Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 1011–1015 **1011**
DOI: 10.1021/ma901994v

Hard−Soft Conversion in Network Polymers: Effect of Molecular Weight of Crystallizable Prepolymer

Kazuki Ishida,[†] Yoshitake Nishiyama, Yuta Michimura, Nobuhiro Oya, and Naoko Yoshie*

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan.
[†]Present address: Syracuse Biomaterials Institute and Department of Biomedical and Chemical Engineering, Syracuse University, 121 Link Hall, Syracuse, NY 13244

Received September 6, 2009; Revised Manuscript Received December 5, 2009

ABSTRACT: A series of hard−soft convertible network polymers were obtained using Diels−Alder reaction between semicrystalline prepolymers, furyl-telechelic poly(ε-caprolactone) with number-averaged molecular weights ranging from 2450 to 8800 (PCL_nF_2; n (degree of polymerization) = 18, 22, 26, 33, and 74), and a tris-maleimide linker (M_3). The reaction between PCL_nF_2 and M_3 was conducted in the semicrystalline state or in the molten state, resulting in two different cross-linked polymers exhibiting harder and softer mechanical properties, respectively ($PCL_nF_2M_3$-CRY^{1st} and $PCL_nF_2M_3$-CL^{1st}). The difference in the properties can be attributed to the difference in size and order of crystalline domains for $n \geq 22$ and that in degree of crystallinity for $n = 18$. The network polymers exhibit the hard−soft conversion behavior via melt/recrystallization process without de-cross-linking. The molecular weight of PCL_nF_2 strongly affects this hard−soft conversion.

Introduction

Physical properties such as hardness, flexibility, and thermal resistance of semicrystalline polymers need to be adjusted for intended applications.[1−3] Incorporation of cross-links into semicrystalline polymers leads to drastic changes in their physical properties and thus is one of the most effective strategies for modifying semicrystalline polymers.[4−8] Cross-links formed in the molten state of a crystallizable polymer effectively limit the crystal growth, resulting in the decrease in degree of crystallinity, crystallite size, and melting temperature compared to the linear homologue.[4,5,7] On the other hand, when cross-linking reaction between polymer chains is conducted in the semicrystalline state, the crystallites interfere with the cross-link formation and affect the resultant network structures.[7,8] Therefore, it is interesting to compare two different network polymers obtained by cross-linking reaction in the molten state and in the semicrystalline state.

In a previous work,[9] we have obtained two network polymers with obviously different thermal and mechanical properties from a prepolymer, furyl-telechelic poly(1,4-butylene succinate-*co*-1,3-propylene succinate) ($PBPSF_2$, $M_n = 4300$) and a tris-maleimide linker by means of Diels−Alder (DA) reaction. The network polymer prepared by cross-linking of the prepolymer in the semicrystalline state was a relatively hard material, while that obtained by cross-linking in the molten state and following crystallization showed softer properties. The thermal reversibility of DA reaction between furan and maleimide moieties[10−15] enabled us the reversible cross-linking and thus the two-way conversion between hard and soft properties in this system by changing the sequencing of crystallization and cross-linking. Moreover, the harder network polymer was also found to convert into softer material by a melting and recrystallization process without de-cross-linking.

Our current interest is focused on the control of the difference between hard and soft mechanical properties of the network polymers. The simplest strategy for this purpose is to alter the molecular weight of the prepolymer, that is, to change the cross-linking density. In this work, the effect of the molecular weight on the hard−soft difference and the conversion is investigated through the comparison of network polymers obtained from five prepolymers, furyl-telechelic poly(ε-caprolactone)s (PCL_nF_2) with molecular weight variation between 2450 and 8800, and a tris-maleimide, M_3 (Scheme 1a).

