

# Network Reorganization of Dynamic Covalent Polymer Gels with Exchangeable Diarylbibenzofuranone at Ambient Temperature

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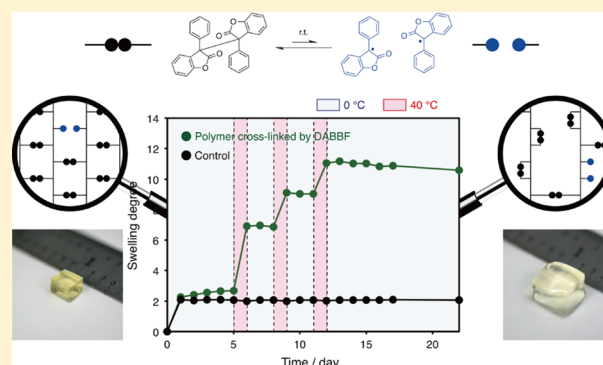
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## Supporting Information

**ABSTRACT:** Reversible bonds and interactions have been utilized to build stimuli-responsive and reorganizable polymer networks that show recyclability, plasticity, and self-healing. In addition, reorganization of polymer gels at ambient temperature, such as room or body temperature, is expected to lead to several biomedical applications. Although these stimuli-responsive properties originate from the reorganization of the polymer networks, not such microscopic structural changes but instead only macroscopic properties have been the focus of previous work. In the present work, the reorganization of gel networks with diarylbibenzofuranone (DABBF)-based dynamic covalent linkages in response to the ambient temperature was systematically investigated from the perspective of both macroscopic and microscopic changes. The gels continued to swell in suitable solvents above room temperature but attained equilibrium swelling in nonsolvents or below room temperature because of the equilibrium of DABBF linkages, as supported by electron paramagnetic resonance measurements. Small-angle X-ray scattering measurements revealed the mesh sizes of the gels to be expanded and the network structures reorganized under control at ambient temperature.



## INTRODUCTION

Cross-linked polymers have a wide range of applications, from hard structural materials to soft rubbers and gels, because of their three-dimensional network structures. The polymer networks are formed by physical associations between polymer chains and/or covalent cross-linking. Reversible non-covalent cross-links afford stimuli-responsive and reorganizable networks, which show recyclability, plasticity, and self-healing, while robust covalent cross-links result in unchangeable networks.<sup>1–4</sup>

Similarly, cross-linked polymers with reversible covalent bonds based on dynamic covalent chemistry<sup>5</sup> can change their structures in response to external stimuli (temperature, pH, light, catalyst, and so on),<sup>6,7</sup> making them processable, self-healable, and environmentally adaptive.<sup>4,8–14</sup> Although these stimuli-responsive properties originate from the rearrangement or reorganization of the polymer networks, researchers in the field of dynamic covalent chemistry have focused only on macroscopic properties such as self-healing, and microscopic structural changes have not been investigated. Several studies have demonstrated reorganization of networks incorporating photo-,<sup>15,16</sup> additive-,<sup>17</sup> or catalyst-responsive<sup>18,19</sup> dynamic

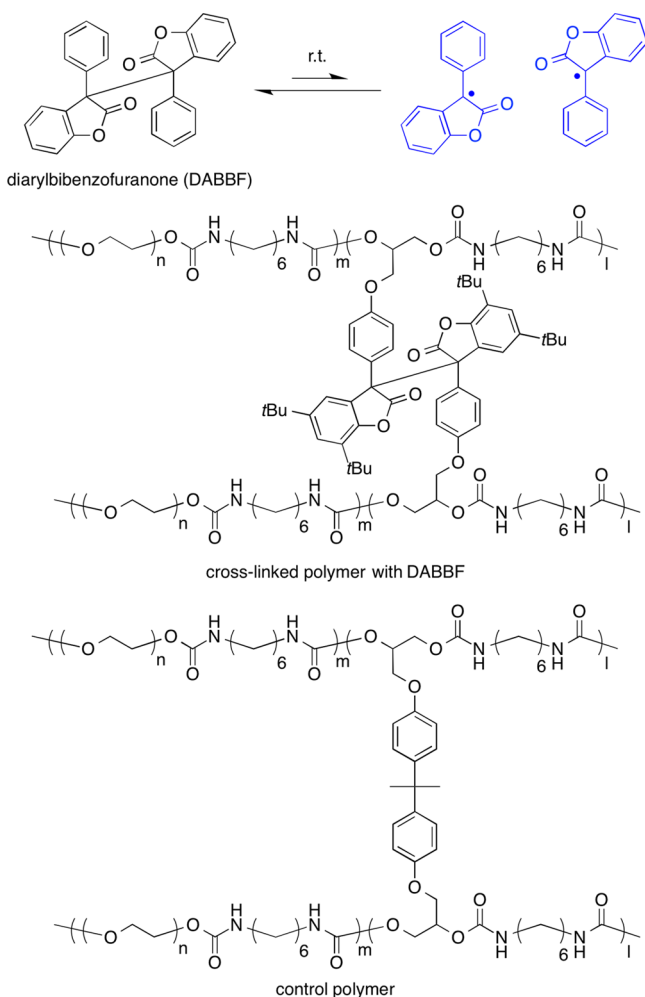
covalent linkages by swelling measurements, small-angle X-ray scattering (SAXS) measurements, and mechanical tests.

