Polymer Journal (2013) 45, 955–961
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ORIGINAL ARTICLE

A crystalline supramolecular polymer with self-healing capability at room temperature

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The healing capability of supramolecular polymers consisting of crystalline poly(ethylene adipate) that has been end-functionalized with quadruple hydrogen-bonding ureidopyrimidinone (PEA-UPy) was studied. PEA-Toly-UPy and PEA-Hex-UPy, in which PEA and UPy are connected via tolylene and hexamethylene units, were synthesized. When these PEA-UPy polymers were torn, the degree of crystallinity at the torn surfaces decreased approximately by the amount of energy that was dissipated in the tearing process. Although the crystallinity was quickly recovered in PEA-Hex-UPy, the reduced crystallinity was maintained for a prolonged period in PEA-Toly-UPy. The dynamic nature of the hydrogen bonds gave PEA-Hex-UPy a healing capability but only at temperatures higher than T_m. Conversely, longer period of reduced crystallinity at the torn surfaces of PEA-Toly-UPy enabled self-healing at room temperature.
Polymer Journal (2013) **45,** 955–961; doi:10.1038/pj.2012.230; published online 23 January 2013

Keywords: crystallization; self-healing polymer; supramolecular polymer

INTRODUCTION

Healing materials, which are capable of repairing cracks in themselves either automatically or upon heat-, photo- or chemical activation, have attracted much interest in recent years.[1] Healing materials increase the lifetime and safeness of the products that contain them, because these materials can maintain their original mechanical properties for a longer period of time than non-healing materials. The healing capability of polymers has been achieved using various methods.[2–4] One of the most promising methods is the introduction of dynamic bonds, such as reversible covalent bonds[5–10] and supramolecular self-assemblies[11–14] into the polymers. These materials are repaired by the reformation of the dynamic bonds between crack surfaces. Therefore, molecular mobility, which allows this bond reformation, is critical for the healing process. In previous papers, healing at room temperature (self-healing) was mostly realized in gels and soft elastic polymers with good molecular mobilities.[8,9,11,12] Healing in stiffer polymers was usually achieved by applying thermal stimuli to promote melting of the crystalline phase, the transition from a glassy to a rubbery state and/or further cleavage of the dynamic bonds near the crack surfaces.[5–7,10,13] Recently, Chen *et al.*[14] proposed a multiphase design for self-healing elastomers with a high modulus and toughness.

In this report, we introduce a new approach to preparing a crystalline polymer with healing capability at room temperature: that is, a self-healing polymer that keeps its bulk crystallinity throughout the healing process. This approach relies on crystallization control. When a crystalline polymer is mechanically broken, the degree of crystallinity at the crack surface is approximately decreased by the dissipated energy amount, which results in a higher molecular mobility near the crack surfaces. Although the degree of crystallinity at the crack surface is recovered over time as a result of recrystallization, a healing mechanism may work in the supercooled liquid state if the crystallization is sufficiently slow.

A supramolecular interaction based on ureidopyrimidinone (UPy) units was used in some healing polymers.[15–18] Owing to the simplicity of UPy synthesis and the supramolecular formation of UPy with a high degree of polymerization, UPy-based materials are commercially available under the trade name SupraB.[17,18] Poly(ethylene adipate) (PEA) is a semicrystalline polyester with a melting point at $\approx 50\,^{\circ}C$. To achieve our proposed self-healing mechanism of crystallization control, a supramolecular polymer made from UPy-telechelic PEA (PEA-UPy) was chosen as the healing crystalline polymer. We attempted to slow down the crystallization of this polymer by inserting a bulky tolylene unit between UPy and PEA (PEA-Toly-UPy, Figure 1). This polymer is a slow-crystallizing polymer with a repeatable healing capability at room temperature.