Experimental Section

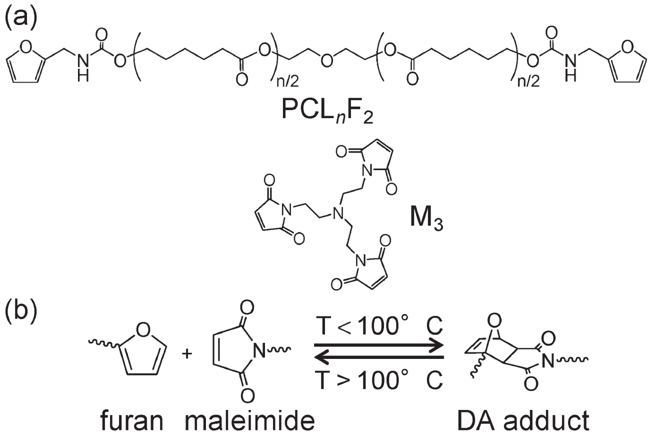
Analytical Procedures. ^{1}H NMR spectroscopy was performed using a JEOL JNM-AL400 FT NMR system on chloroform-*d* solutions at room temperature. Gel permeation chromatography (GPC) was carried out using a Tosoh HLC 8220 equipped with Tosoh TSK-GEL GMH_{HR}-N columns (chloroform, 40 °C, 1 mL/min). Polystyrene standards with low polydispersity were used to construct a calibration curve. Differential scanning calorimetry (DSC) was carried out with Perkin-Elmer Pyris 1 at heating and cooling rates of 10 and −10 °C/min, respectively, under a N_2 atmosphere. The sample of ca. 5 mg in an aluminum pan was measured. The melting (T_m) and crystallization (T_c) temperatures were taken as the peak top of the heating endotherm and the cooling exotherm, respectively. The heat of fusion (ΔH_f) and crystallization (ΔH_c) were taken as the area of the corresponding peaks. Isothermal crystallization was observed at 25 °C after thermally treated at 70 °C for 10 min or 145 °C for 20 min and quenched. 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. Tensile properties were evaluated using a Shimadzu EZ test at a cross-head speed of 1 mm/min at room temperature. Samples of $30 \times 5 \times 0.2$ mm^3 were used. Values of Young modulus, stress at yield, and elongation at break were averaged over the data of at least three samples.

Synthesis of Prepolymers, PCL_nF_2, and a Linker, M_3. Two poly(ε-caprolactone) diols (PCLdiols) with M_n of 1250 and 2000 were purchased from Aldrich and used as-received. Three PCL diols were synthesized by ring-opening polymerization of

---

*Corresponding author. E-mail: yoshie@iis.u-tokyo.ac.jp.

Scheme 1. (a) Chemical Structures of Prepolymers, PCL_nF_2 (n = 18, 22, 26, 33, and 74), and a Cross-Linker, M_3; (b) Thermally Reversible Diels−Alder (DA) Reaction of Furan and Maleimide



ε-caprolactone (ε-CL, Tokyo Chemical Industry) with diethylene glycol (DEG, Tokyo Chemical Industry) as an initiator and stannous octoate ($Sn(Oct)_2$, Aldrich) as a catalyst under a N_2 atmosphere at 130 °C for 24 h. The feed ratios of ε-CL/DEG were 80/1, 25/1, and 15/1, while that of DEG/$Sn(Oct)_2$ was fixed at 25/1. Five samples of furyl-telechelic PCL (PCL_nF_2; n (degree of polymerization) = 18, 22, 26, 33, and 74) were obtained by a modification of end groups of PCL diols by a procedure similar to those for furyl-telechelics of poly(butylene succinate) ($PBSF_2$) and $PBPSF_2$ described in our previous papers.[9,15] Tris(2-maleimidoethyl)amine linker, M_3, was synthesized as previously reported.[11]

Synthesis of Network Polymers, $PCL_nF_2M_3$. Solvent-cast films were made from chloroform solution containing PCL_nF_2 and M_3 (with the molar ratio of furan/maleimide = 1/1) and dried under vacuum for 48 h. Compression-molded samples were prepared from the solvent-cast films between two Teflon sheets with an aluminum spacer (0.2 mm thickness) using a hot press (Imoto Co., Japan) at 145 °C for 20 min under a pressure of 5 MPa. During the cast film preparation, some DA adduct were generated between furan terminals of PCL_nF_2 and maleimide groups of M_3. This reaction history was erased by compression molding at 145 °C.[9,14,15] Cross-linked polymers of PCL_nF_2 and M_3 ($PCL_nF_2M_3$) were prepared from the compression molded sample by three thermal treatments. The crystallization-first sample (CRY^{1st}) was prepared by quenching the molded sample from 145 to 25 °C and kept for 240 h under a N_2 atmosphere. The cross-linking-first sample (CL^{1st}) was prepared by keeping the molded sample at 70 °C for 24−48 h and then at 25 °C for 240 h under a N_2 atmosphere. The recrystallized sample (RECRY) were prepared by keeping a CRY^{1st} sample at 70 °C for 10 min and then at 25 °C for 240 h.

