dynamic properties such as disulfide bonds,[9] cyclopentadiene dimeric adducts,[10] and spiro-orthoesters,[11] the development of network polymer gels with de-cross-linking abilities has been reported. We focused alkoxyamines, which are adducts of styryl radical and nitroxide radical, as covalent bonds with two notable dynamic properties to exchange their units in a radical process[12,13] and to initiate controlled radical polymerization of styrene derivatives.[14,15] We have achieved a structure transformation between linear poly(methacrylate)s and their cross-linked structure via radical crossover reaction of alkoxyamine units by thermal and stoichiometric control.[16]

In the present study, covalently networked polymer gels were designed with two notable functionalities: de-cross-linking by dynamic covalent exchange based on a radical crossover reaction and insertion of monomers into the cross-linkers, as shown in Figure 1.

Experimental Section

Materials. 4-Hydroxy-1-((2′-hydroxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (alkoxyamine diol)[14] and 4-methoxy-1-((1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (**3**)[12] were prepared and purified as previously reported. Anisole (99%) and styrene (99%) were purchased from Wako Pure Chemical Industries and purified by distillation under reduced pressure over calcium hydride. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 95%) and sodium hydride (NaH, 60%) were purchased from Wako Pure Chemical Industries and used without further purification. 4-(Chloromethyl)styrene was kindly supplied by AGC Seimi Chemical Co., Ltd., and used without further purification. *N*,*N*-Dimethylformamide (DMF, 99.5%) was purchased from Wako Pure Chemical Industries and purified with a Glass Contour solvent purification system.

Measurements. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectroscopic measurements were carried out at 25 °C with a JEOL JNM-AL300 spectrometer using tetramethylsilane (TMS)

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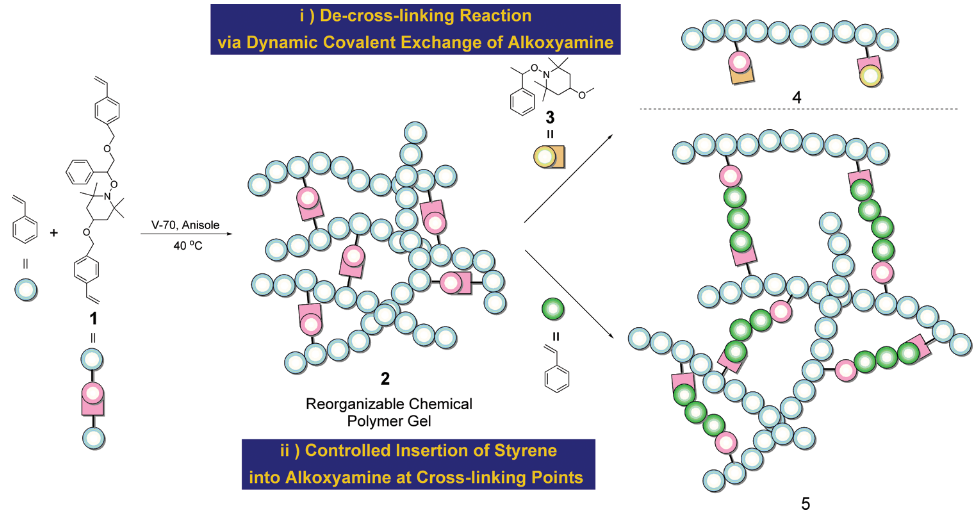


Figure 1. A model of the de-cross-linking reaction via a radical crossover reaction of alkoxyamine units and insertion of styrene into the alkoxyamine units at cross-linking points.

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.

The relative number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymers were estimated by gel permeation chromatographic (GPC) analysis. GPC measurements were carried out at 40 °C on TOSOH HLC-8220 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), and a UV−vis detector (TOSOH UV-8020). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL min^{-1}. Eight polystyrene (PS) standards (M_n = 1060−3 690 000; M_w/M_n = 1.02−1.08) were used to calibrate the GPC system.

