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# Self-Healing of Polymers via Synchronous Covalent Bond Fission/Radical Recombination

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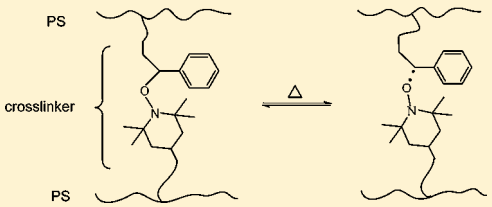
Supporting Information

**ABSTRACT:** The present paper is devoted to preparation of intrinsic self-healing polymeric materials used for structural applications. The authors introduced a novel healing chemistry based on dynamically reversible C−ON bonds, which imitates natural healing in living bodies without affecting their operations. To verify its feasibility, alkoxyamine moieties served as intermolecular links in polystyrene. Upon heating, covalent bond fission and radical recombination synchronously took place among alkoxyamine moieties. Cracked parts were thus reconnected repeatedly, without losing integrity and load bearing ability of the material even above $T_g$.




**KEYWORDS:** *self-healing, synchronous reversibility, alkoxyamines, cross-linked polymer*

## INTRODUCTION

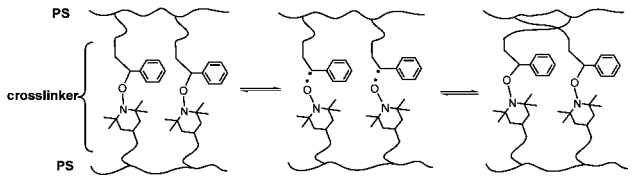
Bioinspired self-healing polymeric materials have attracted more and more research interests.[1−13] Unlike extrinsic self-healing that functions in virtue of embedded healing agent,[3−5] intrinsic self-healing depends only on recombination ability of macromolecules themselves.[6−13] To remend damaged polymer constructed by covalent chemical bonds, thermally reversible Diels−Alder (DA) intermonomer linkages were introduced.[6] Accordingly, cracks in cross-linked polymer made from cycloaddition between multifuran and multimaleimide were repeatedly rebonded. During crack healing, however, the polymer has to be heated up to retro-DA temperature (120 °C) for disconnecting DA bonds (i.e., de-cross-linking), which is generally higher than the glass transition temperature, and then cooled for reconnection of the DA bonds (DA reaction ≈ 80 °C). It means that the material would inevitably lose its shape as a result of (i) molecular cleavage during the first stage of healing (i.e., retro-DA reaction/de-cross-linking) and (ii) drastically increased deformability due to glass transition.[14] It is worth noting that on one hand, breakage of reversible bonds and improved mobility of molecules are necessary for crack healing,[15] whereas on the other, distortion of end-use products is not allowed for structural applications where mechanical strength properties are critical even if self-healing is proceeding. The requirements seem to be contradictory and are hard to be satisfied simultaneously in conventional polymers.

In fact, natural healing in living bodies would not affect their operations. Circulatory system keeps on working, for instance, despite that blood clotting is being formed in an injured vessel. Evidently, mimicking healing process of organisms to a higher degree would further improve performance of artificial self-healing materials. Innovative ideas about molecular structure design and reversible mechanism of molecular fracture and combination should be proposed accordingly.

Here we show the feasibility of using a dynamically reversible C-ON bond as the healing chemistry, which combines the aforesaid covalent bond breakage and reconnection into one step. The possible material deformation in the course of crack remending would thus be avoided even when the healing is carried out above its glass transition temperature. As illustrated in Scheme 1a, C-ON bond in an alkoxyamine moiety

**Scheme 1. (a) Dissociation/Association of Alkoxyamines Derivatives; (B) Dynamic De-Cross-Linking, Crossover Cross-Linking, or Exchange Reactions of PS**

