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Two-Way Conversion between Hard and Soft Properties of Semicrystalline Cross-Linked Polymer

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ABSTRACT: A semicrystalline cross-linked polymer exhibiting two-way conversion between totally different mechanical properties was obtained. Furyl-telechelic poly(1,4-butylene succinate-*co*-1,3-propylene succinate) prepolymer ($PBPSF_2$) was prepared and polymerized with tris-maleimide linker (M_3) by the Diels−Alder (DA) reaction in the bulk state. The DA reactions with M_3 above and below the melting temperature of $PBPSF_2$ gave network polymers with relatively soft and hard properties, respectively, though the degrees of crystallinity of them were very similar. The large difference in mechanical properties was attributed to the difference in size of crystallites. By combining the two dynamic processes of melt−recrystallization and depolymerization−repolymerization, we can freely convert the $PBPSF_2 + M_3$ system back and forth between hard and soft materials.

Introduction

Cross-linked network polymers are industrially important. They are used as various kinds of materials from glassy hard thermosets to soft elastomers. Their physical properties can be regulated by the main-chain structure and the cross-linking density. It is notable that semicrystalline cross-linked polymers have been less studied than amorphous ones, though the cross-linking of a semicrystalline polymer sometimes improve their properties such as mechanical strength and heat resistance.[1,2] The cross-links in a semicrystalline network polymer restrict the molecular motion and the crystal growth in it, which results in the lowering of melting temperature, degree of crystallinity, and crystallization rate, compared to the parent linear polymer. The crystallites in a semicrystalline network polymer, on the other hand, affect the dynamics of the cross-linking formation and the resultant network structures. Therefore, it is interesting to compare the two network polymers obtained by cross-linking of a parent polymer in the molten state and in the semicrystalline state.

Cross-links in polymers given by reversible Diels−Alder (DA) reaction between furan and maleimide moieties are very attractive.[3–11] The cycloaddition (forward DA reaction) proceeds at temperatures lower than ca. 100 °C while the cleavage (retro-DA [rDA]) reaction becomes dominant at higher temperatures. The displacement of equilibrium at a mild temperature range allows the selective de-cross-linking reaction in the network polymers without the cleavage of the parent polymer chains. Thus, the formation and deformation of the network structure based on this thermoreversible DA reaction are well controllable and repeatable in both the solution[3–8] and the bulk state.[9–11]

In this study, we design the network polymer consisting of a telechelic prepolymer of bis-furanic poly(1,4-butylene succinate-*co*-1,3-propylene succinate) ($PBPSF_2$) and a tris-maleimide linker (M_3). The monomers and linkers (succinic acid, 1,4-butanediol, 1,3-propanediol, substituted furans, and substituted maleimides) are producible from bioresources,[12–15] so this network polymer is potentially a highly biobased one. Biodegradability is also expected for this polymer.[16] Since $PBPSF_2$ is a semicrystalline polymer with $T_m =$ ca. 60 °C, cross-linking by the DA reaction in the $PBPSF_2 + M_3$ system can be performed at both higher and lower temperatures than the melting temperature of $PBPSF_2$. We show that these two cross-linking conditions give the products with totally different properties, i.e., hard and soft plastics, respectively. The conversion between hard and soft properties by applying melt/recrystallization and de-cross-linking/re-cross-linking is also shown.

Because it is difficult to analyze the insoluble network polymers quantitatively, the DA reaction of a linear polymer system from $PBPSF_2$ and a bis-maleimide linker (M_2) is studied at first. On the basis of this result, the network polymer system from $PBPSF_2$ and M_3 is then investigated.

Experimental Section

Materials. Furyl-telechelic poly(1,4-butylene succinate-*co*-1,3-propylene succinate) ($PBPSF_2$) was synthesized by a procedure similar to furyl-telechelic poly(1,4-butylene succinate) described in our previous paper.[17] The feed ratio of the monomers was 5/3/3 succinic acid/1,4-butanediol/1,3-propanediol (in mole ratio). GPC ($CHCl_3$, polystyrene equivalents): $M_n = 6900$, $M_w/M_n = 1.26$. ^1H NMR: $M_n = 4300$, 1,3-propylene succinate unit content = 48 mol %. DSC: $T_m = 52$ and 64 °C; $T_g = -30$ °C.