Results and Discussion

Preparation of Prepolymers, PCL_nF_2. Table 1 lists the characteristics of five PCL_nF_2 prepolymers. PCL_nF_2 with n of 18−74 (M_n of 2450−8800) were obtained. Polydispersity index, PDI, of PCL_nF_2 was small (1.1−1.2 for PCL_nF_2 with $n \leq 33$ and 1.5 for $PCL_{74}F_2$), which is suitable for this study investigating the effects of molecular weight of PCL_nF_2. The T_m and ΔH_f values slightly varied with the molecular weight of PCL_nF_2 in the ranges of 49−57 °C and 77−97 J/g, respectively. As for the crystallization during the DSC cooling scan, T_c was gradually depressed with decreasing the molecular weight of PCL_nF_2 in the range of 9−30 °C, while ΔH_c was relatively constant. These data indicate that the five PCL_nF_2 samples are semicrystalline prepolymers having similar crystallizability despite the large molecular weight variation of 2450−8800.

Table 1. Characteristics of Prepolymers, PCL_nF_2

n^a	$M_{n,NMR}{}^b$	$M_{n,GPC}{}^c$	$M_w{}^c$	PDI^c	$T_m{}^d$/ °C	$\Delta H_f{}^d$/ J g^{-1}	$T_c{}^d$/ °C	$\Delta H_c{}^d$/ J g^{-1}
74	8800	9670	14890	1.54	57	94	30	−68
33	4160	6590	8170	1.24	54	90	26	−68
26	3360	4960	5610	1.14	50	97	20	−67
22	2820	4230	5080	1.20	49	86	21	−67
18	2450	3800	4100	1.08	51	77	9	−60

[a] Degree of polymerization determined by ^{1}H NMR. [b] Determined by ^{1}H NMR. [c] Measured by GPC. [d] Measured by DSC.

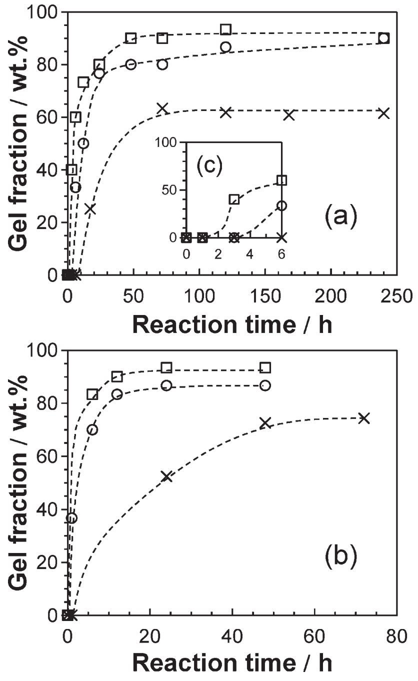


Figure 1. Variations of gel fraction of $PCL_nF_2M_3$ (n = 22 (square), 33 (circle), and 74 (cross)) during the DA reaction at 25 °C (a) and 70 °C (b) against the reaction time. An enlarged view of (a) in the reaction time of 0−6 h (c) is inserted in (a). Data for $PCL_nF_2M_3$ (n = 18 and 26) were almost overlapped with those for $PCL_{22}F_2M_3$ and omitted.

DA Reaction between PCL_nF_2 and M_3. The DA reaction between furan and maleimide moieties can proceed below ca. 100 °C while the retro-DA reaction becomes dominant above the temperature (Scheme 1b).[9−15] Before the preparation of cross-linked polymers, $PCL_nF_2M_3$ were thermally treated at 145 °C for 20 min. Just after the thermal treatment, M_n values of $PCL_nF_2M_3$ were higher (within 1.9 times) than those of PCL_nF_2 (data not shown), indicating that some amounts of DA adducts still remained. $PCL_nF_2M_3$ were, however, sufficiently de-cross-linked and completely soluble in chloroform. The de-cross-linked $PCL_nF_2M_3$ were then quenched to 25 or 70 °C for cross-linking reaction.

In Figure 1 are displayed the time courses of gel fraction of $PCL_nF_2M_3$ (n = 22, 33, and 74) during the DA reaction at 25 °C (a) and 70 °C (b). Plots for the other $PCL_nF_2M_3$ (n = 18 and 26) were almost overlapped with those of $PCL_{22}F_2M_3$ and omitted. The gel fractions increased with the reaction time and reached plateau values less than 100% for all of the samples. The time course strongly depended on the reaction temperature and the molecular weight of PCL_nF_2. During the reaction at 25 °C, insoluble fraction began appearing at 3 h for $PCL_{22}F_2M_3$, 6 h for $PCL_{33}F_2M_3$, and 17 h for $PCL_{74}F_2M_3$, and the gel fractions reached a plateau after 48−72 h as shown in Figure 1a,c. The plateau values were 80−95% for $PCL_nF_2M_3$ with n = 22 and 33 and 60% for $PCL_{74}F_2M_3$. At 70 °C, the gel fractions of $PCL_nF_2M_3$ with