HPLC measurements were carried out with a Shimadzu LC-20AD equipped with a Shimadzu SPD-20A UV−vis detector and a JASCO CrestPak C18S column in a Shimadzu CTO-10AS. A mixed solvent (CH_3CN/H_2O = 3/1, v/v) was used as the eluent at 1.0 mL min^{-1}.

SAXS measurements were carried out at the BL40B2 beamline of SPring-8 using an incident X-ray with the wavelength λ = 1.0 Å. Scattered X-rays were detected using a CCD detector with the resolution of 0.112 mm/pixel and 1877 mm sample-to-detector distance calibrated by the average of 6th, 9th, and 11th peaks of collagen. The polymer gels were swollen in anisole for 72 h and measured in 2 mm capillary. The scattering vector (q) was defined as $4\pi \sin(\theta/\lambda)$.

The dynamic viscoelastic measurements were carried out with a Physica MCR101 with a parallel circular plate 12 mm in diameter in anisole (0.2 g/mL) at 25 °C. The swelling samples were left overnight at room temperature to reach swelling equilibrium. The storage elastic modulus (G') was evaluated based on the average values of five measurements.

4-((4′-Vinylbenzyl)methoxy)-1-((2′-((4′′-vinylbenzyl)methoxy)-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (1). The bifunctional monomer (**1**) was synthesized by a condensation reaction of alkoxyamine diol and 4-(chloromethyl)-styrene. Under a nitrogen atmosphere, alkoxyamine-containing diol (0.735 g, 2.50 mmol), DMF (2.5 mL), and NaH (0.36 g, 15 mmol) were charged into a round-bottom flask at 0 °C and stirred for 1 h. Then, 4-(chloromethyl)styrene (1.27 mL, 9.00 mmol) was added dropwise at 0 °C under a nitrogen atmosphere. After stirring for 2 h, methanol (5 drops) was added. Water and ether were added, the aqueous layer was washed with ether, and the combined organic layer was then evaporated to dryness. The crude product was purified by flash chromatography eluting with ethyl acetate/hexane (1/8, v/v) and dried in vacuo to give divinyl monomer **1** as a colorless oil (1.20 g, 91% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.65 (s, 3H; CH_3), 1.05 (s, 3H; CH_3), 1.20 (s, 3H; CH_3), 1.37 (s, 3H; CH_3), 1.43 (d, J = 12 Hz, 1H; CH_2), 1.50 (d, J = 12 Hz, 1H; CH_2), 1.78 (d, J = 12 Hz, 1H; CH_2), 1.90 (d, J = 12 Hz, 1H; CH_2), 3.58−3.70 (m, 2H; CH_2, CH), 3.96 (dd, J = 10 Hz, 5 Hz, 1H; CH_2), 4.42 (d, J = 3 Hz, 2H; CH_2), 4.48 (s, 2H, CH_2), 4.85 (t, J = 5 Hz, 1H; CH), 5.22 (d, J = 10 Hz, 2H; CH_2), 5.72 (dd, J = 18 Hz, 2 Hz, 2H; CH_2), 6.64−6.75 (m, 2H, CH), 7.09−7.38 (m, 13H, aromatic). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 21.31, 33.98, 34.15, 45.56, 60.08, 60.60, 69.72, 69.97, 72.74, 72.77, 85.57, 113.57, 113.61, 126.05, 126.20, 127.39, 127.53, 127.66, 127.89, 136.58, 136.69, 136.80, 138.05, 138.47, 141.63. IR (neat, cm^{-1}): 2942, 2457, 2253, 1794, 1630 (C═C), 1470, 1364, 1091 (C−O−C), 913, 742, 651. HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{35}H_{44}NO_3$, 526.3321; found, 526.3325.

Network Polymers with Alkoxyamine Units (2). In a typical run, divinyl monomer **1** (0.263 g, 0.5 mmol), styrene (0.469 mL, 4.5 mmol), and anisole (0.946 mL) were charged into a test tube, and the test tube was then immersed in an oil bath thermostated at 40 °C under an argon atmosphere. Anisole solution (0.2 mL) of V-70 (7.71 mg, 0.025 mmol) was dropped via syringe under an argon atmosphere. After 96 h, the cross-linked polymer was purified by Soxhlet extraction with dichloromethane, and the remaining solid was collected and dried under vacuum to give a colorless solid (0.653 g, 89% yield). Elemental analysis: found C, 84.21; H, 7.68; N, 1.06.

