Recyclable Shape-Memory Polymer: Poly(lactic acid) Crosslinked By a Thermoreversible Diels–Alder Reaction

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ABSTRACT: An intelligent shape-memory polymer was made through the synthesis of poly(lactic acid) macromonomers with furanyl groups and crosslinking with linkers with maleimidyl groups. The thermoreversible covalent bonds formed by the Diels–Alder reaction between these groups made this polymer recyclable (i.e., environmentally friendly). The structure of the polymer was also studied. A defect of the structure, a dissociated moiety of the thermoreversible bonding, was strongly affected by the reaction conditions and was investigated with UV spectroscopy, which was used to monitor the concentration of the maleimidyl groups. The relation between the flexibility of the linker and the strength and inner stress of the polymer was also evaluated. Reducing the number of defects and relaxing the inner stress were found to increase the strength of the shape-memory polymer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 876–885, 2009

Key words: Diels-Alder polymers; recycling; renewable resources; structure-property relations

INTRODUCTION

An intelligent and environmentally friendly polymer was developed through the use of the reversible Diels–Alder reaction to link poly(lactic acid) (PLA). Intelligent polymers, which can change their shape or color according to the environmental conditions (pH, light, temperature, chemical presence, electric field, etc.), are remarkable materials with potential applications in many fields. A shape-memory polymer is an intelligent polymer, and a durable shape-memory polymer could be useful in medicine, automobiles, and aerospace engineering. The available durable thermoset polymers, however, are not environmentally friendly materials because they do not have the thermoplasticity needed for recycling. We have therefore developed a polymer made with a reversible reaction for crosslinking and have also made it environmentally friendly by using as a base a polymer that can be made from agricultural products.

There are two kinds of thermally activated shape-memory polymers.[1–3] The thermoset type is durable because its network structure of covalent bonds is strong.[4–6] The thermoplastic type, on the other hand, has been commercialized because it is easy to make, but it has a shape memory that is not stable because of the creep phenomenon.[7,8] The network structure of the thermoplastic type is weak because it has physical bonds such as hydrogen bonds rather than chemical bonds. A thermoplastic polymer therefore does not perfectly recover its permanent shape. We studied a network polymer crosslinked with a thermoreversible reaction and found that it has the properties of both thermoset and thermoplastic polymers: stable shape memory and recyclability.

Thermoreversible reactions were reviewed by Engle and Wagner,[9] and Diels–Alder cycloadditive dimerization of cyclopentadiene[10,11] and Diels–Alder cycloaddition between furanyl and maleimidyl groups[12] are well-known thermoreversible reactions. Many researchers have reported polymers made with the Diels–Alder reaction between furanyl and maleimidyl groups.[13–21] Chen and coworkers[13,14] used it to make a self-healing polymer, and Watanabe and Yoshie[15] used it to make a recyclable and biodegradable polymer. Some researchers have reported low reaction ratios for the Diels–Alder reaction. Kuramoto et al.[16] studied the relation between the reaction conditions and ratio, but the maximum ratio that they reported was only 75%. Imai et al.[17] showed that the maximum reaction ratio in their system was 63% and that the relatively low efficiency of the reaction could be attributed to the dilution of functional groups. In an earlier study intended to help us understand the relation between the mechanical properties and structure of reversibly crosslinked polymers, we investigated not only the conditions of the Diels–Alder reaction but also the flexibility of the crosslinker of the polymer and found evidence that the inner stress of the polymer causes structural weakness.[22]

We used as the base polymer for the new intelligent material reported here one of the environmentally friendly polymers that can be made from renewable plant resources and are starting to be used for durable products as well as disposable products.[23] We selected PLA not only because its use can reduce the consumption of petroleum resources and the production of CO_2 emissions in the manufacturing process[24,25] but also because it has a glass-transition temperature (T_g) suitable for shape-memory polymers. The phase-transition temperature in the programming and recovery processes of a shape-memory polymer must be greater than room temperature. The original shape can be easily deformed in the soft phase above the transition temperature, and the deformed shape can be fixed in the hard phase below it.[3] PLA has a T_g around 60°C.

In this study, we first evaluated the shape-memory behavior of two kinds of polymers based on four-arm macromonomers, one reversibly crosslinked by Diels–Alder bonding and the other irreversibly crosslinked by urethane bonding. The temperature dependence of the elastic modulus and crystallinity of these polymers were measured to investigate the shape-memory property, and the thermal properties of the polymers were measured to confirm the recyclability of the reversibly crosslinked polymer. We then studied the structure of the polymer so that we could make a polymer strong enough for practical uses. The influence of the crosslinking density on the strength was evaluated by the number of macromonomer arms being changed from four to six, and the influence of the crosslinking condition on the reaction ratio of Diels–Alder cycloaddition was also investigated. We evaluated defects in a linking moiety of the structure by using UV spectroscopy to monitor the concentration of the maleimidyl groups and also investigated the ways in which flexible crosslinkers affected the polymer's strength by changing the inner stress of the polymer structure. To confirm the influence of the defects in the linking moiety, we synthesized a six-arm macromonomer whose functional groups were crosslinked in a low linking ratio (65%) by irreversible urethane bonding. It was found that the strength of the shape-memory polymer could be increased by the reduction of the number of defects in the linking moiety and the relaxation of the inner stress.

EXPERIMENTAL

Materials

PLA [Lacty 9030, Shimadzu (Corp., Kyoto, Japan); gel permeation chromatography (GPC): number-average molecular weight (M_n) = 104,000, weight-average molecular weight (M_w) = 230,000, T_g = 62.2°C, and melting temperature (T_m) = 166.6°C] was dried overnight at 100°C, and pyridine (Kanto Corp.) (Tokyo, Japan) was dried with KOH overnight. Hexamethylene diisocyanate (HDI; Kanto), pentaerythritol (Kanto), D-sorbitol (Kanto), tris(2-aminoethyl) amine (Avocado Research Chemicals), hexamethylene diamine (Kanto), dodecamethylene (Heysham, UK) diamine (Kanto), lysine triisocyanate (LTI; Kyowa Hakko Kogyo Co., Ltd.) (Tokyo, Japan), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC; Dojindo Corp.), 2-furfuryl alcohol (Kanto), succinic anhydride (Kanto) (Kumamoto, Japan), exo-3,6-epoxy-1,2,3,6-tetrahydroxyphthalic anhydride (Tokyo Kasei Kogyo Co., Ltd.) (Tokyo, Japan), and various solvents were used as received.