**(a)**




**(b)**

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homolytically cleaves upon heating and produces transient carbon-centered and persistent nitroxide radicals in equal amounts[16−21] with very high frequency factor (e.g., $2.4 \times 10^{14}$ $s^{-1}$ in solution[20]). Meanwhile, the carbon-centered radicals would be rapidly trapped by the nitroxide radicals.[17] As a result, under certain homolysis temperature the C-ON bonds in alkoxyamines frequently cleave but immediately recombine. Moreover, the recombination of radicals involves crossover or exchange reaction between radicals that belong to different alkoxyamine moieties before the chain breakage.[22] Taking advantage of this dynamic equilibrium, nitroxide-mediated radical polymerization has become one of the most useful methods for living radical polymerization[20,21,23,24] and various well-defined and complex molecular architectures, many of which are difficult to prepare via traditional methods, have been synthesized.[21,25−28] For example, a reversible sol−gel was obtained from linear poly(methacrylic ester)s containing alkoxyamine units on the side chain.[29] Upon heating, the cross-linked gel in solvent (10 wt % anisole solution of polymer) was formed through radical exchange reactions of alkoxyamine moieties, releasing alkoxyamine molecules. The retro-reaction, i.e., de-cross-linking, occurred in the presence of an excess amount of alkoxyamine molecules. Although this kind of sol−gel conversion took place in solvent rather than in solid, it theoretically proved that the reversible reaction between alkoxyamine moieties may be useful to construct a reversible cross-linked structure. Nevertheless, in a hard polymer solid, molecular mobility is greatly restricted. As a result, release and incorporation of alkoxyamine molecules are impossible.

To create a novel thermally reversible polymer solid with crack remendability, in this work, we directly incorporate alkoxyamine linkages into cross-linked polymer solid as cross-linkers that cleave and reconnect without byproduct. Because of synchronous scission of alkoxyamine moieties and recombination of resultant radicals, the cross-linked networks would not be completely disrupted during dissociation/association of alkoxyamines derivatives, so that the polymer is allowed to maintain its integrity and load bearing ability whenever the cracked parts are repaired.

## ■ EXPERIMENTAL SECTION

**Chemicals.** Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (98%) and methacryloyl chloride (98%) were purchased from Aldrich and used as received. Styrene (99%) was obtained from Alfa Aesar and purified by distillation under reduced pressure in the presence of calcium hydride. Linear PS (GPPS 685D) was provided by Dow Chemical. All the other reagents and solvents were commercial products and used without further purification.

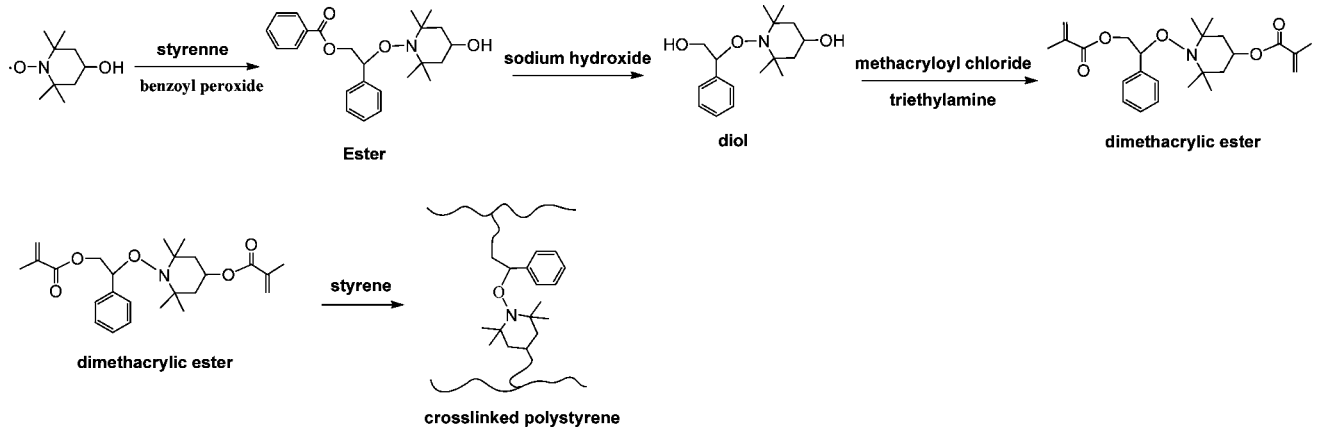
**Synthesis of 4-Hydroxy-1-((2′-hydroxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (Diol).** The diol is a derivative of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), which was prepared and purified as previously reported.[30] The product was characterized by infrared and nuclear magnetic resonance ($^1$H NMR and $^{13}$C NMR) spectroscopy to confirm its molecular structure. FT-IR (KBr/cm$^{-1}$): 3295, 2982, 1453, 1373, 1046. $^1$H NMR ($CDCl_3$): $\delta$/ppm 1.21 (3H, $CH_3$), 1.28 (3H, $CH_3$), 1.31 (3H, $CH_3$), 1.54 (3H, $CH_3$), 1.31−1.98 (4H, $2CH_2$), 3.72 (1H, CH), 4.01 (1H, CH), 4.20 (1H, CH), 5.26 (1H,CH), 7.26−7.34 (5H, aromatic). $^{13}$C NMR ($CDCl_3$): $\delta$/ppm 21.65, 21.94, 33.38, 34.99, 49.08, 49.25, 61.22, 62.19, 63.31, 70.38, 84.46, 127.08, 128.21, 128.56, 138.91. Mass spectrum for $C_{17}H_{27}NO_3$ $[M+1]^+$ found 294.3.