De-Cross-Linking Reaction of Cross-Linked Polymers. In a typical run, cross-linked polymer **2b** (20 mg) and alkoxyamine **3** (20 equiv/alkoxyamine in **2b**) dissolved in anisole (180 μL) were charged into a glass tube. The solution was degassed by five freeze−pump−thaw cycles. Subsequently, the glass tube was sealed off under vacuum and heated at 100 °C for 48 h.

Polymerization of Styrene from Alkoxyamines at Cross-Linking Points. In a typical run, cross-linked polymer **2b** (20 mg), styrene (90 μL), and anisole (90 μL) were charged into a glass tube. The solution was degassed by five freeze−pump−thaw cycles. Subsequently, the glass tube was sealed off under vacuum and heated at 100 °C for 8 h.

Results and Discussion

Preparation of Network Polymers with Alkoxyamine Units at Cross-Linking Points. Network polymers (**2**) with alkoxyamine units at the cross-linking points were prepared by free-radical copolymerization of styrene and alkoxyamine-containing bifunctional monomer **1**. The copolymerization

Table 1. Conversion, Copolymer Composition Ratio of Styrene and Bifunctional Monomer 1, Yield, and Swelling Degree of Cross-Linking Reaction under Several Copolymerization Conditions of Styrene and 1[a]

network polymer	$[St]_0/[\mathbf{1}]_0$	conv/%		[St]/[**1**] in copolymer	yield/%	swelling degree (w/w)
		St	**1**			
2a	9/1	81	97	7.2/1	89	2.9
2b	19/1	63	90	10.6/1	70	8.7
2c	49/1	57	78	17.8/1	25	18.9

[a] The conversion and copolymer composition were estimated by HPLC measurement and elemental analysis, respectively.

was carried out in anisole ([monomer]/[anisole] = 1/2, v/v) at 40 °C with V-70 ([monomer]/[initiator] = 200/1)) as an azo-type radical polymerization initiator that can generate radicals at relatively low temperature. Three different copolymerization conditions of styrene and bifunctional monomer **1** ([styrene]/[**1**] = 9/1, 19/1, and 49/1) were utilized, and gelation of the system was observed in all cases. Table 1 summarizes the conversion, the copolymer composition ratio of styrene and bifunctional monomer **1**, the yield, and swelling degree of network polymers under the three copolymerization conditions. It is obvious that the conversion of styrene and **1** increased under the high-ratio condition of **1**. This increase occurred because the highly viscous diffusion-limited state at high ratios of the bifunctional monomer retarded the termination reaction, which is known as the "Trommsdorff (gel) effect". Importantly, the composition of **1** in copolymers naturally increased with the feed ratio of **1**. The composition was considerably different from the feed ratio because linear polymers and branched polymers with low molecular weight might be completely removed at the purification stages, corresponding to the yields of the network polymers. Additionally, their swelling degree for anisole decreased with increasing ratio of **1** because the gels with lower cross-linking densities could keep more solvent in their network structures.

Cross-Linking States of Network Polymers. The cross-linking states of network polymers (**2**) were evaluated from the viewpoint of gel structures. Scattering measurement was performed, which is one of the most useful methods to give knowledge of network structures in gels.[17] The network polymers swollen by anisole for 72 h were measured by small-angle X-ray scattering (SAXS) measurement, and scattering intensity differences between solution and solvent ($\Delta I(q)$) are discussed. An equilibrium swelling was reached for 12 h in anisole, being confirmed by swollen mass of anisole. Figure 2a shows SAXS profiles of network polymers **2a**, **2b**, and **2c** and their fitting curves by scattering functions, which describes two components as structure of the phase separation (fractal dimension formalism[18]) and the correlation between polymer chains (Ornstein−Zernike formalism[19]), as follows:

$$I(q) = Aq^{-D} + \frac{I_1(0)}{1+q^2\xi^2} \qquad (1)$$

where A and $I_1(0)$ are constant values and D is fractal dimension. ξ is polymer−polymer correlation length, which relates directly to the mesh size of network polymers. Herein, the obtained ξ values are also shown in Figure 2a. With increasing content of **1**, the ξ became shorter. It was obviously because the higher copolymer composition of **1** provided smaller mesh sizes of network polymers. Furthermore, dynamic viscoelasticity measurement was performed by using a rheometer with a parallel circular plate in anisole (0.2 g/mL) at 25 °C. Figure 2b shows G' of network polymers **2a**, **2b**, and **2c** against the angular frequency. The frequency dependence of G' could almost not be observed, which suggests that prepared polymer samples have gel characteristics due to their network structure.[20] Furthermore, G' increased with copolymer composition of **1** higher. This increase occurred because the gels with higher cross-linking densities entered a more solid state,[21] indicating that the value of the elastic modulus corresponding to a gel structure with a high cross-linking density.

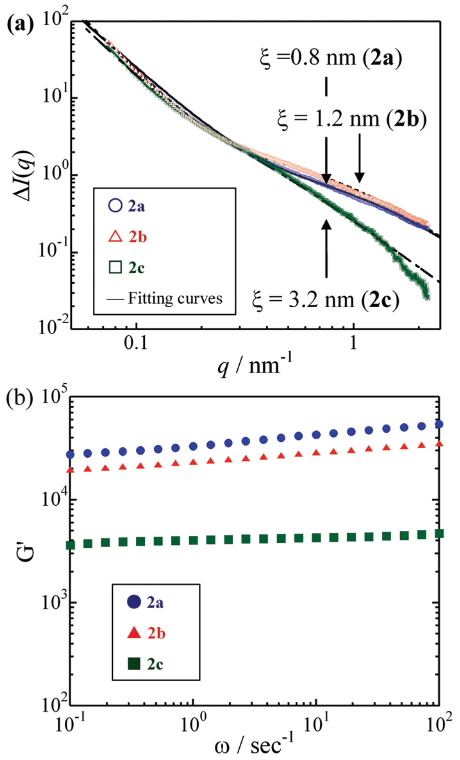


Figure 2. (a) SAXS profiles of network polymers **2a**, **2b**, and **2c** swollen by anisole, and their fitting curves described by eq 1, and (b) G' of cross-linked polymer **2a**, **2b**, and **2c** in anisole (0.2 g/mL) against the angular frequency at 25 °C with a 12 mm diameter parallel circular plate. The plots were the average values of five measurements.

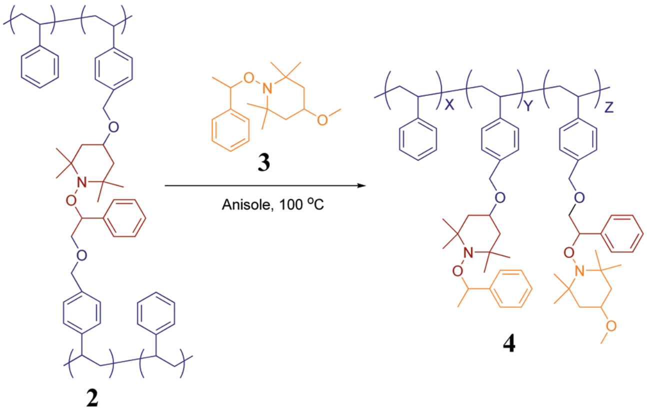
De-Cross-Linking Reaction via Radical Crossover Reaction. In two notable capabilities of alkoxyamine units, the radical crossover reaction enables exchange of alkoxyamine units at cross-linking points of the network polymers. In the presence of an excess amount of alkoxyamine compound, a crossover reaction between the cross-linking point and alkoxyamine compound is expected to occur preferentially and result in de-cross-linking of the network structure. The de-cross-linking reactions were carried out by heating network polymers **2a**−**2c** with an excess amount of alkoxyamine **3** (20 equiv/alkoxyamine at cross-linking points) in anisole (10 wt %) at 100 °C, as shown in Scheme 1. In the case of network polymer **2c** with the lowest cross-linking density, the fluidity of the solution increased with increases in the reaction time, and a macroscopic gel completely disappeared and converted into transparent solution after heating for 6 h. The gel state was entirely fluidized after the reaction in the presence of **3**, although the gel state was kept in the absence of **3**. From these observations, it is obvious that the