To the best of our knowledge, no studies have focused on both macroscopic and microscopic autonomous structural changes of chemically cross-linked polymers at ambient temperature, such as room temperature or body temperature, although these could be suitable for many relevant applications. Soft tissues in the human body, such as tendons, ligaments, cartilage, and muscle are all cross-linked polymers containing water (hydrogels); recently, artificial biocompatible gels with excellent mechanical performance like these soft tissues have been achieved.<sup>20</sup> Therefore, reorganization of polymer gels at ambient temperature has great potential to be applied to biomaterials, actuators, and controlled drug delivery systems.

In the present study, we examined the network reorganization at ambient temperature of polymer gels cross-linked by autonomously exchangeable dynamic covalent linkages, specifically, diarylbibenzofuranone (DABBF) units. DABBF exists in an equilibrium between its dissociated and associated states at room temperature (Figure 1), although usual dynamic covalent

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**Figure 1.** Chemical structures of diarylbibenzofuranone (DABBF) and the cross-linked polymers.

linkages need external stimuli to induce their reversibility.<sup>21,22</sup> A carbon-centered radical formed from cleaved DABBF shows greatly attenuated reactivity toward oxygen compared with other carbon-centered radicals.<sup>23</sup> Therefore, DABBF is a rare dynamic covalent linkage that functions under mild conditions, such as in air at room temperature and physiological temperature. We have previously reported that gels cross-linked by DABBF can macroscopically self-heal and that micelles with DABBF in their inner core are characterized by reversible cross-linking and de-cross-linking in air at room temperature.<sup>24,25</sup> However, structural changes of polymer networks with DABBF have not been evaluated. Thus, in this study, we investigated the reorganization of the network structures in a DABBF-containing cross-linked polymer and the effect of temperature on the structural changes. These were systematically evaluated using swelling, electron paramagnetic resonance (EPR), and SAXS measurements.

## RESULTS AND DISCUSSION

**Preparation of Cross-Linked Polymers.** A polymer cross-linked by DABBF was prepared by polyaddition of poly(ethylene glycol) (PEG) ( $M_n = 1000$ ), hexamethylene diisocyanate (HDI), and a tetrahydric DABBF cross-linker in the presence of di-*n*-butyltin dilaurate (catalyst) in 1,4-dioxane in a manner similar to that previously reported (Figure 1).<sup>24</sup>

The fluidity of the reaction mixture slowly decreased during the course of the reaction. The reaction mixture completely lost fluidity after 48 h, indicating that polymerization was successful. After polymerization, the crude gel was immersed in 1,4-dioxane to remove the catalyst and unreacted monomers and subsequently freeze-dried. A typical cross-linked polymer was prepared and used as a control sample. The control polymer shared the same structure of the cross-linked polymer with DABBF but had no DABBF linkage. It was prepared from PEG, HDI, and tetrahydric 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) in a manner outlined for the polymer cross-linked by DABBF (Figure 1).