**Synthesis of 4-Methacryloyloxy-1-((2′-methacryloyloxy-1′-phenylethyl)oxy)-2,2,6,6-tetramet-hylpiperidine (Dimethacrylic Ester).** The synthesis of dimethacrylic ester followed the published procedures.[26] Triethylamine (5.1 g, 50 mmol) was slowly injected into the solution of methacryloyl chloride (7.8 g, 75 mmol) and diol (7.3 g, 25 mmol) in anhydrous tetrahydrofuran (50 mL). The reaction was carried out with stirring under argon for 10 h at 25 °C, and then evaporated to dryness. The residue was partitioned between saturated sodium chloride solution and dichloromethane in which the aqueous layer was extracted with dichloromethane for several times. The collected organic layers were dried with anhydrous sodium sulfate and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:20 ethyl acetate/hexane (v/v) to give dimethacrylic ester as pale yellow oil (9.4 g, 88% yield). FT-IR (KBr/cm$^{-1}$): 3107−2856, 1719, 1637, 1327, 1166, 763, 701; $^1$H NMR ($CDCl_3$): $\delta$/ppm 0.72 (3H, $CH_3$), 1.16 (3H, $CH_3$), 1.31 (3H, $CH_3$), 1.39 (3H, $CH_3$), 1.49 (3H, $CH_3$), 1.42−2.02 (4H, $2CH_2$), 1.95 (3H, $CH_3$), 2.01 (3H, $CH_3$), 4.63 (1H, CH), 5.29 (1H, CH), 5.49 (1H, CH), 5.52 (1H, CH), 5.82 (1H, vinyl), 5.98 (1H, vinyl) 6.05 (1H, vinyl), 6.23 (1H, vinyl), 7.25−7.35 (5H, aromatic). $^{13}$C NMR ($CDCl_3$): $\delta$/ppm 18.25, 18.59, 21.46, 22.23, 34.20, 34.47, 44.57, 44.81, 59.42, 60.55, 66.88, 84.25, 125.18, 125.89, 127.68, 127.82, 136.12, 136.59, 140.27, 140.49, 166.77, 166.93. Mass spectrum for $C_{25}H_{35}NO_5$ $[M+1]^+$ found 430.4.

**Preparation of Reversibly Cross-Linked PS.** Benzoyl peroxide (58.1 mg, 0.24 mmol) and certain amount of cross-linker dimethacrylic ester were dissolved in styrene (7.8 g, 75 mmol) and then charged into a tube. The tube was evacuated and backfilled with argon for three times. The mixture was cured for 24 h at 80 °C and postcured for 1 h at 100 °C. Three molar feeding ratios of styrene over cross-linker dimethacrylic ester were used: 5/1, 7.5/1, and 9.4/1. FT-IR spectra of the products present following characteristic peaks (KBr/cm$^{-1}$): 3026−2975, 1602, 1364, 1149, 1117, 1043, 699, 758, in which there was no peak of double bond at 1650 cm$^{-1}$, indicating that the polymer has been completely cured. The control material, irreversibly cross-linked PS excluding alkoxyamine moiety, was made following similar procedures by using ethyleneglycol dimethacrylate (EGDMA) as cross-linker.