Table 2. State of the Reaction Mixture before and after De-Cross-Linking of Network Polymers 2 in the Presence of 3 for 48 h and the Molecular Weight and Polydispersities of De-Cross-Linked Polymers 4

	state of reaction mixture		de-cross-linked polymer	
network polymer	before	after (fluid time)	M_n	M_w/M_n
2a	partly swollen	fully swollen	–[a]	–[a]
2b	fully swollen	liquid (30 h)	23 900	4.17
2c	fully swollen	liquid (6 h)	16 500	2.29

[a] A fluid solution was not given even after heating for 48 h.

Scheme 1. De-Cross-Linking Reaction of the Network Polymer via a Radical Crossover Reaction of Alkoxyamine Units in Response to Heating at 100 °C with an Excess Amount of Alkoxyamine 3 in Anisole (10 wt %)



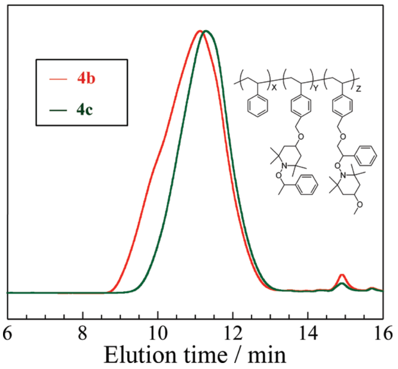


Figure 3. GPC curves of de-cross-linked polymers **4b** and **4c**.

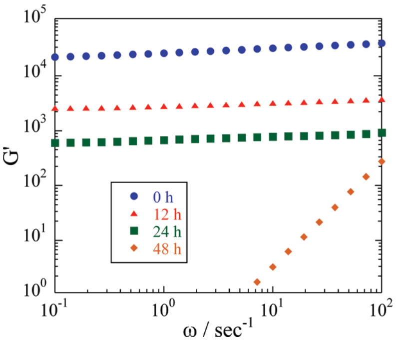


Figure 4. G' of network polymer **2b** and its de-crosslinked polymers in the presence of **3** at 100 °C after 12, 24, and 48 h in anisole (0.2 g/mL) against the angular frequency at 25 °C with a 12 mm diameter parallel circular plate.

de-cross-linking reaction of network polymer **2c** proceeded due to a radical crossover reaction of alkoxyamine units.

In order to evaluate the influence of cross-linking densities on the de-cross-linking behavior, de-cross-linking reactions of network polymers **2a** and **2b** with higher cross-linking densities than that of **2c** were carried out. Similar to **2c**, the solution of **2b** before heating was fully swollen to afford a macroscopic gel, but the gel completely disappeared after heating in the presence of **3** for 30 h. Before the gel states were lost, their swelling degree increased with reaction time because their cross-linking densities came down. In contrast, the solution of **2a** was partly swollen before heating due to its higher cross-linking density, and it kept gel state even after 48 h. Figure 3 shows GPC curves of de-cross-linked polymers **4b** and **4c** after heating **2b** and **2c**, respectively, in the presence of **3** (20 equiv/alkoxyamine at cross-linking points) for 48 h. A peak over the exclusion limit was not observed, and monomodal peaks were obtained for **4c**. The peak for **4b** was accompanied by a small shoulder in higher molecular weight region. Table 2 summarizes the state of the reaction mixture before and after the de-cross-linking reaction had proceeded for 48 h and M_n and M_w/M_n of de-cross-linked polymers **4b** and **4c**. Before heating, the swelling volume was higher with decreasing cross-linking density, which is known as a general property of network polymer gels. A longer reaction time was needed to fluidize the gels in the case of network polymer **4b** with higher cross-linking density compared with network polymer **4c**, and **4a** did not fluidize. Furthermore, both M_n and M_w/M_n of **4b** were larger than those of **4c**. This difference was because small amount of cross-linking points are still remaining in **4b**, and the degree of polymerization was higher due to the gel effect in the preparation stages of **2b**. It is also considered that the diffusion coefficient of alkoxyamine units in cross-linking points was lower with a higher cross-linking density, and the de-cross-linking reaction rate was reduced. From the results obtained above, it is obvious that the state of the reaction mixture and the de-cross-linking behavior strongly depends on the cross-linking density.