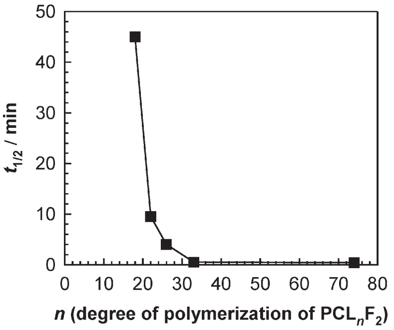


Figure 2. Crystallization half-time ($t_{1/2}$) of $PCL_nF_2M_3$ at 25 °C as a function of n (degree of polymerization) of the prepolymer PCL_nF_2. The crystallization just after the thermal treatment at 145 °C was traced by DSC.

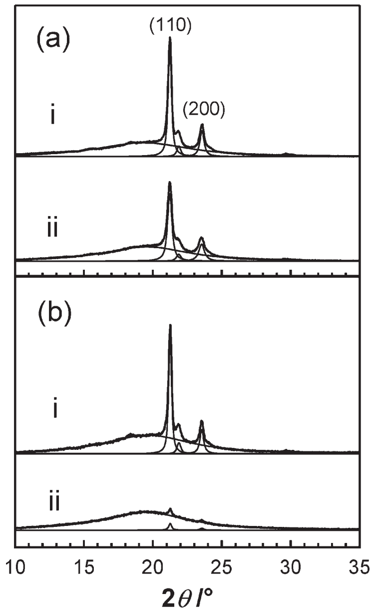


Figure 3. WAXD patterns of CRY^{1st} (i) and CL^{1st} (ii): (a) $PCL_{22}F_2M_3$, (b) $PCL_{18}F_2M_3$.

Table 2. Degree of Crystallinity (X_c) and Mean Crystallite Size (D_{hkl}) along the [hkl] Direction of $PCL_nF_2M_3$-CRY^{1st}, $PCL_nF_2M_3$-CL^{1st}, and $PCL_nF_2M_3$-RECRY

	$X_c{}^a$/%				$D_{hkl}{}^a$/nm		
sample	CRY^{1st}	CL^{1st}	RECRY		CRY^{1st}	CL^{1st}	RECRY
$PCL_{74}F_2M_3$	41	39	ND[b]	D_{110}	26	24	ND[b]
				D_{200}	21	20	ND[b]
$PCL_{33}F_2M_3$	41	39	39	D_{110}	27	23	25
				D_{200}	22	18	21
$PCL_{26}F_2M_3$	37	33	36	D_{110}	28	24	25
				D_{200}	22	18	20
$PCL_{22}F_2M_3$	34	29	31	D_{110}	29	23	23
				D_{200}	23	17	19
$PCL_{18}F_2M_3$	29	2	29	D_{110}	33	ND[b]	29
				D_{200}	27	ND[b]	23

[a] Determined by WAXD. [b] Not determined.

$n = 22$ and 33 reached the plateau at 85−95% after 24 h, while $PCL_{74}F_2M_3$ required 48 h to reach the plateau at 75%, as shown in Figure 1b. These results indicate that PCL_nF_2 prepolymers with $n \leq 33$ can react with M_3 effectively at both 25 and 70 °C to form cross-linked network polymers, while the reactivity is relatively low between M_3 and $PCL_{74}F_2$ having chain much longer than the other PCL_nF_2.

Isothermal crystallization of $PCL_nF_2M_3$ was traced with DSC at 25 °C just after de-cross-linking at 145 °C. Crystallization half-times ($t_{1/2}$) were plotted against n of PCL_nF_2 in Figure 2. The crystallization rate of $PCL_nF_2M_3$ decreased with decreasing the molecular weight of PCL_nF_2. The $t_{1/2}$ values of $PCL_nF_2M_3$ with $n \geq 22$ were less than 10 min, while $PCL_{18}F_2M_3$ showed a slower crystallization ($t_{1/2} = 45$ min). As shown in Figure 1c, $PCL_nF_2M_3$ kept completely soluble in chloroform within at least 1 h at 25 °C, indicating that crystallization of $PCL_nF_2M_3$ was completed before substantial cross-linked network structures were formed. Therefore, in the CRY^{1st} samples, which were prepared by keeping the de-cross-linked $PCL_nF_2M_3$ at 25 °C, the cross-linking reaction proceeded in the semicrystalline state. We could also prepare the CL^{1st} samples by cross-linking in the molten state at 70 °C and following crystallization at 25 °C.