Synthesis of four-arm hydroxyl-terminated poly(lactic acid) (4HP) and four-arm furanyl-terminated poly(lactic acid) (4FP)

4HP and 4FP were synthesized as shown in Scheme 1. First, succinic acid monofuran-2-ylmethyl ester (SFE) was synthesized by the refluxing of a chloroform solution [including furfuryl alcohol (1.02 mol), succinic anhydride (1.12 mol), and a catalytic amount of pyridine] for 15 h and then washing with aqueous hydrochloric acid. After separation, the organic layer was mixed with aqueous NaOH, the water layer was separated, and its pH was adjusted to 4 by the addition of hydrochloric acid. The acidified aqueous mixture was then extracted with chloroform, and the resultant organic layer was concentrated *in vacuo* to produce SFE with a yield of 83%.

^{1}H-NMR [CDCl$_3$, δ (ppm)]: 2.68 (m, 4H, —OCOCH$_2$CH$_2$—COOH), 5.09 (s, 2H, furanyl—CH$_2$—O—), 6.36, 6.41 [dd, 2H, J (Hz) = 3.2, 3.2, =HC—CH= of furanyl], 7.42 (s, 1H, —HC=CH—O— of furanyl). ^{13}C-NMR [CDCl$_3$, δ (ppm)]: 28.7, 28.8 (—OCOCH$_2$CH$_2$—COOH), 58.4 (furanyl—CH$_2$—O—), 111 (—HC=CH— of furanyl), 143 (—HC=CH—O— of furanyl), 149 [—HC=C(C)O— of furanyl], 172 (—OCO—CH$_2$CH$_2$—), 178 (—CH$_2$CH$_2$—COOH). Acid value: 4.88 mmol/g (purity: 96.6%).

4HP was then synthesized by an ester exchange reaction between pentaerythrytol (1.41 mol) and PLA (2530 g) at 200°C for 4.5 h. Macromonomer 4HP was purified by reprecipitation with chloroform and methanol. Its molecular weight was measured by GPC with polystyrene as the standard, and its composition was calculated from ^{1}H-NMR data by a comparison of the integrals of the peaks related to the composition ratios of hydroxyls (δ = 3.57 and 4.36) and repeating units of lactic acid (δ = 5.16) and pentaerythritol (δ = 3.57 and 4.17).

GPC: M_n = 4200, M_w/M_n = 1.6. NMR: molecular weight (MW) = 3200. ^{1}H-NMR [CDCl$_3$, δ (ppm)]: 1.60 (121H, m, CH_3 of PLA), 3.57 (1.77H, br,
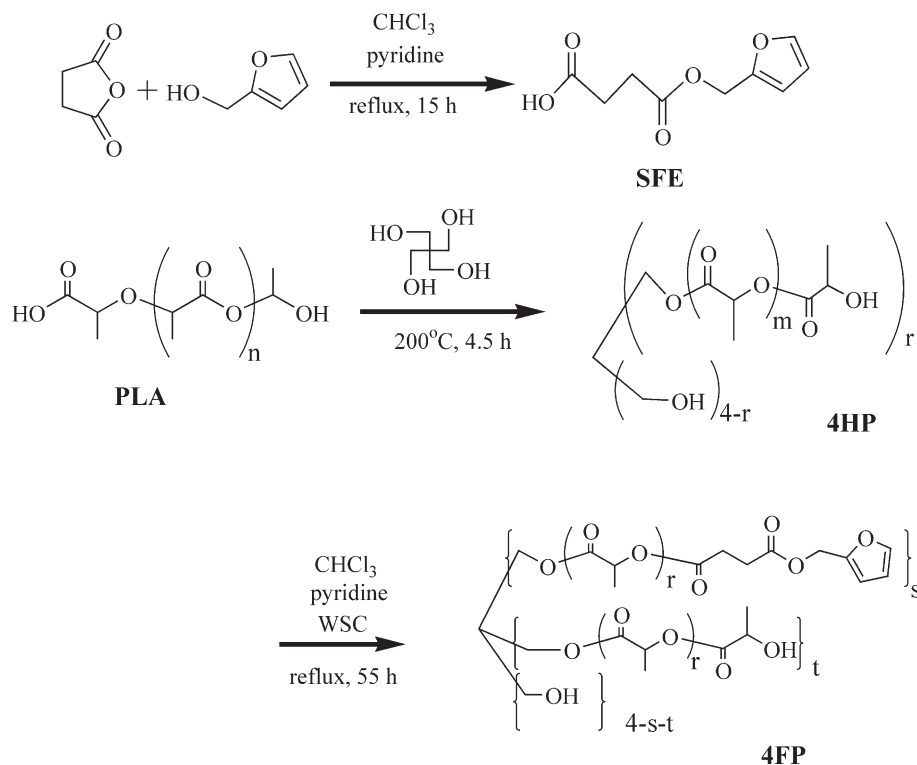
Scheme 1 Synthesis of the four-arm macromonomers.

—CCH₂—OH), 4.17 (6.23H, br, —CCH₂—O—PLA), 4.36 [3.11H, q, PLA—CH(CH₃)OH], 5.16 (39.4H, m, CH of PLA). Acid value: 0.0478 mmol/g. ¹³C-NMR [CDCl₃, δ (ppm)]: 16.6 (CH₃ of PLA), 20.4 (—CCH₂—O—PLA), 66.6 (—CCH₂—O—PLA), 68.9 (CH of PLA), 170 (COO of PLA). Differential scanning calorimetry (DSC): $T_g = 39°C$, $T_m = 131°C$.