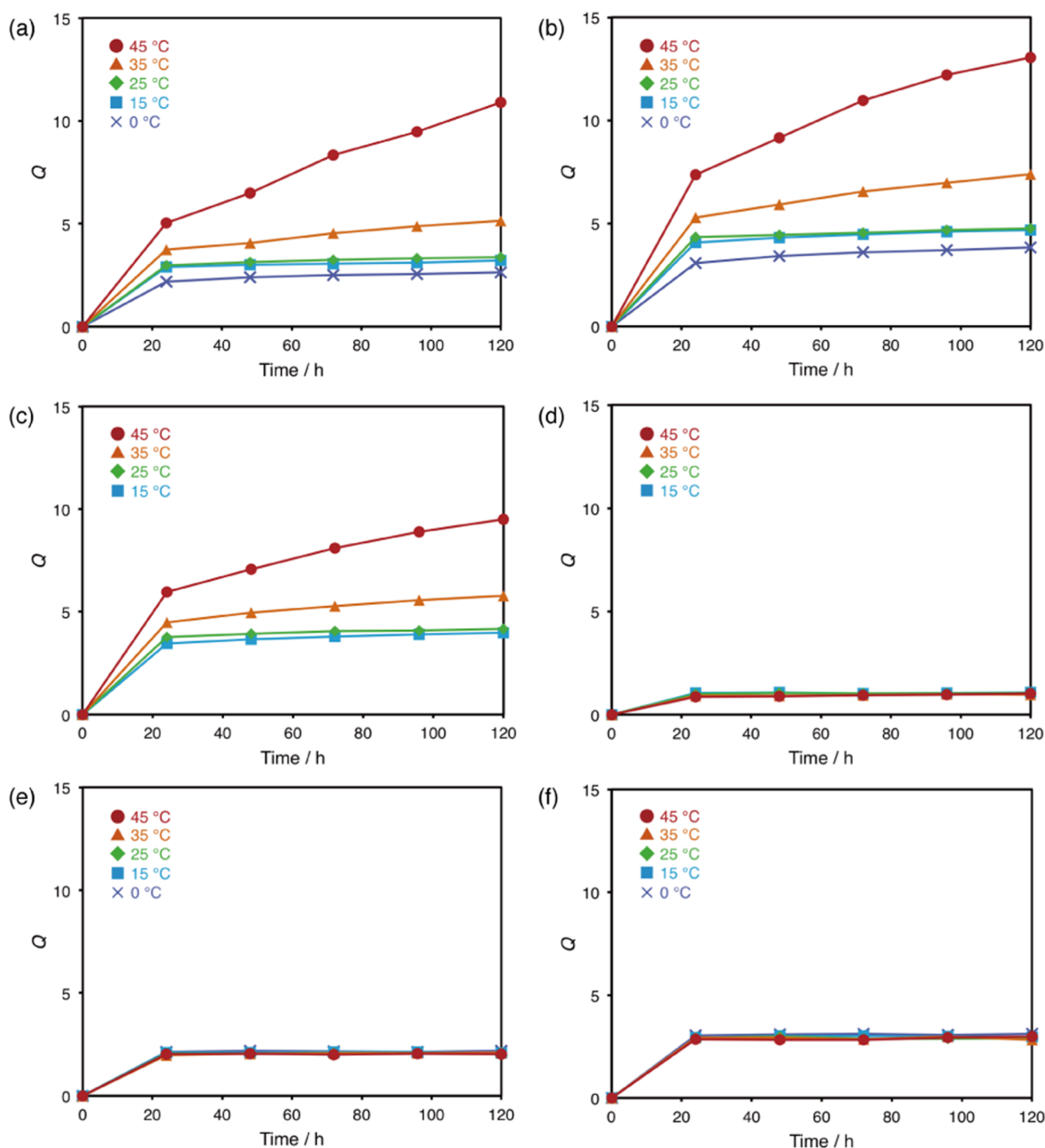
**De-Cross-Linking of Cross-Linked Polymers.** To determine whether DABBF linkages in the cross-linked polymer were in a state of equilibrium and able to exchange their bonds with one another, a de-cross-linking reaction was performed in tetrahydrofuran (THF) in air at room temperature by addition of an excess of another DABBF derivative, as published elsewhere.<sup>24,25</sup> After the de-cross-linking reaction (42 h), a THF-soluble high-molecular-weight component ( $M_n = 6600$ ) was detected by gel-permeation chromatography (GPC) measurements (Figure S1 in the Supporting Information). This was expected to be a linear polymer and/or a cross-linked oligomer. Although we tried to perform a detailed analysis by fractionation of this component, cross-linking occurred again after fractionation. However, the <sup>1</sup>H NMR spectrum of the solution without fractionation after de-cross-linking clearly indicated the presence of soluble PEG and HDI, which constitute the polymer network (Figure S2 in the Supporting Information). Consequently, we confirmed that the DABBF linkages in the polymer network were in an equilibrium state in air at room temperature and that de-cross-linking of the cross-linked polymer occurred through bond exchange of the DABBF linkages.