Physical Properties of $PCL_nF_2M_3$ Prepared under Different Conditions. Figure 3 displays WAXD patterns of representative CRY^{1st} (i) and CL^{1st} (ii) ($PCL_{22}F_2M_3$ (a) and $PCL_{18}F_2M_3$ (b)). These patterns showed three diffraction peaks at $2\theta = 21.4°$, 22.0°, and 23.7°, ascribable to the (110), (111), and (200) planes of the orthorhombic unit cell of PCL, respectively.[16] The degree of crystallinity (X_c) was calculated by curve resolution of these patterns, in which the diffraction peaks from the crystalline phase and an amorphous halo were separated (Table 2). The X_c value gradually decreased with the decrease in molecular weight of the prepolymer, PCL_nF_2. The decline in X_c was larger for CL^{1st} than for CRY^{1st}. As a result, the difference in X_c between CRY^{1st} and CL^{1st} of $PCL_{18}F_2M_3$ was significant (29% and 2%, respectively), while X_c of CRY^{1st} and CL^{1st} were similar for $PCL_nF_2M_3$ with $n \geq 22$.

The peak width of the (hkl) diffraction in the WAXD pattern is related to the mean crystallite size along the [hkl] direction, D_{hkl}, which can be calculated with the Scherrer equation.[9,17] The D_{110} and D_{200} values, which are crystallite sizes along the lateral growth directions (D_{hk0}), are listed in Table 2. The crystallite size of CL^{1st} (D_{110}: 23−24 nm; D_{200}: 17−20 nm) was smaller than that of CRY^{1st} (D_{110}: 26−33 nm; D_{200}: 21−27 nm), indicating that the preformed cross-links in CL^{1st} disturbed the crystal growth. With the decrease in molecular weight of PCL_nF_2, the D_{110} and D_{200} values of CRY^{1st} gradually increased, while those of CL^{1st} showed a trend of slight decrease. As shown in Table 1, T_m of PCL_nF_2 slightly decreased with decreasing the molecular weight. This means that in CRY^{1st} of $PCL_nF_2M_3$ with smaller n, crystallization proceeds under lower degree of supercooling, and the resulting crystalline phase has more ordered structure with fewer defects, which results in the gradual increase in the mean crystallite size along the lateral growth directions. On the other hand, in CL^{1st} of $PCL_nF_2M_3$ with smaller n, crystallization is more disturbed due to higher degree of cross-linking. The slight decrease in D_{hk0} values of CL^{1st} with decreasing n of PCL_nF_2 indicates that CL^{1st} with smaller n has smaller crystallites and less ordered crystalline phase structure. Consequently, the difference in size and order of crystalline domains of CRY^{1st} and CL^{1st} slightly expanded with the decrease in molecular weight of PCL_nF_2.

Figure 4 shows DSC thermograms of CRY^{1st} (i) and CL^{1st} (ii) of $PCL_nF_2M_3$ (n = 74 (a), 33 (b), 26 (c), 22 (d), and 18 (e)) during the heating scans. The T_m and ΔH_f values are listed in Table 3. The T_m and ΔH_f values of $PCL_nF_2M_3$-CRY^{1st} were higher than those of $PCL_nF_2M_3$-CL^{1st} with the same n. Furthermore, the shape of melting peaks of CL^{1st} was obviously broader than that of CRY^{1st}. These results indicate that the preformed cross-links in CL^{1st} restrict the crystallization and cause less ordered crystalline phase,

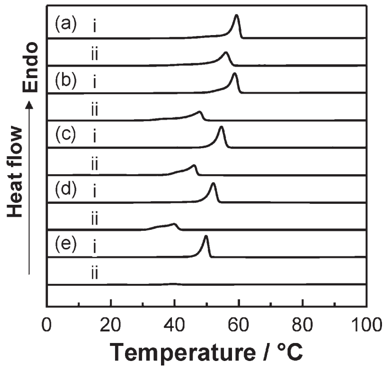


Figure 4. DSC curves during heating scans of CRY^{1st} (i) and CL^{1st} (ii): (a) $PCL_{74}F_2M_3$, (b) $PCL_{33}F_2M_3$, (c) $PCL_{26}F_2M_3$, (d) $PCL_{22}F_2M_3$, and (e) $PCL_{18}F_2M_3$.