4FP was then synthesized through the refluxing of a chloroform solution including SFE (0.336 mol), 4HP (0.0451 mol), WSC (0.326 mol), and pyridine (0.320 mol) for 55 h and washing with water. The polymeric product was reprecipitated by the addition of methanol and purified by silica gel flash chromatography (chloroform/ethyl acetate = 1 : 3). The filtrate was evaporated *in vacuo* to give the product 4FP. The degree of furanyl group substitution was calculated from NMR data to be 3.1 equiv/mol, the molecular weight was measured by GPC with polystyrene as the standard, and the composition was calculated from ¹H-NMR data by a comparison of the integrals of the peaks related to the composition ratios of furanyl (δ = 7.42), hydroxyls (δ = 3.57 and 4.35), and repeating units of lactic acid (δ = 5.04–5.24) and pentaerythritol (δ = 3.74 and 4.16).

GPC: $M_n = 6900$, $M_w/M_n = 1.2$. NMR: MW = 4400. ¹H-NMR [CDCl₃, δ (ppm)]: 1.62 (191H, m, CH₃ of PLA), 2.71 (12.4H, m, —OCO—CH₂CH₂—COO—), 3.74 (0.278H, s, —CCH₂—OH), 4.16 (7.72H, br, —CCH₂—O—), 4.35 [0.91H, q, PLA—CH(CH₃)OH],

5.04–5.24 (52.1H, m, furanyl—CH₂—O—, CH of PLA), 6.36, 6.40 [6.18H, dd, J (Hz) = 1.2, 1.6, =HC—CH= of furanyl], 7.42 (3.09H, s, —HC=CH—O— of furanyl). Acid value: 0.0193 mmol/g. DSC: $T_g = 36°C$, $T_m = 128°C$.

Synthesis of six-arm hydroxyl-terminated poly(lactic acid) (6HP) and six-arm furanyl-terminated poly(lactic acid) (6FP)

As shown in Scheme 2, 6HP was synthesized by an ester exchange reaction between D-sorbitol (0.974 mol) and PLA (1990 g) at 230°C for 15 h. Polymer 6HP was purified by reprecipitation with chloroform and methanol. Its molecular weight was measured by GPC with polystyrene as the standard, and its composition was calculated from ¹H-NMR data by a comparison of the integrals of peaks related to the composition ratios of hydroxyls (δ = 4.35) and repeating units of lactic acid (δ = 5.18) and sorbitol (δ = 4.10–4.50).

GPC: $M_n = 4700$, $M_w/M_n = 1.42$. NMR: MW = 6500). ¹H-NMR [CDCl₃; δ (ppm)]: 1.56 (m, 262 H, CH₃ of PLA), 4.10–4.50 (br, 4 H, —CCH₂—O—PLA), 4.35 [q, 6 H, PLA—CH(CH3)OH], 5.18 (m, 85.5 H, CH of PLA, —CCH—O—PLA). Acid value: 0.07392 mmol/g. DSC: $T_g = 48.8°C$, $T_m = 132°C$.

6FP was then synthesized by the refluxing of a chloroform solution including SFE (0.374 mol), 6HP (0.0204 mol), WSC (0.376 mol), and pyridine (0.388
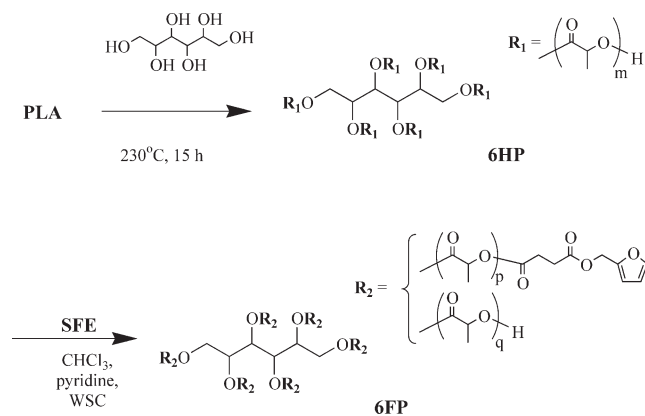
Scheme 2 Synthesis of the six-arm macromonomers.

mol) for 43 h and washing with water. The polymeric product was reprecipitated by the addition of methanol and purified by silica gel flash chromatography (chloroform/ethyl acetate = 1 : 3). The filtrate was evaporated *in vacuo* to give the product 6FP. The degree of furanyl group substitution was calculated from NMR data to be 5.78 equiv/mol, the molecular weight was measured by GPC with polystyrene as the standard, and the composition was calculated from ^{1}H-NMR data by a comparison of the integrals of the peaks related to the composition ratios of furanyl (δ = 7.42), hydroxyls (δ = 4.35), and repeating units of lactic acid (δ = 5.00–5.40) and sorbitol (δ = 4.10–4.50).

GPC: M_n = 6940, M_w/M_n = 1.27. NMR: MW = 6774. ^{1}H-NMR [CDCl$_3$;δ(ppm)]: 1.54 (m, 275 H, CH_3 of PLA), 2.60–2.80 (m, 23.1 H, —OCO— CH_2CH_2—COO—), 4.10–4.50 (br, 4 H, —CCH_2— O—PLA), 4.35 [q, 0.22 H, PLA—CH(CH$_3$)OH], 5.00–5.40 (m, 93.6 H, furanyl—CH_2—O—, CH of PLA), 6.36, 6.40 [dd, 11.6 H, J (Hz) = 1.6, =HC—CH= of furanyl], 7.42 (s, 5.78 H, —HC=CH—O— of furanyl). Acid value: 0.01204 mmol/g. DSC: T_g = 42.5°C, T_m = 124°C.