**Characterization.** Fourier transform infrared (FT-IR) spectra were recorded by a Bruker EQUINOX55 Fourier transformation infrared spectrometer coupled with an infrared microscope spectrometer. $^1$H NMR and $^{13}$C NMR spectra were measured by a VARIAN Mercury-Plus 300 (300 MHz) with $CDCl_3$ as solvent. Mass spectra were obtained by Shimadzu LCMS-2010A. Electron spin resonance (ESR) spectroscopy study was performed on a JEOL JES-FA200 spectrometer equipped with nitrogen heating setup operating at 8.85 Hz. Modulation frequency and amplitude were 100 kHz and 0.1 mT, respectively. Dynamic mechanical analysis (DMA) was conducted on a Mettler Toledo DMA/SDTA861 using single cantilever mode under 1 Hz at a heating rate of 2 °C min$^{-1}$ in nitrogen. Thermomechanical analysis (TMA) was performed on TA/DMA2980 instrument in penetration mode under a pressure of 0.35 MPa at a heating rate of 2 °C min$^{-1}$ in nitrogen. Thermal degradation habits of the materials were determined by a TA-Q50 thermogravimeter (TGA) in $N_2$ at a heating rate of 10 °C min$^{-1}$. To evaluate healing efficiency of the materials, double cleavage drilled compression (DCDC) tests[14] were conducted using a SANS CMT 6000 universal tester. The specimen was a column of a rectangular cross-section (length $L$ = 50 mm, width $w$ = 16 mm, thickness $t$ = 9.1 mm) with a circular hole (radius $R$ = 2 mm) drilled through its center. Prior to the test, a blade was wedged into the central hole of the DCDC specimen to create precracks 0.5 mm deep at the upper and lower crowns. Then, a restraining clamp was placed around the specimen and axial compression was applied. The lateral confinement offered by the clamp prevented the cracks from growing beyond a length, $l$ ($l/R$ = 0.8), from the crowns of the hole. Afterward, the clamp was removed and the specimen was reloaded in compression at a crosshead rate of 0.2 mm/min to record the critical force, $\sigma_{crit}$, and crack length, $l$, of the subsequent fracture event. The test was paused at increments of 60 $\mu$m in crosshead displacement and, after an equilibration period of 10 s, the peak load over that period was recorded and a photo was taken for determining crack length. After the test, the specimen was placed in a preheated oven at 130 °C in argon for 2.5 h, followed by cooling to room temperature. Finally, the healed specimen was tested again

**Scheme 2. Synthetic Route of Alkoxyamine-Based Cross-Linked Polystyrene**




following the above procedure. Healing efficiency was calculated from the ratio of the fracture toughness of the healed specimen over that of the virgin specimen.[31]

## ■ RESULTS AND DISCUSSION

To verify our consideration mentioned in the Introduction, we synthesize cross-linked polystyrene (PS) in which alkoxyamine moiety acts as the reversible cross-linker (Scheme 1b). First, the reaction between diol and methacryloyl chloride produces dimethacrylic ester (Scheme 2). Then cross-linked PS is yielded via bulk polymerization of styrene with dimethacrylic ester as cross-linking agent and benzoyl peroxide (BPO) as initiator, respectively. Molecular structures of the related substances are confirmed by infrared and nuclear magnetic resonance ($^{1}$H NMR and $^{13}$C NMR) spectroscopy (see Experimental Section), respectively. The resultant cross-linked PS possesses similar mechanical properties as conventional cross-linked PS with ethyleneglycol dimethacrylate (EGDMA) as cross-linking agent. When the molar feeding ratio of styrene over cross-linker is fixed at 10/1, for example, flexural strength and modulus of the former are 99.4 MPa and 5.0 GPa, whereas those of the latter are 93.0 MPa and 5.2 GPa.