Table 3. Thermal Properties of $PCL_nF_2M_3$-CRY^{1st} and $PCL_nF_2M_3$-CL^{1st}

	$T_m{}^a$/°C		$\Delta H_f{}^a$/J g^{-1}	
sample	CRY^{1st}	CL^{1st}	CRY^{1st}	CL^{1st}
$PCL_{74}F_2M_3$	59	56	84	73
$PCL_{33}F_2M_3$	59	48	72	57
$PCL_{26}F_2M_3$	55	46	65	48
$PCL_{22}F_2M_3$	52	40	60	37
$PCL_{18}F_2M_3$	50	40	54	2

[a] Determined by DSC.

which corresponds with the D_{hkl} data. As the molecular weight of PCL_nF_2 decreased, the T_m and ΔH_f values of both CRY^{1st} and CL^{1st} decreased, though the declines of these values were larger for CL^{1st} than for CRY^{1st}. As a result, $PCL_{18}F_2M_3$-CL^{1st} exhibited a negligible melting endotherm (ΔH_f = 2 J/g) while $PCL_{18}F_2M_3$-CRY^{1st} showed much larger one (ΔH_f = 54 J/g). This tendency corresponds well to the X_c results mentioned above.

Figure 5 shows stress−strain curves of CRY^{1st} (i) and CL^{1st} (ii) obtained by tensile test (n = 33 (a), 26 (b), 22 (c), and 18 (d)). Young modulus, stress at yield, and elongation at break of the samples are listed in Table 4. The mechanical properties of CRY^{1st} and CL^{1st} were different. CRY^{1st} is harder and relatively brittle materials with higher Young modulus, higher and clear yield point with larger stress depression, and short elongation at break, while CL^{1st} is softer and ductile materials with long elongation at break. Since CRY^{1st} and CL^{1st} of $PCL_nF_2M_3$ with the same n (and $n \geq 22$) have similar degree of crystallinity, the difference in mechanical properties must be ascribed to the difference in the size and order of crystalline domains. On the other hand, for $PCL_{18}F_2M_3$, the difference in mechanical properties between CRY^{1st} and CL^{1st} is obviously due to the different X_c.

The difference in mechanical properties between CRY^{1st} and CL^{1st} tended to expand with decreasing the molecular weight of the prepolymer PCL_nF_2. The Young modulus of CL^{1st} (E_{CL}) was divided by that of CRY^{1st} (E_{CRY}), and the E_{CL}/E_{CRY} ratio was plotted as a function of n of PCL_nF_2 in Figure 6. The ratio was depressed continuously with the decrease in n, which clearly shows the expansion of the hard−soft difference between CRY^{1st} and CL^{1st} with the decrease in n. The differences in stress at yield and elongation at break between CRY^{1st} and CL^{1st} had similar expansion behavior as shown in Table 4. These trends correspond well with the X_c, D_{hkl}, T_m, and ΔH_f data shown above. It is notable that $PCL_{18}F_2M_3$-CL^{1st} displayed a completely elastomeric tensile curve, while $PCL_{18}F_2M_3$-CRY^{1st} exhibited a curve similar to those of the other CRY^{1st} samples.

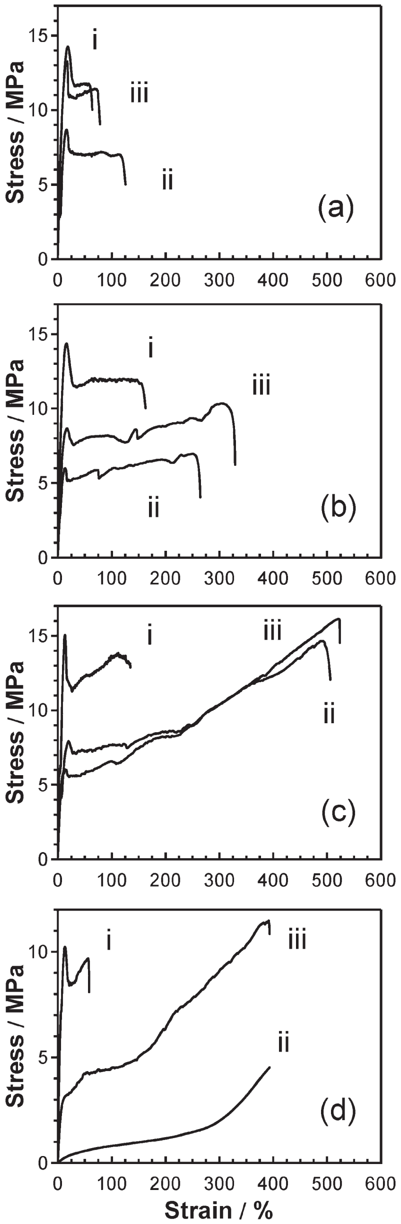


Figure 5. Stress−strain curves of CRY^{1st} (i), CL^{1st} (ii), and RECRY (iii): (a) $PCL_{33}F_2M_3$, (b) $PCL_{26}F_2M_3$, (c) $PCL_{22}F_2M_3$, and (d) $PCL_{18}F_2M_3$.