Additionally, the change in the network structure was evaluated by dynamic viscoelasticity. Figure 4 shows G' of network polymer **2b** in anisole against the angular frequency in the time course of the de-cross-linking reaction. The G' decreased with increasing reaction time, and characteristic angular frequency dependence for linear polymers was confirmed after heating for 48 h. These data strongly support that the network structure was gradually broken down with the progress of the crossover reaction.

Polymerization of Styrene from Alkoxyamine at Cross-Linking Points. Alkoxyamine derivatives have been used frequently as initiators for nitroxide-mediated radical polymerization (NMRP) of monomers such as styrene derivatives and acrylates. In the present system, monomer insertion into the cross-linking points was expected to drastically change the network structure. Insertion of styrene into the cross-linking points was carried out by heating network polymers **2a** and **2b** swollen by styrene and anisole ([styrene]/[anisole] = 1/1, v/v, 10 wt %) at 100 °C, as shown in Scheme 2. Figure 5a shows kinetic plots of $\ln[M]_0/[M]$ versus reaction time in the case of polymerization of styrene from network

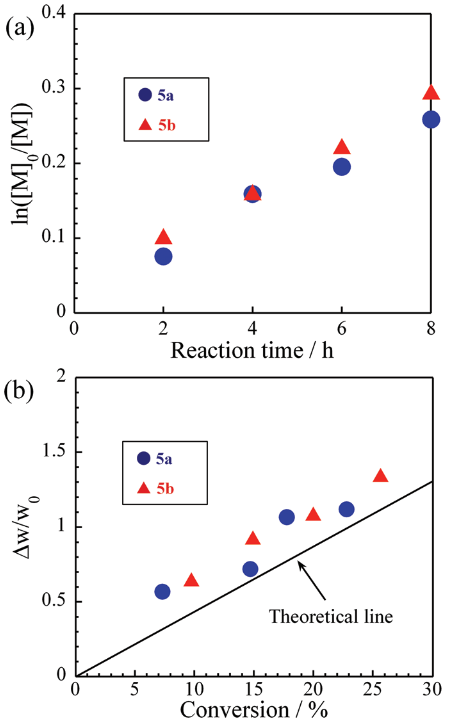
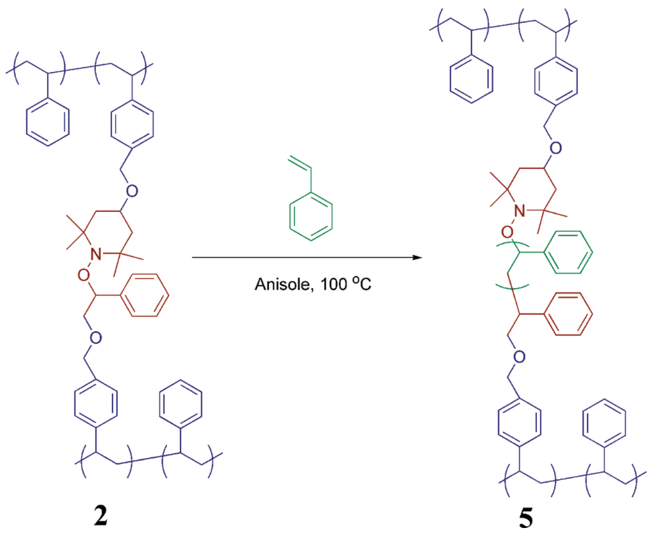


Figure 5. (a) Kinetic plots and (b) $\Delta w/w_0$ versus conversion plots in the polymerization of styrene from alkoxyamines at the cross-linking points. Polymerization was carried out by heating network polymers **2a** and **2b** in styrene and anisole (1/1, v/v, 10 wt %) at 100 °C to afford **5a** and **5b**, respectively.