Electron spin resonance (ESR) spectroscopy measurement, a technique for studying free radicals, is carried out at different temperatures to examine fission behavior of the cross-linker dimethacrylic ester in cross-linked PS. As shown in Figure 1,

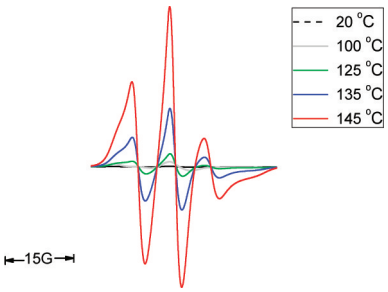



**Figure 1.** Typical ESR spectra of reversibly cross-linked PS (with molar feeding ratio of styrene over cross-linker dimethacrylic ester of 7.5/1) measured at various temperatures.

there is no evident absorption until 100 °C, and then the relative ESR signal intensity drastically increases with a rise in temperature, indicating that homolytic cleavage of alkoxyamine moiety (C-ON bond) starts at about 125 °C. It is noted that at each temperature the signal intensity is kept on certain level within a fixed testing time. Therefore, the ESR spectra can be used to describe radical concentration in the material, as suggested by Sylvain et al.[32] To highlight reversibility of the C-ON bonds, Figure 2a gives the normalized absorptions

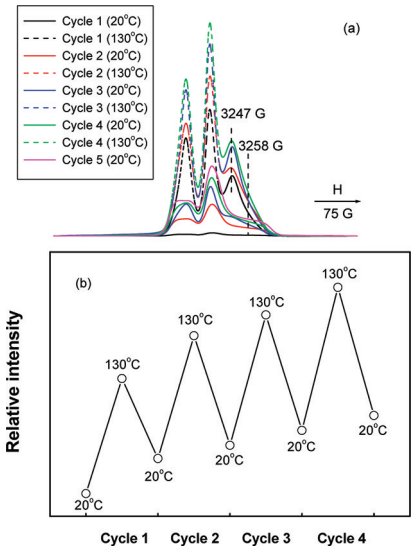



**Figure 2.** (a) Normalized absorption lines obtained from ESR data of reversibly cross-linked molar PS (with molar feeding ratio of styrene over cross-linker dimethacrylic ester of 7.5/1), measured during heating−cooling cycles between 20 and 130 °C. (b) Relative ESR signal intensities calculated from integral area of the normalized absorption lines.

recorded by cyclic ESR measurements between 20 and 130 °C. Accordingly, relative intensity of the radical signal estimated from the area under each curve in Figure 2a is plotted in Figure 2b. It is seen that when temperature alternates between 20 and 130 °C, the amount of free radicals fluctuates as a result of scission of alkoxyamine moiety and recombination of the radicals. These processes are fully reversible, despite the fact that both peak and valley values of the relative intensity slightly increases with the thermal cycles. The latter phenomenon might be attributed to permanent dissociation of a few alkoxyamines caused by irreversible combination of methylene radicals, which results in remainder of nitroxide radicals. This can be detected by the temperature dependence of the absorption at around 3247 G (Figure 2a). It peaks up at 130

°C, but becomes a wide shoulder centered at 3258 G under 20 °C, manifesting that the radicals at elevated temperature consist of two types of radicals (i.e., methylene and nitroxide radicals) but only remainder of nitroxide radicals at room temperature (Scheme 1).

Although radicals are detected as of 125 °C and the amount of radicals increases with increasing temperature, the temperature of homolytic cleavage cannot be unlimitedly raised. At ∼250 °C thermal degradation of linear PS derived from scission of alkoxyamine moieties is triggered (see the Supporting Information and Figure 3). Nevertheless, the reversibly cross-linked PS keeps stable below 200 °C.

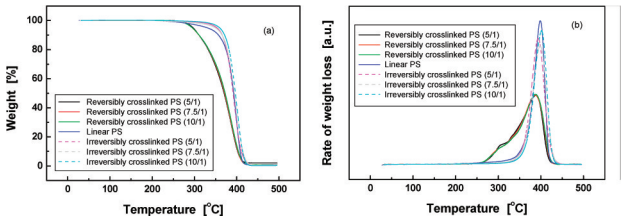



**Figure 3.** Pyrolytic behaviors of linear PS, reversibly cross-linked PS, and irreversibly cross-linked PS. The numerals in parentheses represent molar feeding ratio of styrene over cross-linker.