1,2-Bis(maleimido)ethane (M_2)[18] and tris(2-maleimido ethyl)-amine (M_3)[9] were synthesized as previously reported.

Analytical Procedures. Gel permeation chromatography (GPC) was carried out using Tosoh HLC 8220 GPC system equipped with Shodex LF-804 columns ($CHCl_3$, 40 °C, 1 mg/mL). Polystyrene standards with low polydispersity were used to construct a calibration curve. Differential scanning calorimetry (DSC) was carried out with Perkin-Elmer Pyris 1 at a heating rate of 10 °C/min under a N_2 atmosphere. The sample of ca. 6 mg in an aluminum pan was measured. The T_m value was taken as the peak top of the melting endotherm, and the T_g value was taken as the midpoint of the heat capacity change. The heat of fusion (ΔH_f) was taken as the area of the melting endotherm. Wide-angle X-ray diffraction (WAXD) measurement was performed with Rigaku RINT-2000 diffractometer (40 kV and 40 mA) at room temperature. Nickel-filtered Cu Kα radiation ($\lambda = 0.154$ nm) was used. WAXD patterns were recorded in a 2θ range of 5°−40° at a scanning speed of 2.0°/min. Mechanical properties of films were evaluated using a tensile testing machine, SHIMAZU EZ test, at a cross-head speed of 1 mm/min at room temperature. Samples of $30 \times 5 \times 0.1$ mm^3 were used. Values of Young modulus, stress at yield, and elongation at break were averaged over the data of at least five samples.

DA and rDA Reactions. Solvent-cast films were prepared from $CHCl_3$ solution containing $PBPSF_2$ and a linker, M_2 or M_3 (with furan/maleimide = 1/1), on a Teflon Petri dish. During this procedure, DA reaction between furan terminals of $PBPSF_2$ and

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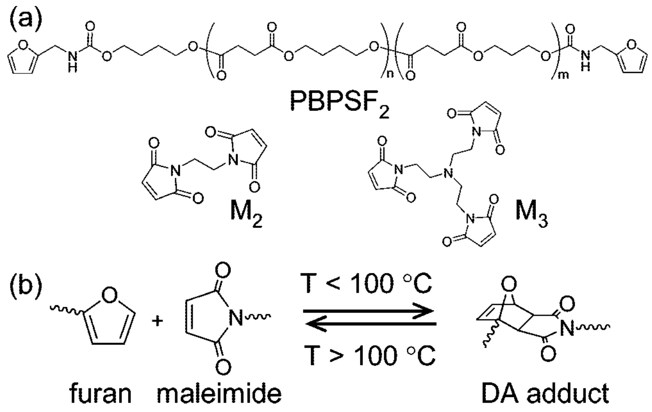
Scheme 1. (a) Chemical Structures of the Prepolymer $PBPSF_2$ and the Linkers M_2 and M_3; (b) Thermally Reversible DA Reactions of Furan and Maleimide



maleimide groups of the linker partially proceeded. This reaction history was erased by keeping the film at 145 °C for 20 min under a N_2 atmosphere just before the DA reaction. The DA reaction was carried out in an oven kept at 25 or 70 °C under a N_2 atmosphere. For the DA products, molecular weight was measured with GPC. Though the linear polymer obtained from $PBPSF_2$ and M_2 ($PBPSF_2M_2$) were soluble in $CHCl_3$, the network polymer from $PBPSF_2$ and M_3 ($PBPSF_2M_3$) became insoluble as the reaction proceeded. GPC measurements of the latter samples were performed only for the soluble fractions.

Reversibility of the DA reaction of $PBPSF_2M_2$ and $PBPSF_2M_3$ was analyzed by applying multiple cycles of DA and rDA reactions to them. The DA and rDA reactions were carried out at 25 °C for 48 h and at 145 °C for 20 min, respectively, under a N_2 atmosphere. After each reaction, the sample was immediately dissolved in $CHCl_3$ at room temperature and analyzed with GPC.