**Effect of Temperature on Reorganization of Polymer Networks.** The reorganization of the polymer networks was evaluated by monitoring the swelling behavior in several solvents at ambient temperatures (0, 15, 25, 35, and 45 °C). The swelling degree ( $Q$ ) is defined as the weight ratio of the amount of absorbed solvent to that of the dry polymer, as follows (eq 1):

$$Q = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  are the weights of the dried and wet gels, respectively.<sup>26</sup>

Figure 2 shows the swelling behavior of the cross-linked polymers containing DABBF and bisphenol A in different solvents at 0, 15, 25, 35, and 45 °C. The cross-linked polymer with DABBF was swollen with THF, and the obtained gel attained equilibrium swelling within 24 h at low temperatures such as 0, 15, and 25 °C (Figure 2a). At relatively higher temperatures such as 35 and 45 °C, however, the gel did not reach equilibrium swelling but continued to swell. The swelling degree in THF after 120 h increased with increasing temperature. In contrast, the bisphenol A-containing control polymer was swollen with THF, and the gel attained equilibrium swelling within 24 h at all temperatures (Figure 2e). The swelling degree showed almost the same value at all temperatures, which was close to that of the DABBF-containing gel at 0 °C. This is a significant difference between dynamic covalent and covalent systems. Thus, our data clearly indicated



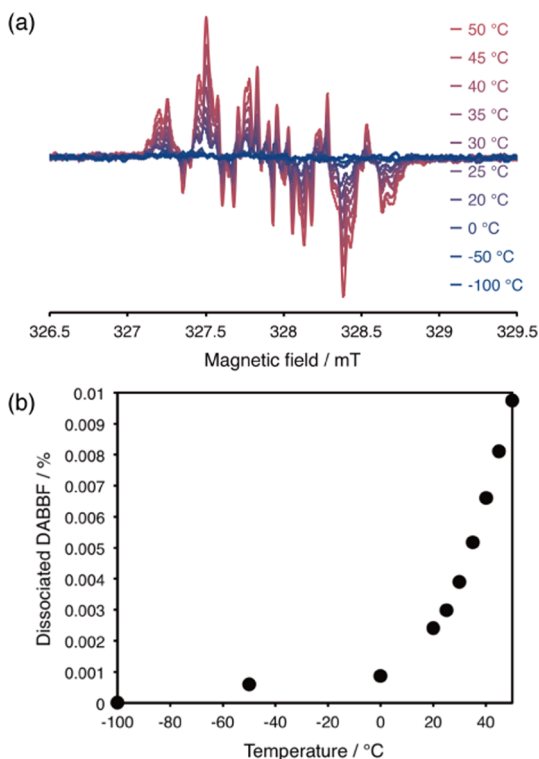
**Figure 2.** Swelling behavior of the cross-linked polymers at ambient temperatures (0, 15, 25, 35, and 45 °C). Shown are plots of swelling degree ( $Q$ ) vs time for the DABBF-containing cross-linked polymer in (a) THF, (b) DMF, (c) 1,4-dioxane, and (d) water and for the control cross-linked polymer in (e) THF and (f) DMF.

that the network structure incorporating DABBF reorganized and expanded at relatively higher temperatures as a result of the bond exchange of the DABBF linkages, with this unique behavior originating from the equilibrium.

As shown in Figure 2b,c, the swelling behavior and the swelling degrees of the DABBF-containing cross-linked polymer in *N,N*-dimethylformamide (DMF) and in 1,4-dioxane were similar to those in THF, and the polymer finally dissolved in THF, DMF, and 1,4-dioxane at 50 °C within 1 day, while the cross-linked polymer was hardly swollen with water and the swelling degrees were unaffected by temperature (Figure 2d). In neutral polymer gels, the increase in entropy associated with polymer solvation leads to stretching of the polymer chains between cross-linking points, despite their restorative forces.<sup>27</sup>

This suggests that the swelling is caused by the imbalance between the repulsive forces among polymer chains and the contractile stretching forces of the elastically active networked structures. The polymer chains showed less compatibility with water because water is a nonsolvent for the polymer. Therefore, the repulsive forces were not generated, and the network structure was not affected by temperature. The swelling behavior of the control cross-linked polymer in DMF was similar to that in THF and unaffected by temperature (Figure 2f). The swelling behavior and the swelling degrees of the DABBF-containing cross-linked polymer in other solvents at room temperature are shown in Figure S3 and Table S1 in the Supporting Information.