Hard−Soft Conversion via Melt/Recrystallization. In Figure 5 are also shown stress−strain curves of RECRY of $PCL_nF_2M_3$ (iii). The X_c, D_{110}, and D_{200} values and the data of mechanical properties for RECRY are also listed in Tables 2 and 4. RECRY samples, which were prepared by the melting and recrystallization process of CRY^{1st}, exhibited similar X_c values, smaller D_{hk0} values, and softer mechanical properties compared to CRY^{1st} with the same n. As discussed above, in $PCL_nF_2M_3$-CRY^{1st}, well-ordered crystallites grew under the conditions where the network structure had been hardly formed yet, followed by the network structure construction by the progress of the DA reaction. By heating $PCL_nF_2M_3$-CRY^{1st} to 70 °C, the ordered crystallites in it melt without breaking the cross-links. During the subsequent treatment at 25 °C to obtain $PCL_nF_2M_3$-RECRY, the remaining network structure disturbs the recrystallization, and thus less ordered crystallites are then formed in $PCL_nF_2M_3$-RECRY. Hence, CRY^{1st} can convert their harder mechanical properties to softer ones by the melting/recrystallization process.

Table 4. Tensile Properties of $PCL_nF_2M_3$-CRY^{1st}, $PCL_nF_2M_3$-CL^{1st}, and $PCL_nF_2M_3$-RECRY

	Young modulus/MPa			stress at yield/MPa			elongation at break/%		
sample	CRY^{1st}	CL^{1st}	RECRY	CRY^{1st}	CL^{1st}	RECRY	CRY^{1st}	CL^{1st}	RECRY
$PCL_{33}F_2M_3$	217 (±10)	140 (±6)	173 (±12)	15 (±1)	8 (±1)	13 (±1)	44 (±10)	108 (±8)	67 (±8)
$PCL_{26}F_2M_3$	232 (±17)	94 (±9)	127 (±4)	14 (±1)	6 (±0)	9 (±0)	103 (±54)	207 (±37)	307 (±31)
$PCL_{22}F_2M_3$	276 (±13)	93 (±3)	109 (±7)	15 (±0)	5 (±1)	8 (±0)	74 (±37)	466 (±83)	432 (±69)
$PCL_{18}F_2M_3$	182 (±13)	2 (±0)	49 (±2)	10 (±1)	—[a]	3 (±0)	77 (±42)	345 (±45)	398 (±48)

[a] Not observed.

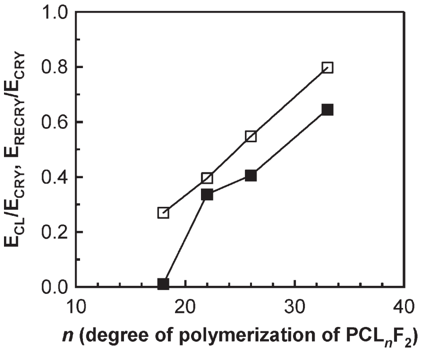


Figure 6. Ratios of Young modulus of CL^{1st} and RECRY to that of CRY^{1st} (E_{CL}/E_{CRY}, ■; E_{RECRY}/E_{CRY}, □) as a function of n (degree of polymerization) of the prepolymer PCL_nF_2.

The ratio of Young modulus of RECRY to that of CRY^{1st} (E_{RECRY}/E_{CRY}) is also plotted in Figure 6. The ratio was depressed continuously with the decrease in n, which is similar behavior with the E_{CL}/E_{CRY} ratio, but the former kept higher than the latter in the whole n range. Figures 5 and 6 and Tables 2 and 4 show that the crystalline phase structure and mechanical properties of RECRY were not coincident with CL^{1st} of the same n, although RECRY crystallized in the presence of cross-links like CL^{1st}. RECRY exhibited slightly larger D_{hk0} values and harder mechanical properties than CL^{1st}. This result indicates that microstructures like entanglements in CL^{1st} are different from those in RECRY. To further consider this indication, crystallization rates of CL^{1st} and RECRY were analyzed at 25 °C after melting at 70 °C for 10 min. The crystallizations of $PCL_nF_2M_3$-CL^{1st} with $n = 33$, 26, and 22 were completed in approximately 6, 40, and 240 min, respectively, and those of $PCL_nF_2M_3$-RECRY with $n = 33$, 26, and 22 were done in approximately 2, 24, and 75 min, respectively. $PCL_{18}F_2M_3$-CL^{1st} did not crystallize within the observation time of 7 h while $PCL_{18}F_2M_3$-RECRY showed crystallization peak which was too small and broad to determine the crystallization time. RECRY samples obviously had higher crystallization rates than CL^{1st} with the same n. It is reasonable to consider that, in CRY^{1st}, chain folding and disentanglement occur during the crystallization before cross-linking. Thus, CRY^{1st} has fewer entanglements than CL^{1st}, which are carried over to the melt at 70 °C and following crystallization at 25 °C to prepare RECRY. The more ordered crystalline structure and slightly harder mechanical properties of RECRY than those of CL^{1st} can be attributed to the fewer entanglements in RECRY than those in CL^{1st}.