Preparation of Films by Various Thermal Treatments. Three $PBPSF_2M_3$ samples were prepared from a melted sample by different thermal treatments. The melted sample of $PBPSF_2M_3$ was prepared by compression-molding of the solvent-cast films composed of $PBPSF_2$ and M_3 (with furan/maleimide = 1/1) between two Teflon sheets with an aluminum spacer (0.1 mm thickness) using a hot press (Imoto Co., Japan) at 145 °C for 20 min under a pressure of 5 MPa. $PBPSF_2M_3$-25 was prepared by quickly moving the melted sample from the hot press to an oven at 25 °C and kept for 120 h under a N_2 atmosphere. $PBPSF_2M_3$-70-25 was prepared by keeping the melted sample at 70 °C for 6 h first and then at 25 °C for 120 h under a N_2 atmosphere. $PBPSF_2M_3$-25-70-25 was prepared by keeping $PBPSF_2M_3$-25 at 70 °C for 10 min and then at 25 °C for 120 h.

Results and Discussion

DA Reaction between $PBPSF_2$ and M_2 and Its Reversibility. Chemical structures of the prepolymer, $PBPSF_2$, and the linkers, M_2 and M_3, are shown in Scheme 1a. The bulk chain extension (polymerization) of $PBPSF_2$ with M_2 and M_3 and the depolymerization are conducted by utilizing the reversible DA reaction between furan terminals of the prepolymer and maleimide groups of the linkers. The DA and rDA reactions can be controlled simply by the thermal condition, as shown in Scheme 1b.

The DA reaction proceeds not only in bulk but also in solution. The DA reaction between the prepolymer and the linkers proceeded to some extent during the preparation of the cast film of them. This reaction history was erased by keeping the cast film under the conditions where the rDA reaction proceeds (at 145 °C for 20 min). Just after the erase of the reaction history, however, M_n of $PBPSF_2M_2$ was 8900 (GPC), which is slightly larger than that of the original prepolymer (6900). Prolonged thermal treatment at 145 °C did not induce further change in the molecular weight of this sample. These results indicate that even in the thermal equilibrium state at 145 °C, a few DA adduct moieties remain. The sample after the thermal treatment at 145 °C for 20 min is referred to as rDA0. The first DA reaction (DA1) for the $PBPSF_2 + M_2$ system was applied just after this thermal treatment.

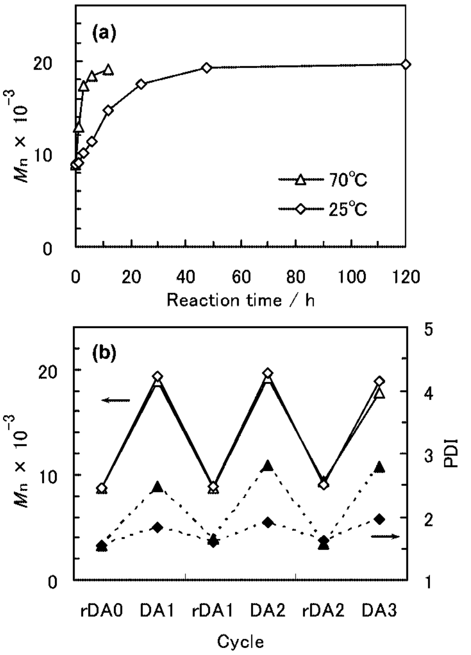


Figure 1. (a) Variations of M_n of $PBPSF_2M_2$ during the DA reaction at 70 (triangle) and 25 °C (square) against the reaction time. (b) Variations of M_n (open) and PDI (closed) of $PBPSF_2M_2$ during the cycles of DA and rDA reactions. The rDA reaction was performed at 145 °C for 20 min. The DA reactions were performed at 70 °C for 6 h (triangle) or 25 °C for 48 h (square).