To investigate the equilibrium state of the DABBF linkages in the gel network, variable-temperature EPR measurements were performed. Figure 3a shows EPR spectra of the DABBF-



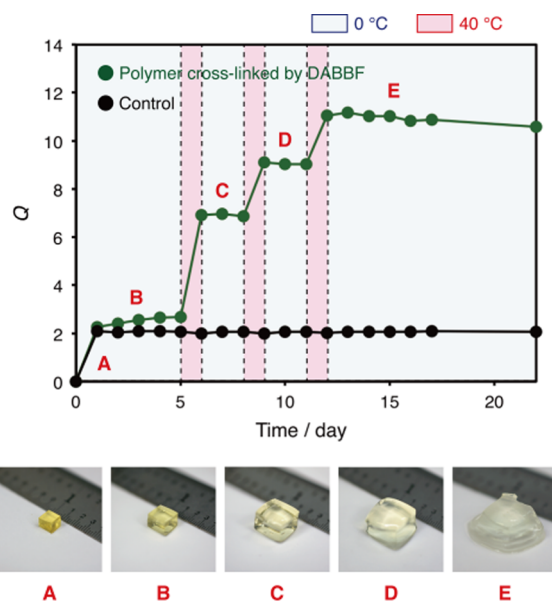
**Figure 3.** (a) EPR spectra of the DABBF-containing cross-linked polymer swollen with THF and (b) percentage of dissociated DABBF linkages at different temperatures.

containing cross-linked polymer swollen with THF measured over the temperature range from  $-100$  to  $50$  °C. The  $g$  values of these spectra were determined to be 2.0040, suggesting the presence of oxygen radicals and carbon radicals. Therefore, the detected spectra were derived from these radicals, which were formed from cleaved DABBF units. The chemical structures of plausible generated radicals are shown in Figure S4 in the Supporting Information. The intensity of the peaks increased with increasing temperature, indicating that the equilibrium of DABBF shifted to the dissociated side. We assumed that the equilibrium simply involves the associated DABBF and the dissociated radicals without irreversible side reactions; under this assumption, we calculated the ratio of dissociated DABBF from the peak intensity by using 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as a standard (Figure 3b). Although the amount of dissociated radicals was extremely low below  $0$  °C (less than 0.001%), the amount of dissociated radicals exponentially increased above  $0$  °C. The steep increase in the ratio of the dissociated DABBF linkages reduced the contractile restorative forces generated by swelling, resulting in continuous swelling. This indicated that the above-mentioned unique and temperature-dependent reorganization is caused by the extreme sensitivity of the equilibrium to the temperature.

Notably, the amount of dissociated radical was found to be less than 0.01% even at  $50$  °C. The DABBF-containing gels attained equilibrium swelling at low temperature because almost all of the DABBF linkages were connected. The slight increase in the percentage of the dissociated DABBF upon heating, however, led to macroscopic changes in the material

properties. The amount of the dissociated radical at  $50$  °C was certainly larger than that at  $0$  °C, but the change was very small in the material, from 0.001% to 0.01%.

**Reorganization of Networks with Reversible Temperature Changes.** To provide a deeper understanding of the effect of temperature on the network reorganization, the swelling behavior with reversible temperature changes was investigated. As shown in Figure 4, the polymer cross-linked by



**Figure 4.** Swelling behavior of the cross-linked polymers with reversible temperature changes ( $0$  and  $40$  °C): (top) swelling degrees of the DABBF-containing cross-linked polymer (green) and the control cross-linked polymer (black) in THF and (bottom) photographs of the swelling behavior of the DABBF-containing cross-linked polymer.

DABBF and the control polymer were swollen with THF at  $0$  °C (light-blue area) and  $40$  °C (pink area). As expected, the swelling degrees of the control polymer did not change with temperature. While little change was also observed in the swelling degree of the DABBF-containing gel at  $0$  °C, the gel was drastically swollen at  $40$  °C, and the swelling degree significantly increased. The temperature-dependent swelling was confirmed by the volume changes shown in the photographs in Figure 4. The changes were irreversible, and the gel attained new equilibrium states. This may be due to the compatibility of the polymer chains with THF, which leads to high repulsive forces, and to the network, which reorganized upon swelling at  $40$  °C. Reversible volume changes of some hydrogels with physical cross-links in response to external stimuli have been reported.<sup>28–31</sup> The networks had stable covalent cross-links, and the number of cross-links drastically changed in response to external stimuli by dissociation and association of physical cross-links, resulting in reversible changes with upper volume limits. This may be due to the DABBF-containing gel, which shows no stable cross-links, and to the fact that the number of cross-links hardly changed when the external stimulus was applied. Similar behavior was also observed in the DABBF-containing cross-linked polymer swollen with DMF, although the response was slightly worse than that in THF (Figure S6 in the Supporting Information). These results indicated that the gels cross-linked by DABBF