Scheme 2. Polymerization of Styrene from Alkoxyamine at the Cross-Linking Points



polymers **2a** and **2b**. Both plots linearly increased with reaction time, indicating that the concentrations of radicals in the reaction systems remained constant. As already mentioned, alkoxyamine is one of the initiators for controlled radical polymerization, and the concentrations of radicals are constant in the heating condition if a side reaction does not occur. In the present system, styrene was polymerized from alkoxyamine units, and the polymerization proceeded with little evidence of side reactions such as C−C coupling. Indeed, the relative weight increase ($\Delta w/w_0$) of the network polymers linearly increased with conversion, as shown in Figure 5b. This result supports that the insertion of styrene into alkoxyamines at the cross-linking points proceeded, and the mesh sizes could be controlled by reaction time.

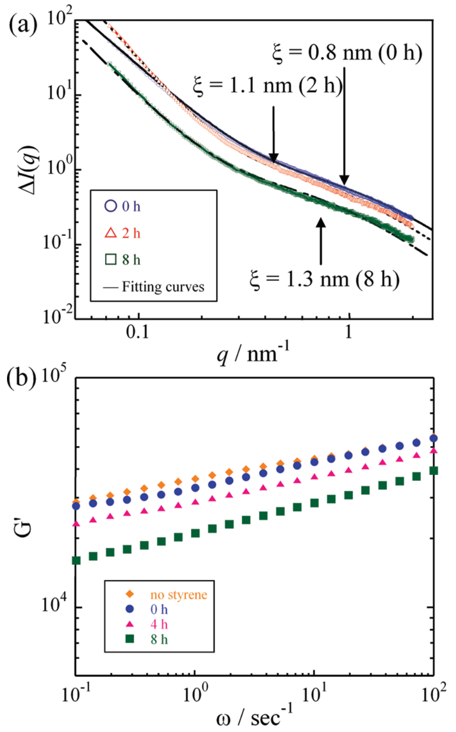


Figure 6. (a) SAXS profiles of network polymers **5a** prepared by heating gel **2a** with styrene for 2 and 8 h, and their fitting curves described by eq 1, and (b) G' against the angular frequency of network polymer **5a** (in anisole) prepared by radical polymerization of styrene for 4 and 8 h at 100 °C.

In the present systems, because it was expected that the mesh sizes of network polymers changed, the variation was estimated by SAXS. Figure 6a shows SAXS profiles of **5a** in anisole prepared by heating **2a** with styrene for certain times. The ξ grew from 0.8 nm (0 h) to 1.3 nm (8 h), which indicated that the mesh sizes got larger. This result supports that the added styrene was polymerized by alkoxyamine at cross-linking points, and the distance between cross-linking points became longer. To obtain further insight into the state of the resulting network polymer, dynamic viscoelastic measurement was carried out. Figure 6b shows G' against the angular frequency of network polymer **5a** (in anisole) prepared by radical polymerization for certain time. In the absence of styrene (see no styrene), the change in G' was hardly observed compared with the parent network polymer (shown as 0 h). In contrast, G' gradually decreased with increasing reaction time after polymerization of styrene. This decrease was due to the decrease in the cross-linking density in the network structure. This result also revealed that styrene was successfully inserted into alkoxyamine units at the cross-linking points.

Conclusion

We have demonstrated the characteristic reaction of network polymers whose cross-linking states could be dynamically changed under heating conditions; a de-cross-linking reaction and a polymerization of styrene were successfully performed to change the cross-linking states. The de-cross-linking reaction was carried out by heating network polymers with excessive alkoxyamine compound in anisole, and it was shown that the de-cross-linking reaction occurred more easily with lower cross-linking densities. In addition, the polymerization of styrene was performed by heating the network polymers swollen by styrene and anisole, and it was revealed that polymerization proceeded to expand the mesh sizes of network polymers. We believe that such dynamic chemical gel systems have the advantage of providing a stable network structure in the absence of external stimuli, whereas one can change their network structures under certain conditions like physical gel systems.

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