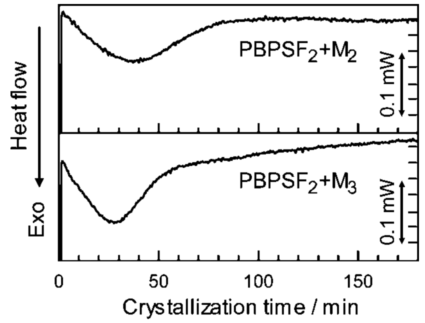


Figure 2. DSC curves of $PBPSF_2 + M_2$ and $PBPSF_2 + M_3$ during the isothermal crystallization at 25 °C just after the thermal treatment at 145 °C for 20 min.

The DA reactions in the $PBPSF_2 + M_2$ system were performed at 25 and 70 °C. Figure 1a shows the time courses of M_n during the reaction at 25 and 70 °C. The molecular weight of $PBPSF_2M_2$ increased with the reaction time and reached its equilibrium in 48 h at 25 °C and in 6 h at 70 °C. The equilibrium M_n values at both 25 and 70 °C were ca. 19 000.

$PBPSF_2$ shows two-peak melting behavior with peak tops at 52 and 64 °C in DSC thermogram (see Figure S1 of the Supporting Information). So, at 70 °C, the $PBPSF_2 + M_2$ system has kept molten state throughout the DA reaction. On the other hand, at 25 °C, the crystallization can proceed. Figure 2 shows DSC curves during isothermal crystallization of the $PBPSF_2 + M_2$ system at 25 °C just after the thermal treatment at 145 °C for 20 min. The crystallization of this system takes only about 1 h while the molecular weight increase by the DA reaction

Table 1. Tensile Properties of $PBPSF_2M_3$ Films after DA Reaction during Multiple Cycles of DA and rDA Reactions[a]

cycle	Young modulus/MPa	stress at yield/MPa	elongation at break/%
DA1	138 ± 7	10 ± 1	61 ± 16
DA2	112 ± 10	8 ± 1	67 ± 17
DA3	107 ± 12	8 ± 1	54 ± 13

[a] DA and rDA reactions were performed at 25 °C for 48 h and at 145 °C for 20 min, respectively. At the final DA reaction, the film was kept at 25 °C for 120 h for equilibrium crystallization.

lasts for 48 h at 25 °C. Hence, even in the presence of the crystalline domains, the DA reaction between the chain ends of $PBPSF_2$ and M_2 can proceed.

The reversibility of this polymer was tested by applying multiple cycles comprising polymerization by the DA reaction at 25 and 70 °C and depolymerization by the rDA reaction at 145 °C. Figure 1b shows a variation of M_n of $PBPSF_2M_2$ during the cycles of DA and rDA reactions. During the three cycles, M_n after the DA and rDA reactions, respectively, kept almost constant values, i.e., ca. 19 000 and ca. 9000, respectively. A good reversibility with no degradation of $PBPSF_2$ prepolymer was confirmed in this polymer system.

DA Reaction between $PBPSF_2$ and M_3 and Its Recyclability. The DA reaction in the $PBPSF_2 + M_3$ system was also performed at 25 and 70 °C. At both temperatures, the reaction proceeded, and the products gradually became insoluble to $CHCl_3$, indicating the formation of network structures. Totally insoluble products were obtained in 48 h at 25 °C and in 6 h at 70 °C, respectively. Similar to the $PBPSF_2 + M_2$ system, crystallization of $PBPSF_2$ proceeds in the $PBPSF_2 + M_3$ system at 25 °C. As shown in Figure 2, the isothermal crystallization of this system takes only ca. 1 h at 25 °C. This is much shorter than the time taken for insolubilization of the product by the cross-linking. So, the progress of the DA reaction in the semicrystalline state was confirmed.

To evaluate the reversibility of the DA reactions in the $PBPSF_2 + M_3$ system, multiple thermal cycles of DA and rDA reactions were applied. The products of every rDA reaction kept almost constant M_n of 9000, indicating any unfavorable degradation of $PBPSF_2$ did not occur by the repetition of thermal cycles of DA and rDA reactions. As listed in Table 1, the mechanical properties of the recycled $PBPSF_2M_3$ films were hardly changed by the thermal cycles. So, a good recyclability of $PBPSF_2M_3$ was confirmed.