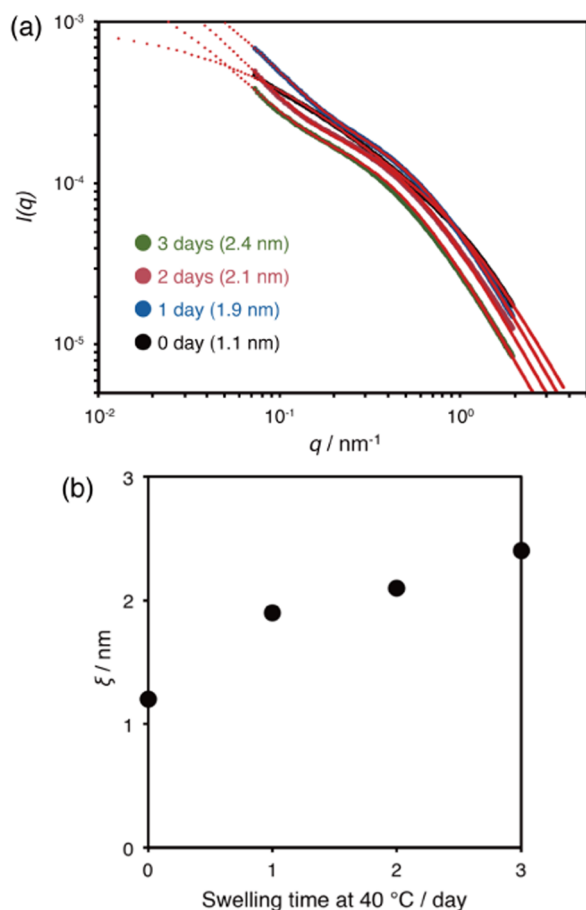


swelled and reorganized in response to the ambient temperature and that the network structures can be easily controlled with the ambient temperature.

If the network structure reorganizes, its mesh size is expected to change. Therefore, the variations of the network structures in the DABBF-containing gels were investigated by SAXS, and the correlation lengths ( $\xi$ ) of the gels were evaluated. The latter represents the mesh size consisting of polymer chains in a semidilute solution, which was determined by fitting eq 2 to SAXS profiles.<sup>32,33</sup> Equation 2 consists of two components, namely, randomly distributed noninteracting domains in the networks (stretched exponential formalism) and the correlation between the polymer chains (Ornstein–Zernike formalism), as follows:

$$I(q) = I_{\text{ex}}(0) \exp[-(q\Xi)^\alpha] + \frac{I_{\text{soln}}(0)}{1 + \xi^2 q^2} \quad (2)$$

where  $I_{\text{ex}}(0)$  and  $I_{\text{soln}}(0)$  are constant values,  $\alpha$  is also a positive constant in the range of 0.7 to 2,  $\Xi$  is the mean size of static nonuniformities or the mean size of static concentration fluctuations, and  $q$  is the scattering vector. Figure 5a shows SAXS profiles, fitting curves described by eq 2, and the correlation lengths of the gel swollen with THF for 0 to 4 days at 40 °C. In all cases, the fitting curves successfully represented



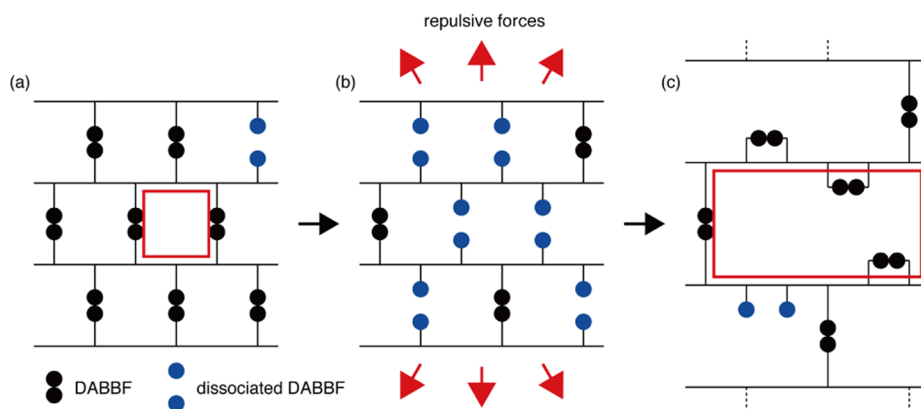
**Figure 5.** (a) SAXS profiles of the DABBF-containing cross-linked polymer swollen with THF at 40 °C for different reaction times, their fitting curves described by eq 2, and the values of the correlation length ( $\xi$ ). (b) Values of  $\xi$  associated with the DABBF-containing cross-linked polymer swollen with THF at 40 °C for different swelling times. The scattering vector is defined as  $q = 4\pi \sin(\theta/\lambda)$ .