To further ascertain dynamic feature of the reversibly cross-linked PS, we compared its temperature dependences of loss factor, measured by dynamic mechanical analysis (DMA), with those of irreversibly cross-linked PS (with EGDMA as cross-linker) in Figure 4a. For the latter polymers, their glass

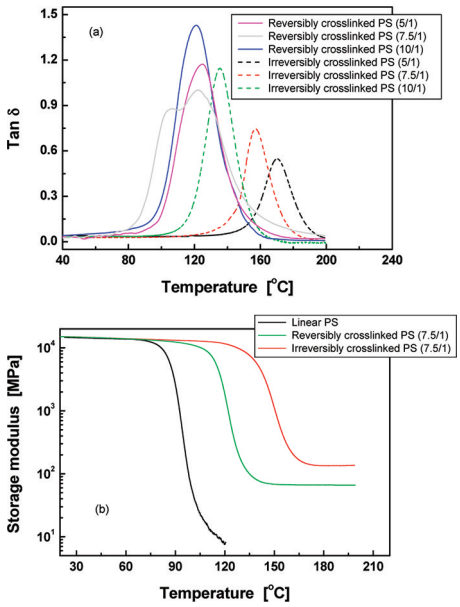



**Figure 4.** Temperature dependences of (a) loss factor of reversibly cross-linked PS and irreversibly cross-linked PS, and (b) storage modulus of linear PS, reversibly cross-linked PS and irreversibly cross-linked PS. The numerals in parentheses represent molar feeding ratio of styrene over cross-linker.

transition temperatures, $T_g$, determined from tan $\delta$ peak positions, significantly increase with the cross-linker content as usual, because of the increase in cross-linking density. On the contrary, the reversibly cross-linked PS shows similar $T_g$ at around 125 °C regardless of dimethacrylic ester content. This abnormality reflects dual role of the reversible cross-linkage in the polymer. On one hand, the cross-links are in a dynamic equilibrium state of random dissociation/association resulting from the synchronous cleavage and recombination of the C-ON bonds. The relative molecular weight between cross-links has to rapidly change so that its effect on $T_g$ is not statistically definite enough as compared with the irreversibly cross-linked PS. On the other hand, the cross-links still take the responsibility of networking PS chains. Otherwise, complete cleavage of cross-linked sites should result in transformation from cross-linked PS to the linear version that has glass transition at ∼100 °C. This argument is supported by the dependence of area under tan $\delta$ peak on cross-linker content of the materials. For either irreversibly or reversibly cross-linked PS, the area under tan $\delta$ peak decreases with a rise in cross-linker content, because higher cross-linking density leads to less entanglement and friction between PS chains. Additionally, the storage modulus curve of reversibly cross-linked specimen shows an elastic plateau above $T_g$ similar to irreversibly cross-linked PS (Figure 4b), which strongly suggests the existence of cross-linked network even at a temperature of as high as 200 °C. However, the lower storage modulus at temperatures above $T_g$ of reversibly cross-linked PS in comparison with irreversibly cross-linked PS reveals that cross-link density of the former should be lower than the later. This behavior is consistent with the dynamic equilibrium feature of reversible cross-linkage.

A careful survey of Figure 4a indicates that the PS reversibly cross-linked by dimethacrylic ester with molar feeding ratio of styrene over cross-linker of 7.5/1 exhibits two maxima during glass transition. In addition to the maximum corresponding to $T_g$ at ∼125 °C as mentioned above, another one appears at about 105 °C, which is quite close to the $T_g$ of linear PS. It might be related with the heterogeneous network structure derived from dynamic cross-linking/de-cross-linking processes. That is, the maximum at 105 °C should originate from segment motion of free linear PS chains generated by random disconnection of the reversible cross-links. When the polymer involves more reversible cross-linker (e.g., molar feeding ratio of styrene over cross-linker = 5/1); however, lengths of the disconnected chains produced by fission of alkoxyamine moieties have to be rather short, which cannot afford to form to a new damping peak. Accordingly, only single peak is observed on the loss factor spectrum. As for the polymer with less reversible cross-linker (e.g., molar feeding ratio of styrene over cross-linker = 10/1), the cleft chains are long (or flexible) enough to be immediately reconnected, so that the tan $\delta$ peak is still unimodal.