Physical Properties of $PBPSF_2M_3$ Films Prepared under Different Conditions. As described in the previous section, $PBPSF_2$ can react with M_3 not only in the molten state (70 °C) but also under the conditions in which the crystallization proceeds simultaneously (25 °C). In $PBPSF_2M_3$-70-25, the dynamic processes of cross-linking and crystallization were clearly separated. The DA reaction at 70 °C was followed by the crystallization of the $PBPSF_2$ chains at 25 °C. On the other hand, in $PBPSF_2M_3$-25, the crystallization proceeds simultaneously with the DA reaction at the earliest stage at 25 °C. The crystallization, however, takes only ca. 1 h while the insolubilization by cross-linking of $PBPSF_2M_3$-25 requires 48 h. So, the crystallization occurs in the $PBPSF_2 + M_3$ system where substantial network structures have not been formed yet. The subsequent DA reaction, which proceeds in the semicrystalline state, contributes the network structure formation.

Figure 3 shows WAXD patterns of $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25. By curve resolution of these patterns, several diffraction peaks from the crystalline phase and an amorphous halo were separated. There was no difference in the degree of crystallinity, X_c, between $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25 (26 and 27%, respectively). The peak positions of these samples were almost identical and also corresponded to those of the PBS homopolymer.[19] The three strong diffraction peaks located at 2θ of 19.6°, 21.8°, and 22.4° are ascribed to the (020), (021), and (110) planes of the monoclinic unit cell of PBS, respectively.

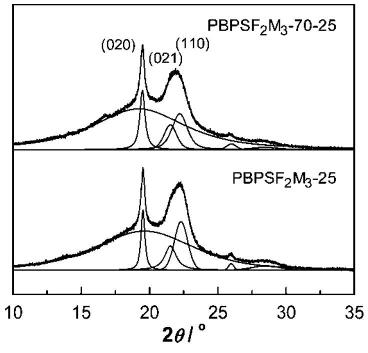


Figure 3. WAXD patterns of $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25.

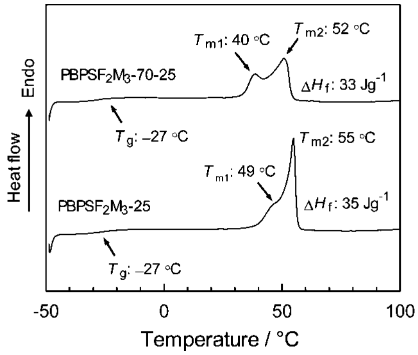


Figure 4. DSC curves of $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25 during the heating scan at a rate of 10 °C/min.

An obvious difference between $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25 was observed in the width of the diffraction peaks. For example, the full width at the half-maximum (fwhm) of the (020) diffraction of $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25 were 0.46 and 0.34, respectively. The difference in the width of diffraction peaks can be attributed to the difference in the crystallite sizes. To estimate the crystallite sizes, the Scherrer equation was used:[20]

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}\cos\theta} \tag{1}$$

where D_{hkl} is the mean crystallite size along the $[hkl]$ direction, K is the shape factor (the Scherrer constant, equals 0.94 in this study), λ is the wavelength (0.154 nm), β_{hkl} is the line breadth (usually taken as the fwhm of a (hkl) diffraction), and θ is the half-scattering angle. By this equation, the crystallite sizes along the [020] direction of $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25 were estimated to be ca. 19 and 26 nm, respectively. The crystallite sizes in other directions of $PBPSF_2M_3$-70-25 were also smaller than those of $PBPSF_2M_3$-25. So, the smaller crystallites are formed in $PBPSF_2M_3$-70-25 than in $PBPSF_2M_3$-25.

Figure 4 shows DSC thermograms of $PBPSF_2M_3$-70-25 and $PBPSF_2M_3$-25 during heating at a rate of 10 °C/min. Both of them had two melting peaks (T_{m1} and T_{m2}), while the peak top positions were different. Obviously, T_ms of $PBPSF_2M_3$-70-25 are lower than those of $PBPSF_2M_3$-25. On the other hand, the total areas of the melting peaks, i.e., the heat of fusion, of those samples were similar. These results are consistent with the WAXD results. The crystallites in $PBPSF_2M_3$-70-25 are smaller than those in $PBPSF_2M_3$-25 while the degrees of crystallinity of them are similar. The difference in T_m also suggests that the crystallites in $PBPSF_2M_3$-70-25 contain more defects.