the experimental results. Figure 5b shows the time dependence of the correlation length obtained from the fitting curves. The correlation length increased with increasing swelling time, from 1.1 to 2.4 nm after 4 days. Similar behavior was observed in the swelling of the DABBF-containing gel in DMF (Figure S7 in the Supporting Information). These results support the concept that the networks reorganized and the mesh sizes expanded through the bond exchange of the DABBF linkages in response to the ambient temperature. Therefore, the polymer networks and the mesh sizes can be controlled using the swelling time and the ambient temperature.

A plausible mechanism for the network reorganization in response to the ambient temperature is shown in Figure 6. Below room temperature, the gel attains the equilibrium swelling because the repulsive forces among the polymer chains and the contractile forces due to stretching of elastically active networked structures become equal in magnitude. The ratio of dissociated DABBF increases while the contractile restorative forces decrease with increasing temperature. These changes lead to an imbalance between the repulsive forces and the contractile forces, resulting in expansion of the network (continuous swelling). After the reorganization, the gel attains a new state of equilibrium at low temperatures. In the extreme case of increased intramolecular cross-linking due to the reorganization, the cross-linked polymers can completely dissolve in some solvents at ambient temperature.

## CONCLUSIONS

We have shown the network reorganization of gels covalently cross-linked by DABBF linkages at ambient temperature. The gels were successfully prepared by polyaddition of PEG, HDI, and a DABBF cross-linker. De-cross-linking occurred at room temperature upon the addition of an excess of another DABBF into the gels, as the DABBF linkages in the gels were in an equilibrium state and could exchange their bonds. The gels continued to swell at ambient temperatures above room temperature but attained equilibrium swelling at temperatures lower than room temperature. EPR measurements revealed that the temperature-dependent swelling and the network reorganization are due to the sensitivity of the equilibrium of the DABBF linkages to temperature. The amount of dissociated DABBF in the gels increased from 0.001% at 0 °C to 0.01% at 50 °C. The increase in the ratio reduced the contractile restorative forces generated by swelling, resulting in continuous swelling. The slight increase led thus to macroscopic changes in the swelling behavior. The gel networks irreversibly reorganized with reversible temperature changes. SAXS measurements showed that the mesh sizes of the gels expand through bond exchanges of the DABBF linkages and that the network structures can be easily controlled via the swelling time and the ambient temperature. Evaluation of the change in network structures is crucial, since exchange reactions of reversible covalent bonds and resulting network reorganization in polymer gels and cross-linked polymers have been widely applied in the past decade to the production of smart materials. In addition, we believe that the network reorganization of the DABBF-containing gel in response to the ambient temperature can find applications in a diverse range of fields in which smart materials are used, such as biomaterials, controlled release, and drug delivery systems.



**Figure 6.** Proposed mechanism for the network reorganization of the DABBF-containing gel in response to the ambient temperature: (a) below room temperature; (b) upon heating; (c) upon cooling to temperatures lower than room temperature.

## MATERIALS AND METHODS

**Synthesis of Cross-Linked Polymers.** In a sample tube, a solution of tetrahydic DABBF (1.00 g, 1.22 mmol) and PEG ( $M_n = 1000$ ) (2.43 g, 2.43 mmol) in 1,4-dioxane (4.11 mL) was prepared. HDI (0.78 mL, 4.86 mmol) and a 50 vol % solution of di-*n*-butyltin dilaurate in THF (3 drops) were added to the solution under a nitrogen atmosphere at room temperature. After 48 h, the obtained gel was purified by immersing it in water for 24 h and in 1,4-dioxane for several days and then freeze-drying it to afford a yellow solid (4.23 g, quantitative yield).