The dynamic cross-linking behavior, or synchronous reversibility, has become an intrinsic performance of the dimethacrylic ester cross-linked PS, as demonstrated by the multiple cyclic DMA scans within temperature range between 20 and 200 °C (Figure 5). The marginal increase of $T_g$ with testing cycles is probably due to appearance of small amount of irreversible connection between methylene radicals. Nevertheless, most of the reversible links must still remain; otherwise, their $T_g$ should be significantly increased to the values of irreversibly cross-linked PS. The subsequent multiple remendability tests also support the argument. According to the results of Figure 1, it is known that crack healing of the PS can be conducted at a temperature higher than 125 °C, allowing synchronous fission of the cross-linkages and radical recombination. Therefore, we set the healing temperature at 130 °C for quantitative characterization of the ability of mechanical

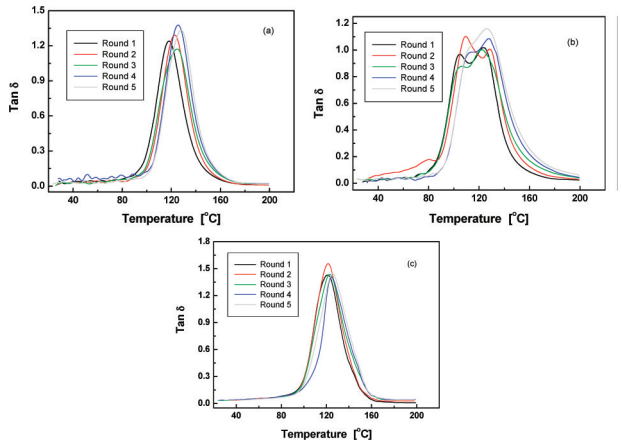



**Figure 5.** DMA spectra of reversibly cross-linked PS measured by repeated scans between 20 and 200 °C. Molar feeding ratio of styrene over cross-linker dimethacrylic ester: (a) 5/1, (b) 7.5/1, and (c) 10/1.

property restoration in terms of double cleavage drilled compression (DCDC) tests (see the Experimental Section).

Figure 6 depicts typical crack length dependences of stress of virgin and healed specimens measured by multiple tests under

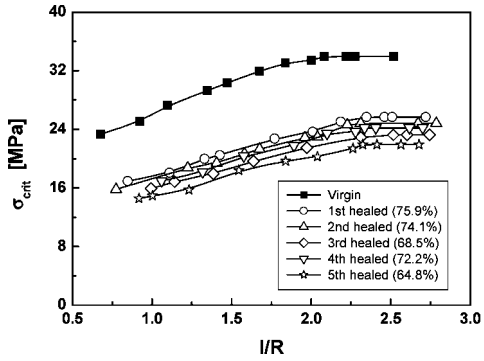



**Figure 6.** Typical critical stress, $\sigma_{crit}$, versus crack length, $l/R$, of reversibly cross-linked PS specimen with molar feeding ratio of styrene over cross-linker dimethacrylic ester of 7.5/1. The numerals in parentheses represent healing efficiency. Crack healing temperature and time: 130 °C, 2.5 h.

fixed healing time of 2.5 h. At molar feeding ratio of styrene over cross-linker of 7.5/1, the specimens can be repeatedly healed, and the efficiency of the first healing event is 75.9%. The mild decline in healing efficiency with healing/refracture cycles might originate from heterogeneity of dynamic recombination of alkoxyamine moieties at the fractured surfaces or reduction of reversible alkoxyamine moieties due to permanent connection of methylene radicals. When the healing time is prolonged to 6 and 9 h, the healing efficiencies are 75.3 and 75.7%, respectively. It means that 2.5 h is sufficient for crack healing under 130 °C, as thermal equilibrium between dissociation and association of alkoxyamine moieties is reached.[32]