In $PBPSF_2M_3$-25, the crystallization occurs at the earliest stage of the DA reaction, at which network structures have not

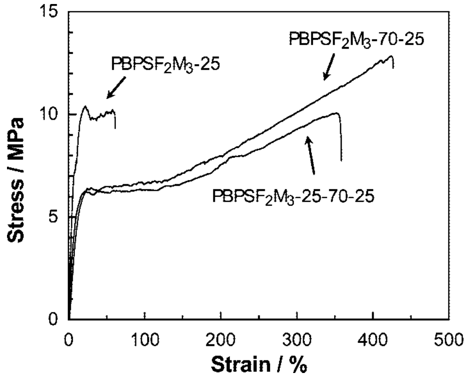


Figure 5. Stress−strain curves of PBPSF$_2$M$_3$-70-25, PBPSF$_2$M$_3$-25, and PBPSF$_2$M$_3$-25-70-25 in tensile test.

Table 2. Tensile Properties of PBPSF$_2$M$_3$ Films Prepared under Three Different Conditions

sample	Young modulus/MPa	stress at yield/MPa	elongation at break/%
PBPSF$_2$M$_3$-70-25	70 ± 4	6 ± 1	464 ± 37
PBPSF$_2$M$_3$-25	138 ± 7	10 ± 1	61 ± 16
PBPSF$_2$M$_3$-25-70-25	67 ± 3	6 ± 1	380 ± 29

been formed yet. Thus, relatively large crystallites can grow. In PBPSF$_2$M$_3$-70-25, on the other hand, the network structures that have been already formed in the molten state (70 °C) should disturb the growth of the crystallites at 25 °C.

Figure 5 shows stress−strain curves of PBPSF$_2$M$_3$-70-25 and PBPSF$_2$M$_3$-25 obtained by tensile tests. Young modulus, stress at yield, and elongation at break of the samples are listed in Table 2. These two samples showed completely different properties. PBPSF$_2$M$_3$-25 is a hard and brittle material with relatively high Young modulus and short elongation at break. On the other hand, PBPSF$_2$M$_3$-70-25 is a soft and ductile material with long elongation at break. Since degrees of crystallinity of PBPSF$_2$M$_3$-70-25 and PBPSF$_2$M$_3$-25 are similar, the difference in mechanical properties between them must be ascribed to the difference in the crystallite size.

As a cross-linked semicrystalline polymer, PBPSF$_2$M$_3$ is potentially a shape memory material.[21,22] Actually, after being deformed to 50% strain at room temperature, both PBPSF$_2$M$_3$-70-25 and PBPSF$_2$M$_3$-25 films showed the strain recovery at 70 °C within 5 min.[23] The in-depth investigation of the shape memory property of PBPSF$_2$M$_3$ is now in progress.

Two-Way Conversion of Mechanical Properties in PBPSF$_2$M$_3$. If the assumption that the mechanical properties of PBPSF$_2$M$_3$ alter depending on the crystallite size is correct, a heat treatment for PBPSF$_2$M$_3$-25 at a temperature high enough to melt the crystallites and low enough not to break the labile cross-links will change the mechanical properties. PBPSF$_2$M$_3$-25 was annealed at 70 °C for 10 min and recrystallized at 25 °C for 120 h. The stress−strain curve of this sample, i.e., PBPSF$_2$M$_3$-25-70-25, is shown in Figure 5. Interestingly, PBPSF$_2$M$_3$-25-70-25 showed the curve similar to that of PBPSF$_2$M$_3$-70-25.

DSC thermogram shows that the melting points, T_{m1} and T_{m2}, of PBPSF$_2$M$_3$-25-70-25 are 39 and 50 °C with $\Delta H_m = 32$ J/g (data not shown). WAXD analysis shows X_c and fwhm of the (020) diffraction of this sample were 25% and 0.43, respectively (data not shown). These values are almost the same as the values of PBPSF$_2$M$_3$-70-25, indicating the similarity in the crystalline structure between PBPSF$_2$M$_3$-25-70-25 and PBPSF$_2$M$_3$-70-25.