Interestingly, as shown in Figures 5 and 6 and Tables 2 and 4, the hard−soft conversion behavior was strongly affected by the molecular weight of PCL_nF_2. The crystalline phase structures and mechanical properties of RECRY tended to approach to those of CL^{1st} with the decrease in n from 33 to 22, indicating that the microstructure of RECRY approaches to that of CL^{1st} with altering n from 33 to 22. As for $PCL_{18}F_2M_3$, the difference in mechanical properties between RECRY and CL^{1st} became larger again, though the E_{RECRY}/E_{CRY} value continued to decrease with decreasing n from 22 to 18. This is obviously due to the absence of crystallinity in CL^{1st} with $n = 18$. In conclusion, the prepolymer molecular weight in this system is very important to control the hard−soft difference and the conversion behavior.

Conclusion

In this study, we prepared a series of hard−soft convertible network polymers using semicrystalline furyl-telechelic prepolymers, PCL_nF_2, with n of 18−74 (M_n of 2450−8800) and a tris-maleimide linker, M_3, and analyzed the effect of prepolymer molecular weight on the difference between hard and soft mechanical properties of the network polymers. The hard−soft conversion behavior via melt/recrystallization procedure was also examined. For $n \geq 22$, the difference of thermal and mechanical properties between hard (CRY^{1st}) and soft (CL^{1st}) samples expanded with the decrease in n due to the slight expansion of the difference in size and order of crystalline domains. In the case of $n = 18$, the hard−soft difference became drastically large owing to the absence of crystalline phase in the soft sample. The hard−soft conversion behavior turned out to be strongly influenced by the molecular weight of the prepolymer. We can widely control and convert the thermal and mechanical properties of the semicrystalline network polymer system by controlling the molecular weight of the prepolymer and temperature.

Acknowledgment. We thank Professor Araki and Professor Ogura at Institute of Industrial Science at the University of Tokyo for supporting DSC and WAXD measurements, respectively.

References and Notes

(1) Lendlein, A.; Kelch, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2034–2057.
(2) Liu, C.; Qin, H.; Mather, P. T. *J. Mater. Chem.* **2007**, *17*, 1543–1558.
(3) Han, S.-S.; Kang, S.-W.; Kim, B.-S.; Im, S. S. *Adv. Funct. Mater.* **2005**, *15*, 367–374.
(4) Han, S.-S.; Im, S. S.; Kim, D. K. *Polymer* **2003**, *44*, 7165–7173.
(5) Kang, H.; Lin, Q.; Armentrout, R. S.; Long, T. E. *Macromolecules* **2002**, *35*, 8738–8744.
(6) Andjelić, S.; Richard, R. E. *Macromolecules* **2001**, *34*, 896–906.
(7) Peacock, A. J. *J. Macromol. Sci., Polym. Rev.* **2001**, *C41*, 285–323.
(8) Chodák, I. *Prog. Polym. Sci.* **1998**, *23*, 1409–1442.
(9) Ishida, K.; Yoshie, N. *Macromolecules* **2008**, *41*, 4753–4757.
(10) Chujo, Y.; Sada, K.; Saegusa, T. *Macromolecules* **1990**, *23*, 2636–2641.
(11) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698–1702.
(12) Gheneim, R.; Perez-Berumen, C.; Gandini, A. *Macromolecules* **2002**, *35*, 7246–7253.
(13) Chen, X.; Wudl, F.; Mal, A. K.; Shen, H.; Nutt, S. R. *Macromolecules* **2003**, *36*, 1802–1807.
(14) Watanabe, M.; Yoshie, N. *Polymer* **2006**, *47*, 4946–4952.
(15) Ishida, K.; Yoshie, N. *Macromol. Biosci.* **2008**, *8*, 916–922.
(16) Nojima, S.; Hashizume, K.; Rohadi, A.; Sasaki, S. *Polymer* **1997**, *38*, 2711–2718.
(17) Alexander, L. E. *X-ray Diffraction Methods in Polymer Science*; Wiley-Interscience: New York, 1969.