Synthesis of the linkers

The linkers tris(2-maleimidoethyl) amine (TMEA), hexamethylene dimaleimide (HDM), and dodecamethylene dimaleimide (DDM) were synthesized as shown in Scheme 3 and described in detail elsewhere.[13,26]

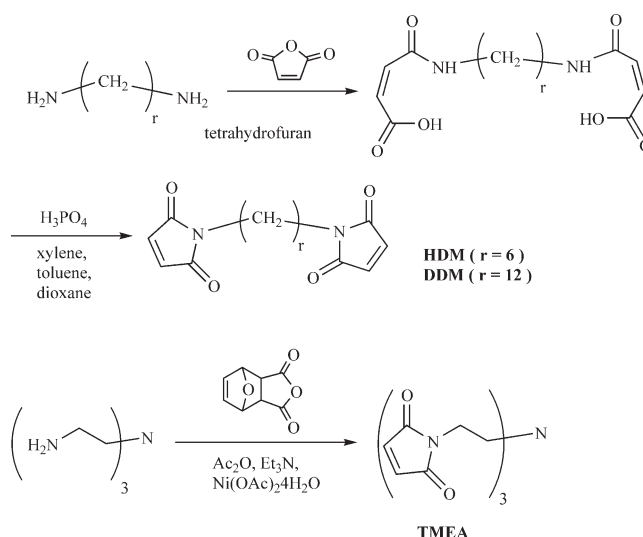### Polymerization of the macromonomers and preparation of the test plates

Test plates were made through the mixing of the synthesized furanyl-terminated macromonomers with linkers (at molar ratios giving a 1 : 1 ratio of the furanyl moiety in the macromolecule to the maleimidyl moiety in the linker) and polymerization in molds under various conditions. As shown in the upper part of Scheme 4, the crosslinked polymer

(4FP–TMEA) was formed by the mixing of the macromonomer 4FP with TMEA at 160°C and crosslinking in a mold at 100°C for 1 h. The T_g of 4FP–TMEA was measured by DSC to be 65°C, higher than the T_g of the macromonomer (36°C), and the crosslinking made 4FP–TMEA insoluble in CHCl$_3$. The polymers 6FP–TMEA, 6FP–HDM, and 6FP–DDM were formed by the mixing of the macromonomer 6FP with TMEA, HDM, or DDM at 160°C and crosslinking of the monomers in molds under conditions I and II (listed in Table I).

Comparison test plates of the polymers crosslinked with HDI or LTI were also formed by the mixing of 4FP with HDI and 6FP with LTI at 170°C and crosslinking of the macromonomers in molds at 170°C for 1 h (condition III); this yielded the polymers 4FP–HDI and 6FP–LTI.

Measurements

GPC was carried out on a Shimadzu 10A-VP equipped with a GPC-8025C and two GPC-80MC columns. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) (Shimadzu, Kyoto, Japan) spectra were obtained on a Bruker Avance 400 spectrometer. DSC was carried out on a DSC 6200 (SII Nanotechnology, Inc.) (Buruker, Faellanden, Switzerland). Samples were repeatedly heated from −20 to 180°C at 10°C/min and cooled to −20°C at 50°C/min. Dynamic mechanical analysis (DMA) of samples (40 × 5 × 1 mm^3) was carried out at a frequency of 10 Hz on a DMS 6100 (SII Nanotechnology) (Chiba, Japan) at a heating rate of 2°C/min under an N$_2$ atmosphere. The mechanical properties of 20 × 35 × 1.6 mm^3 polymer samples at room temperature were evaluated with an Instron 5567 universal testing machine (Instron, Norwood, MA) at a crosshead speed of

Scheme 3 Synthesis of the linkers.
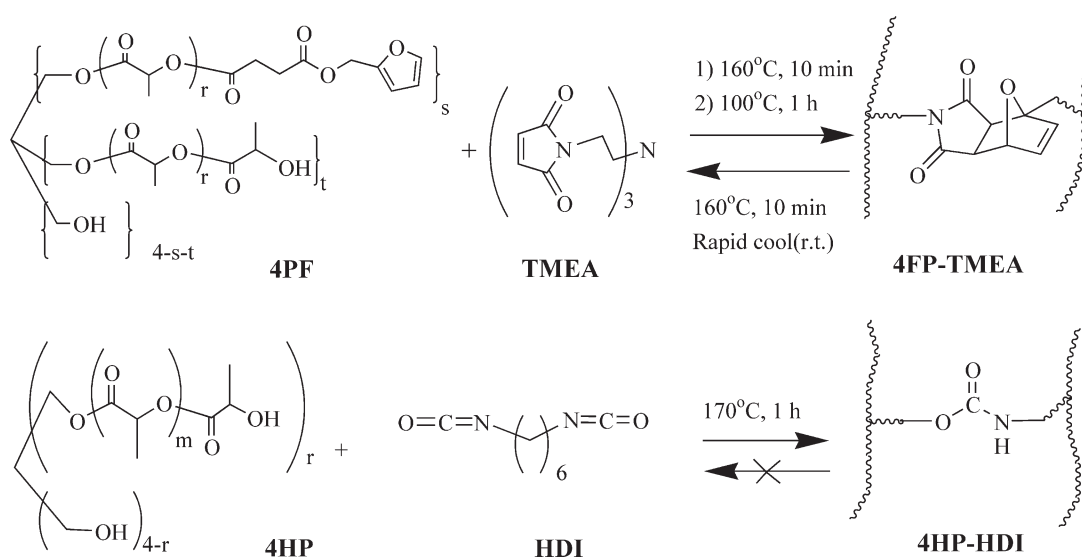
Scheme 4 Polymerization of the macromonomers (r.t. = room temperature).