It is worth noting that the crack healing temperature (130 °C) is higher than $T_g$ of the polymer, but the specimens do not show creep distortion during healing. Thermal mechanical analysis (TMA) and DMA data further manifest that at the rubbery state the reversibly cross-linked PS has similar deformation resistance as irreversibly cross-linked PS (Figure 7 and Figure 4b). Simple load bearing test also confirm the

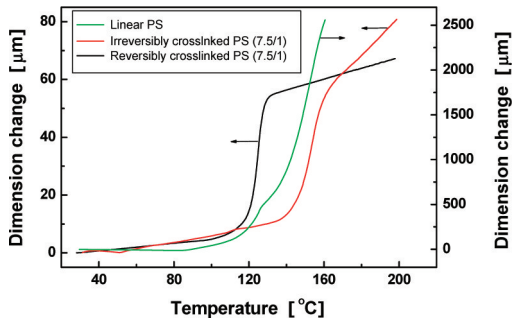



**Figure 7.** Temperature dependences of dimensional change for linear PS, reversibly cross-linked PS and irreversibly cross-linked PS. The numerals in parentheses represent molar feeding ratio of styrene over cross-linker. The curves were measured by TMA.

material can stand against pressure at elevated temperature (see the Supporting Information, Figure S1). These suggest that the concept of synchronous covalent bond fission/radical recombination indeed works in developing self-healing polymer, which is robust enough even when macromolecular chains are temporarily cleft.

For the reversibly cross-linked PS with molar feeding ratio of styrene over cross-linker of 5/1, low healing efficiency of 26.4% is obtained, which seems to be contrary to expectation because the polymer containing more alkoxyamine moieties. This can be explained by the fact that the higher cross-linking density of the polymer reduces range of motion of radicals. Consequently, exchange reactions (scrambling) of alkoxyamine moieties (Scheme 1b) across the crack interfaces are limited. In fact, healing efficiency of the polymer can be increased to 70.1% when healing temperature is raised to 145 °C. The increased radical concentration and reduced restraint on range of motion of radicals account for the improvement.

With respect to the reversibly cross-linked PS with molar feeding ratio of styrene over cross-linker of 10/1, the measured healing efficiency (32.6%) is also low. It should be attributed to the insufficient amount of radicals despite that range of motion of the radicals is large enough as a result of lower cross-linked density.

Considering that thermal treatment itself might contribute to the healing effect, control DCDC tests were performed on irreversibly cross-linked PS. No healing was detected when the specimens with cracks were heated at a temperature 20 °C higher than $T_g$ of the polymer. It is thus confirmed that chemical reconnection of fractured bonds on crack surfaces dominates the crack healing.

## ■ CONCLUSIONS

The synchronous bond fission/radical recombination feature of alkoxyamines has been successfully introduced into cross-linked PS. It enables the polymer to repeatedly self-heal cracks without deformation induced by chain scission, and provides the polymer with mechanical stability at elevated temperature as well. Moreover, the healing can be conducted within a wide temperature range (i.e., between the onset temperatures of homolysis and pyrolysis). These characteristics allow damaged products made from the polymer to be unconsciously repaired using the heat out of operating environment, where temperature always has to be fluctuating in practice.

Because bond fission/radical recombination temperature of alkoxyamines can be tuned by changing their molecular

structures (e.g., by altering side groups),[24] new self-healing polymers with even wider healing temperature range or room temperature healability might be produced accordingly. On the other hand, because alkoxyamine moieties can be easily incorporated into various monomers, a series of existing polymers would be provided with self-healing property based on C-ON bonds. When alkoxyamines are attached to the monomers carrying double bonds, for example, all radical or ionic chain polymerizations are allowed to proceed. If alkoxyamines are linked with different functional groups (like hydroxyl/carboxyl, or isocyanate/hydroxyl), their polymerizations could proceed via step polymerization. Additionally, from the point of view of molecular structure, alkoxyamines are able to take effect no matter whether they appear in linear or cross-linked polymers. In this context, the family of self-healing polymers would be remarkably expanded to meet actual application requirements.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figure S1, described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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