The control polymer was synthesized in a similar manner. In a sample tube, a solution of tetrahydic bisphenol A (185 mg, 0.49 mmol) and PEG ( $M_n = 1000$ ) (984 mg, 0.98 mmol) in 1,4-dioxane (1.45 mL) was prepared. HDI (0.32 mL, 1.97 mmol) and di-*n*-butyltin dilaurate (1 drop) were added to the solution under a nitrogen atmosphere at room temperature. After 48 h, the obtained gel was purified by immersing it in water for 72 h and in 1,4-dioxane for several days and then freeze-drying it to afford a white solid (1.42 g, 94% yield).

**De-Cross-Linking Reaction.** The cross-linked polymer with DABBF (20 mg) and a THF solution (2.23 mL) of dihydic DABBF (20 equiv of DABBF linkages in the cross-linked polymer) were placed in a sample tube. The mixture was then stirred under air at room temperature. After 42 h, the reaction mixture was evaluated by GPC analysis at 40 °C using the following experimental setup: a guard column (Tosoh TSK guard column Super H-L), three columns (Tosoh TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. THF was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ( $M_n = 4920\text{--}3000000$ ;  $M_w/M_n = 1.02\text{--}1.03$ ) were used to calibrate the GPC system.  $^1\text{H}$  NMR (400 MHz) spectroscopic measurements were carried out to evaluate the mixture at 25 °C using a 400 MHz Bruker spectrometer with tetramethylsilane as an internal standard in chloroform-*d* ( $\text{CDCl}_3$ ).

**Measurement of Swelling Degrees.** Sliced cross-linked polymers were placed in various organic solvents at several temperatures, and the  $Q$  values of the cross-linked polymers were calculated from the weights of the cross-linked polymers in the dry and gel states. Temperature was controlled using an oil bath and an ethanol bath. The weights of the cross-linked polymers in gel states were measured by taking the gel out of the solution, removing excess solution from the gel surface, and weighing. Gels were kept in darkness during the entire process.

**EPR Measurements.** Variable-temperature EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. The measured gels swollen with THF were contained in 3 mm glass capillaries, and the capillaries were sealed after being degassed. Spectra were measured using a microwave power of 0.5 mW and a field modulation of 0.01 or 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.05 or 0.25

mT/s. The concentration of the radicals formed from cleaved DABBF was determined by comparing the area of the observed integral spectrum with that of TEMPOL in the same solvent under the same experimental conditions; the  $\text{Mn}^{2+}$  signal was used as an auxiliary standard. The concentration of DABBF linkages was calculated by using the gel volume after swelling for 5 days at room temperature with the assumptions that the density of the cross-linked polymer in the dry state was  $1\text{ g/cm}^3$  and that the composition of the polymer was similar to that of the reaction mixture because the polymer was obtained in quantitative yield, as shown in Figure S5 in the Supporting Information. The  $g$  value was calculated according to the following equation:

$$g = h\nu/\beta H$$

where  $h$  is the Planck constant,  $\nu$  is the microwave frequency,  $\beta$  is the Bohr magneton, and  $H$  is the magnetic field.

**SAXS Measurements.** SAXS measurements were carried out on beamline BL40B2 at SPring-8 using incident X-rays with wavelength of  $\lambda = 0.1\text{ nm}$ . Scattered X-rays were detected using a  $300\text{ mm} \times 300\text{ mm}$  imaging plate with a resolution of  $0.1\text{ mm/pixel}$  and a 2158 mm sample-to-detector distance calibrated by the average of three peaks of silver behenate. The measured gels were swollen in THF and DMF and contained in 2 mm quartz capillaries. The scattering intensity of the polymer  $[\Delta I(q)]$  was calculated by subtracting the scattering intensity of the solvent  $[I_{\text{solv}}(q)]$  from that of the solution  $[I_{\text{soln}}(q)]$  after the intensities were adjusted using the transmittances ( $T_{\text{solv}}$  and  $T_{\text{soln}}$ , respectively), according to the equation  $\Delta I(q) = I_{\text{soln}}(q)/T_{\text{soln}} - I_{\text{solv}}(q)/T_{\text{solv}}$ . The scattering vector was defined as  $q = 4\pi \sin(\theta/\lambda)$ .

## ASSOCIATED CONTENT

### Supporting Information

De-cross-linking reaction, swelling behavior of the DABBF-containing gels in other solvents at room temperature, swelling behavior with reversible temperature changes in DMF, and SAXS profiles of the DABBF-containing gels in DMF after reaction at 40 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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