1 mm/min. X-ray diffraction (XRD) spectra were measured with a Shimadzu XRD-6100 (Shimadzu, Kyoto, Japan), the extent of the reaction between furanyl and maleimidyl groups was determined by the calculation of the reaction ratio from data measured with a Hitachi U-2010 UV spectrophotometer (Hitachi, Tokyo, Japan), and the urethane reaction was confirmed with a Spectrum 1000 IR spectrophotometer (PerkinElmer, Inc.) (Waltham, MA).

RESULTS AND DISCUSSION

Recyclable shape-memory polymer

Shape-memory behavior and recyclability

The reversibly crosslinked polymer 4FP–TMEA was evaluated as a shape-memory polymer, as shown in Figure 1. When the polymer was heated from 60 to 100°C, the I shape in which the polymer had been molded was easily transformed into a temporary C shape that could be fixed by the cooling of the poly-

mer to room temperature. The polymer returned to its permanent shape, however, when its temperature was increased to 60°C for only 10 s. These programming and recovery processes were repeatable. Heating the 4FP–TMEA sample to not less than 160°C caused link disconnection and erased the memory of the permanent shape. A new memory of a permanent sheet shape was produced by the remolding of the sample, and this recycled polymer behaved as a shape-memory polymer again. Although the polymer in which the four-arm PLA macromonomers were irreversibly crosslinked by urethane bonds (4HP–HDI) also showed shape-memory behavior, it was not recyclable because it could not be remolded.

Temperature dependence of the elastic modulus

DMA thermograms revealed that crystallization increased the elastic modulus of PLA above T_g ($T_g = 62.2°C$; Fig. 2). Amorphous and crystallized PLAs were measured at temperatures between 20°C and

TABLE I
Mechanical Properties of the Crosslinked Polymers

Sample	Reaction condition[a]	Reaction ratio (%)[b]	Flexural strength (MPa)	Flexural modulus (GPa)	T_g (°C)
4FP–TMEA	I	70	41	2.7	65
6FP–DDM	I	66	39	3.2	51
6FP–HDM	I	66	19	2.3	50
6FP–TMEA	I	65	40	3.8	59
6FP–DDM	II	78	102	3.5	54
6FP–HDM	II	83	62	3.1	61
6FP–TMEA	II	77	62	3.9	64
6HP–LTI	III	100	143	3.6	61
6HP–LTI(65)	III	65	119	3.9	60

[a] Condition I, 100°C for 1 h; condition II, 100°C for 1 h and then 75°C for 20 h; and condition III, 170°C for 1 h.
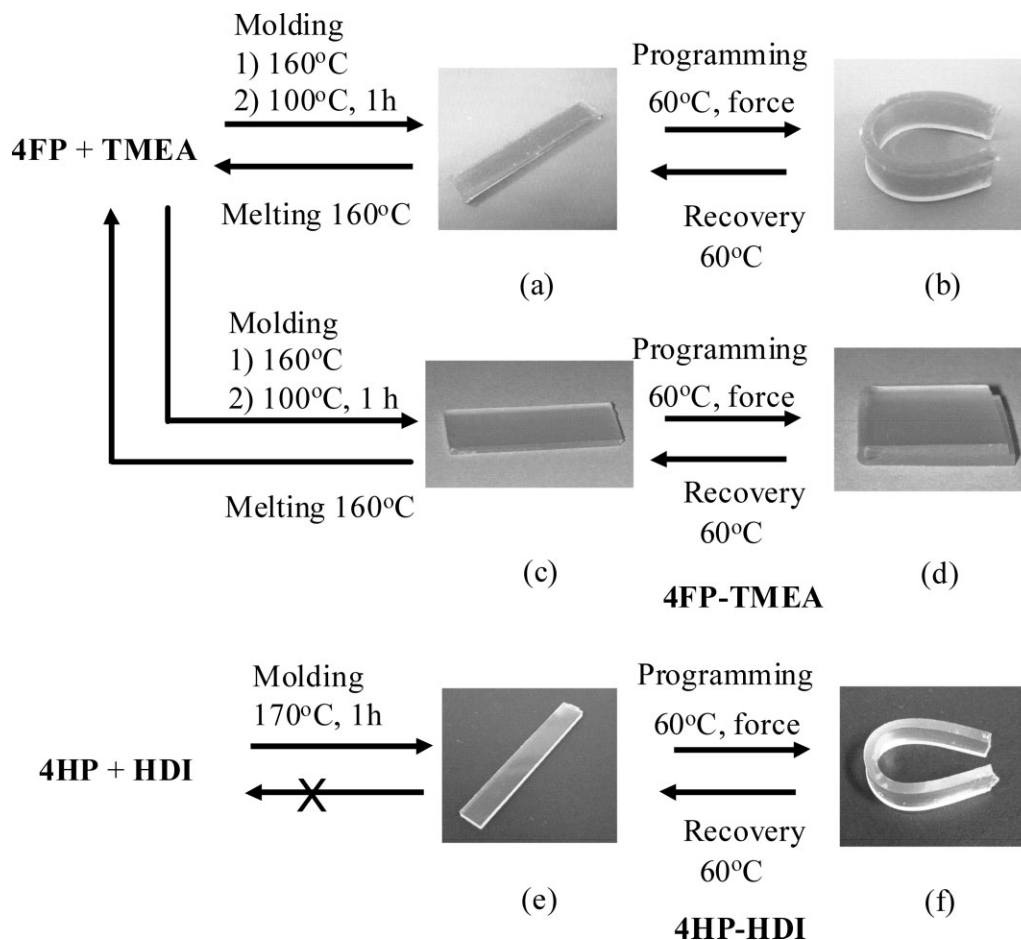[b] The reaction ratio was determined by the use of UV spectroscopy to monitor the maleimidyl group.