In PBPSF$_2$M$_3$-25, larger crystallites grew under the conditions where the DA reaction had hardly proceeded yet, followed by the network structure construction by the progress of the DA reaction. By heating PBPSF$_2$M$_3$-25 to 70 °C, the large crystallites in it melt without breaking the cross-links. During the subsequent treatment at 25 °C to obtain PBPSF$_2$M$_3$-25-70-25, the remaining network structure disturbs the regrowth of the large crystallites. Only small crystallites can be formed. Therefore, the root cause of the thermoresponsive alteration of the mechanical properties is the time lag given by the two dynamic processes, i.e., cross-linking reaction and crystallization. The similarity in the tensile properties between PBPSF$_2$M$_3$-25-70-25 and PBPSF$_2$M$_3$-70-25 indicates the similarity in the network structure such as the density and distribution of the cross-links of them. The thermoresponsive conversion in PBPSF$_2$M$_3$ is schematically represented in Figure 6.

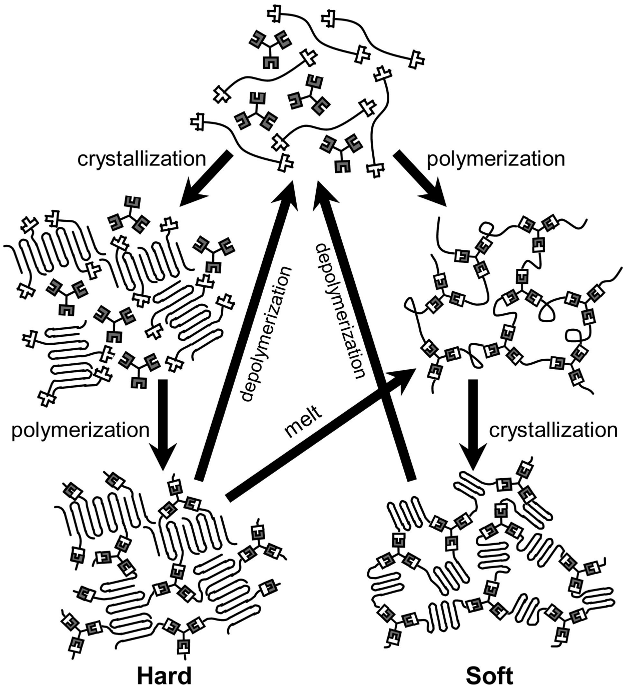


Figure 6. Schematic representation of two-way conversion between hard and soft mechanical properties in PBPSF$_2$M$_3$ induced by controlling the dynamics of melt/crystallization and polymerization/depolymerization.

As mentioned above, the network polymer system from PBPSF$_2$ and M$_3$ can be de-cross-linked at 145 °C to produce the prepolymer and the linker, which can be then polymerized to reproduce the network polymer. Combining the melt−recrystallization and the depolymerization−repolymerization of the PBPSF$_2$ + M$_3$ system, we can freely alter the PBPSF$_2$ + M$_3$ system back and forth between hard and soft properties. Thus, we have obtained a unique network polymer showing two-way conversion between totally different mechanical properties.

Conclusion

In this study, we have synthesized a biobased network polymer with switchable mechanical properties. A prepolymer, PBPSF$_2$, was prepared and polymerized with a tris-maleimide linker, M$_3$, by the DA reaction to give a network polymer, PBPSF$_2$M$_3$. The polymerization can occur not only in the molten state (70 °C) but also under the condition where crystallization can proceed (25 °C). Two different sequences of thermal treatments resulted in materials with totally different mechanical properties. This differentiation is derived from the difference in size and distribution of crystallites generated by the time lag given by the two dynamic processes, i.e., cross-linking reaction and crystallization. Therefore, by controlling the two reversible processes of melt−recrystallization and depolymerization−repolymerization, we can freely alter back and forth between hard and soft materials.

Supporting Information Available: DSC thermogram of $PBPSF_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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