Figure 1 Recyclable shape memory of thermoreversibly crosslinked PLAs. (a,e) I-shaped test pieces of 4FP–TMEA and 4HP–HDI were transformed into (b,f) temporary C shapes, and (a,e) they recovered to their permanent shapes without any creep phenomenon. (c) The memory of only 4FP–TMEA was erased, and a new shape memory was produced by remolding. (c,d) This recycled polymer also exhibited shape-memory behavior.
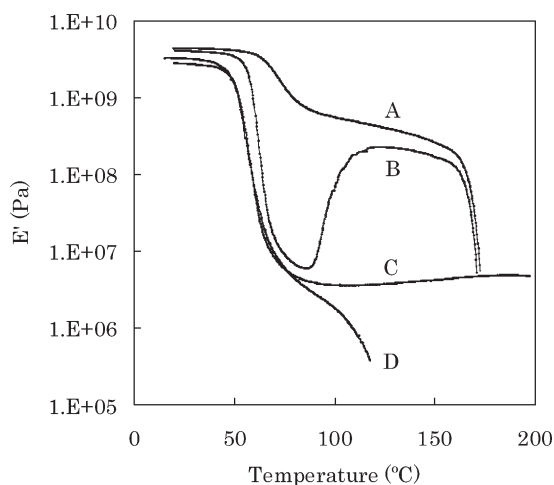

Figure 2 DMA thermograms of the crosslinked polymers (measured at 10 Hz and a heating rate of 2°C/min): (A) annealed PLA (100°C, 1 h), (B) amorphous PLA, (C) 4HP–HDI, and (D) 4FP–TMEA. The clasic modului (E) were measured at 10 Hz and a heating rate of 2°C/min.

T_m (166.6°C). The elastic modulus of amorphous PLA first showed a large drop at temperatures above T_g but then increased again at temperatures above 90°C. The elastic modulus of PLA that had been annealed at 100°C for 1 h did not show a large drop because that PLA was crystallized. This crystallization would make the programming process (Fig. 1) difficult because the crystallized PLA remains hard above the transition temperature.

Figure 2 also shows DMA thermograms of reversibly and irreversibly crosslinked PLAs (4FP–TMEA and 4HP–HDI). Like amorphous PLA, these polymers showed drops in the elastic modulus just above T_g. For these polymers, however, the elastic modulus remained low at temperatures above 90°C. We think that crosslinking prevented the PLA moieties of these polymers from crystallizing, maintained the large difference between the elastic moduli below and above T_g, and made the programming process easy.
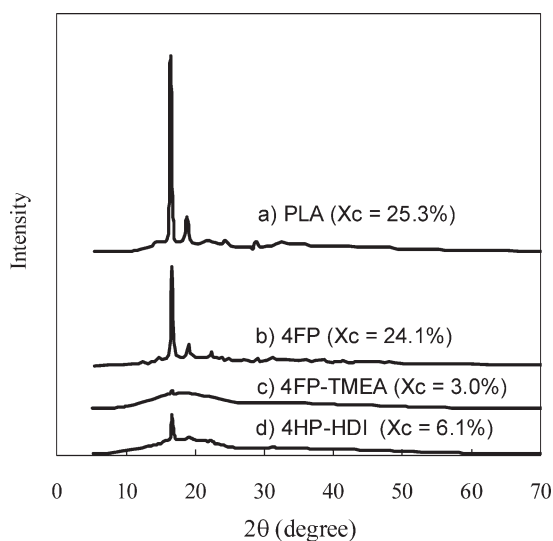
Figure 3 XRD spectra of PLA, a macromonomer, and crosslinked polymers. The crystallinity (X_c) was defined by the ratio of the crystalline peak areas to the noncrystalline harrow area observed between 5 and 70°. The crystallinities of the macromonomer (4FP) were reduced by crosslinking. PLA, 4HP, and 4FP–TMEA were annealed or crosslinked at 100°C for 1 h. The polymer 4HP–HDI was crosslinked at 170°C for 1 h.

Crystallinity of the crosslinked polymer

We can see from the XRD spectra in Figure 3 that crosslinking decreased the crystallinity of PLA. Sharp peaks at 16.6° were observed in the spectra of PLA and 4FP, and the crystallinities of these PLAs were estimated to be 25.3 and 24.1%, respectively. The spectra of the crosslinked PLAs, on the other hand, had smaller peaks, and the crystallinities of 4FP–TMEA and 4HP–HDI were estimated to be 3.0 and 6.1%, respectively. We think that the crosslinking in these structures restrains molecular motion and hinders the generation of lamellar and crystalline domains. This would be the reason for the low elastic moduli of 4FP–TMEA and 4HP–HDI above T_g.

Recyclability

The DSC thermograms of two crosslinked PLAs (4HP, 4HP–HDI, and 4FP–TMEA) are shown in Figure 4. Like ordinary PLA, the macromonomer 4HP exhibited exothermic and endothermic peaks that could be assigned to the formation and disappearance of a crystalline domain. Because neither peak was observed in the crosslinked polymer 4HP–HDI, crosslinking seems to hinder the generation of the crystalline domain, as described in the previous section. The thermogram of 4FP–TMEA showed evidence of a reversible reaction in the PLA-based polymer. Exothermic and endothermic peaks were observed in the thermograms of the reversibly cross-

linked polymer 4FP–TMEA. As shown in the previous section, the crystallinity of this polymer (3.0%) was lower than that of 4HP–HDI (6.1%). These peaks were therefore assigned to association (at 100°C) and dissociation (at 160°C) of the furanyl and maleimidyl groups participating in the reversible Diels–Alder reaction. Both peaks were observed in repetitive measurements carried out during heating (10°C/min) following rapid cooling (−50°C/min). In addition, the areas of the peaks stayed the same during the repetitive measurements. These results show that polymer recycling is possible because the Diels–Alder reaction in this system can be reversed repeatedly.

Structure and strength

Crosslinking density of the shape-memory polymer

Comparing the mechanical strength of a polymer made from a four-arm macromonomer (MW = 4400, 3.1 equiv of furanyl/mol) with that of a polymer made from a six-arm macromonomer (MW = 6800, 5.8 equiv of furanyl/mol) (Table I), we found the strength of 6FP–TMEA (40 MPa) to be almost the same as that of 4FP–TMEA (41 MPa) when both polymers were made under condition I. Although we expected the greater number of arms to increase the crosslinking density of the polymer structure
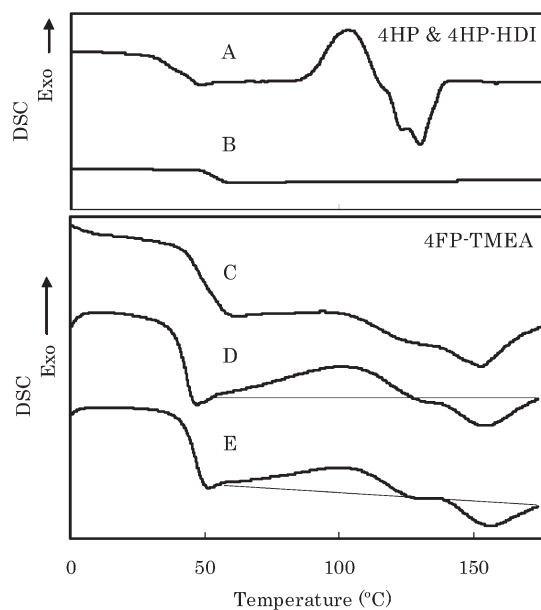

Figure 4 DSC thermograms of crosslinked PLA samples repeatedly heated from −20 to 180°C (10°C/min) and quenched to −20°C (50°C/min): (A) 4HP, (B) 4HP–HDI, (C) 4FP–TMEA, (D) dissociated 4FP–TMEA, and (E) dissociated 4FP–TMEA after five heating cycles. The exothermic peaks at 100°C and the endothermic peaks at 160°C were assigned to furan–maleimide association and dissociation, respectively.

and enhance its strength, the arm number did not affect the strength in this thermoreversible system. The strength of 6HP–LTI (made under condition III), in contrast, was much greater: 143 MPa. The monomers in 6HP–LTI are irreversibly crosslinked by urethane bonds between isocyanate and hydroxyl functional groups, and this bonding is a very fast reaction. Unreacted isocyanate functional groups (2265 cm^{-1}) were not detected by IR spectroscopy after crosslinking under condition III. The monomers in 4FP–TMEA, on the other hand, are crosslinked by a slow reversible Diels–Alder reaction between furanyl and maleimidyl groups, and the maximum reaction ratio of this reaction is not high.[16,17] We therefore think that the network structure of the thermoreversible polymer did not grow enough in this system and the increase in the arm number from four to six might be too small to cover defects in the linking points.

Reaction ratio of reversible cycloaddition

The UV spectra of 0.10-mm-thick 6FP–TMEA on a quartz plate are shown in Figure 5. The absorption at 294 nm was assigned to the double bond of the maleimidyl moiety, and the changes in it were monitored during the crosslinking reaction. It decreased as the maleimidyl group was consumed by the Diels–Alder reaction. Dissociated 6FP–TMEA, which was produced by rapid cooling after heating ($>160°C$), showed a strong absorbance that we assigned to the released and unassociated maleimidyl moiety. The strength of the absorbance returned to the original level before crosslinking. This indicates that the thermoreversible crosslinking worked well in this polymer based on PLA, just as in other polymers.[13–21]

The maximum reaction ratio, however, was estimated to be only 65%, which is too low to generate a strong network polymer. This reaction ratio was calculated from the absorption of unreacted maleimidyl groups with the molar absorptivity in a solid polymer. The absorptivity in a solid polymer was estimated with a partially crosslinked polymer because this polymer was soluble in $CHCl_3$ and the maleimidyl content necessary for the estimation was easily confirmed. Thermoreversible crosslinking in the polymer was observed as an equivalent reaction between 30 and 65%. This means that one-third of the maleimidyl groups do not connect with furanyl groups. The crosslinking point needs three arms, and TMEA, which loses one of its three maleimidyl groups, cannot serve as a crosslinking point. The unreacted maleimidyl group generated a lot of defects in the network structure of the reversibly linked polymer and resulted in poor strength.
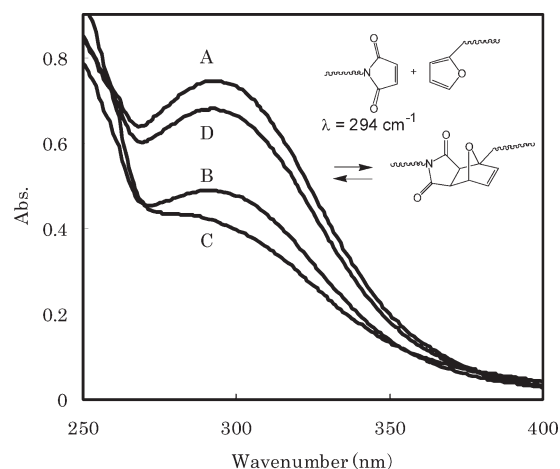

Figure 5 Change in the maleimidyl concentration in 6FP–TMEA during a thermal cycle: (A) initial dissociated 6FP–TMEA, (B) 6FP–TMEA crosslinked for 10 min, (C) 6FP–TMEA crosslinked for 60 min, and (D) thermally dissociated 6FP–TMEA. The maleimidyl absorbance ($λ = 294$ nm) after crosslinking at $100°C$ was measured with a UV spectrometer.

Reaction conditions of reversible cycloaddition

The reaction ratios and flexural strength of 6FP polymers produced under two reaction conditions are listed in Table I. The flexural strengths of the reversibly crosslinked polymers 6FP–DDM, 6FP–HDM, and 6FP–TMEA produced under condition I ($100°C$ for 1 h) were lower than that of the base PLA (120 MPa). These insufficient flexural strengths were likely caused by defects due to low ratios of the cycloaddition reactions. We therefore tried to identify conditions resulting in higher reaction ratios. Increasing the reaction time at $100°C$ from 1 to 20 h did not increase the ratios of the Diels–Alder reactions (data not shown). This means that the ratio had already reached the maximum limited by chemical equilibrium at $100°C$ of the reaction. The reaction ratio was, however, greatly increased by the lowering of the reaction temperature from 100 to $75°C$ and then the continuation of the reaction for another 20 h (condition II). The strengths of the polymers produced under condition II were also much greater than those of the polymers produced under condition I. The increased reaction ratios are thought to be mainly due to the slower retro-Diels–Alder reaction at $75°C$. The increased reaction ratio increases the strength of the polymers, but reactions at temperatures lower than $75°C$ are not efficient for increasing the reaction ratio and strength because they are close to the T_g of 6FP–TMEA crosslinked under condition II ($64°C$), so they would reduce the molecular motion of the polymer.
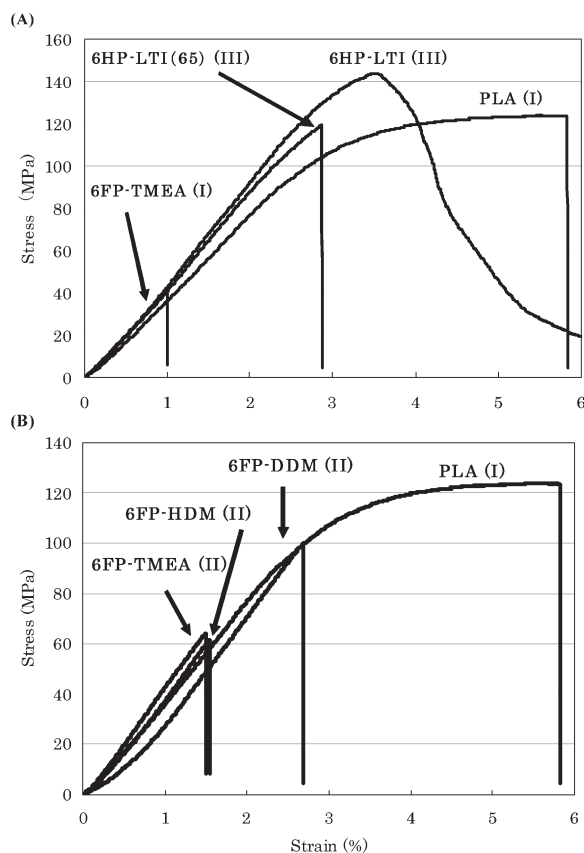
Figure 6 Stress–strain curves of crosslinked PLAs. Crosslinking and annealing conditions are indicated in parentheses.

Flexibility of the linker

We investigated the influence of the type of the maleimidyl linker on the strength of the polymers, and the stress–strain curves of PLA and the reversibly and irreversibly crosslinked polymers 6FP–TMEA and 6HP–LTIs are shown in Figure 6. The imperfect polymer, 6HP–LTI(65), was a crosslinked polymer with 6HP and LTI (with hydroxyl/isocyanate = 1/0.65). No peak at 2256 cm^{-1} assignable to unreacted isocyanate functional groups was detected in the IR spectra of 6HP–LTIs after crosslinking. The defect ratio in the linking moiety of 6HP–LTI(65) was therefore the same as that in the linking moiety of 6FP–TMEA, and 6FP–TMEA was quite a bit weaker than 6HP–LTI and 6HP–LTI(65). Although 6HP–LTI included the urethane functional group, which could form an intermolecular hydrogen bond and confer strength greater than that of PLA, the difference between the strengths of 6HP–LTI and 6HP–LTI(65) was not large. This result suggested that the weakness of 6FP–TMEA was due not only to defects but also to the weakness of the bonding produced by cycloaddition. Polymer 6FP–DDM made under condition II with the longest chain crosslinker (Scheme 3) exhibited high strength (102 MPa), but 6FP–HDM and 6FP–TMEA made with shorter crosslinkers were much weaker than PLA. The reaction ratio of 6FP–TMEA was higher than that of 6FP–DDM. TMEA has three maleimidyl groups, whereas DDM has only two, so 6FP–TMEA should have been stronger than 6FP–DDM. This means that the difference in the strengths of the thermoreversible polymers cannot be explained by the density of crosslinking points.

We think that the reversibly linked polymers have higher inner strains when they are made under conditions in which the reaction ratios are high because their network structures are twisted by the cycloaddition between furanyl and maleimidyl groups, which results in steric hindrance of the linking moiety. Therefore, relaxing the inner strain by the use of DDM with a flexible dodecamethylene segment appeared to be effective in increasing the strength of 6FP–DDM. 6FP–HDM and 6FP–TMEA, however, which had flexible units shorter than DDM, were insufficient to relax the inner strain of the thermoreversible polymers. The reduction in the inner stress of the polymer structure increased the strength of this polymer, and this is necessary for practical uses. Several authors have reported the reaction ratios and reaction conditions of the reversible Diels–Alder reaction,[13,15–17] and the reactions ratios in the polymer were lower than those of the model reactions because the polymers had low concentrations of functional groups. We guess that the low reaction rates in the polymers might have been caused by the steric hindrance of the linking moiety as well as a low density of functional groups.

CONCLUSIONS

Polyfuranyl PLAs and polymaleimidyl linkers were synthesized and crosslinked with each other to form recyclable shape-memory polymers. The stability of the reversible reaction was confirmed by DSC and UV spectroscopy. XRD and DMA revealed that the easy transformation in the shape-memory programming process was caused by the low crystallinity of the PLA moiety, which was in turn due to crosslinking. These polymers were also enhanced in their mechanical strength up to a level sufficient for practical use. Their structures were investigated by the study of the influences of the reaction ratio, crosslinking density, and linker flexibility. Reducing the number of defects by modification of the reaction conditions and relaxation of the inner stress with a flexible crosslinker increased the strength of the reversibly crosslinked polymer. We think this polymer is an intelligent and environmentally friendly new material with potential applications in many fields.

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