EXPERIMENTAL PROCEDURES

Materials

Hexamethylene diisocyanate, 2-amino-4-hydroxy-6-methylpyrimidine, and dibutyltin dilaurate were purchased from Tokyo Chemical Industry Co Ltd. (Tokyo, Japan). Tolylene 2,4-diisocyanate-terminated poly(ethylene adipate) (PEA-Toly) was purchased from Sigma-Aldrich (St Louis, MO, USA). Adipic acid and ethylene glycol were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Chloroform and methanol were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Anhydrous chloroform was purchased from

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Received 28 August 2012; revised 14 November 2012; accepted 15 November 2012; published online 23 January 2013

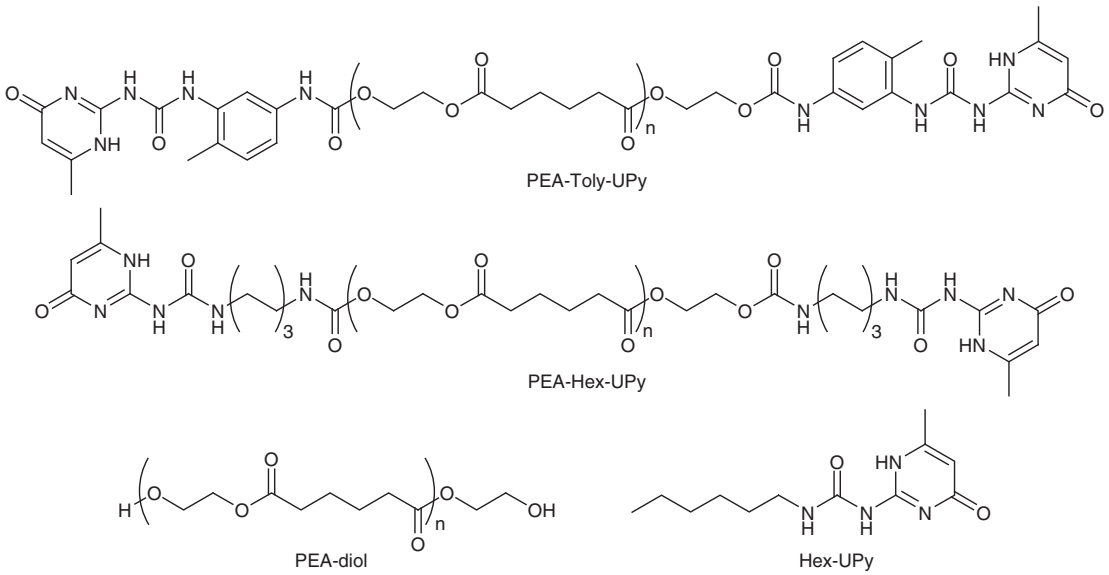

Figure 1 Chemical structures of the telechelic polymer, PEA-UPy, and of the supramolecular interaction inhibitor, Hex-UPy.

Kanto Chemical Co. (Tokyo, Japan). All reagents and solvents were used as received. *N*-Hexyl-*N*-(1,4-dihydro-4-oxo-6-methyl-2-pyrimidinyl)-urea (Hex-UPy)[19] and 2-(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H] pyrimidinone[16] were synthesized as previously reported.

Synthesis of UPy-tolylene-telechelic poly(ethylene adipate) [PEA-Toly-UPy]

Under an N_2 atmosphere, PEA-Toly (6.182 g) and 2-amino-4-hydroxy-6-methylpyrimidine (1.720 g per excess) were dissolved in 60 ml of dehydrated chloroform. The reaction mixture was stirred for 22 h under reflux and then cooled to room temperature. A volume of 30 ml of *N*,*N*-dimethylformamide was added to the mixture, and the chloroform was removed by evaporation. The product was filtered, precipitated with excess water at room temperature and dried under vacuum at 80 °C to obtain PEA-Toly-UPy. Yield: 5.830 g. ATR-IR (cm^{-1}): 3339, 2955, 1731, 1620, 1600, 1445, 1384, 1279, 1137, and 822. ^{1}H NMR [$CDCl_3$] (δ/p.p.m.): 1.67 (br, CH_2), 2.22 (s, CH_3), 2.28 (s, CH_3), 2.36 (br, CH_2), 4.2–4.33 (m, CH_2), 5.83 (s, CH), 6.71 (br, NH), 7.13–8.00 (m, aromatic, overlapping $CHCl_3$ peaks), 11.79 (br, CH), 12.36 (br, NH), and 12.99 (br, NH). ^{13}C NMR (δ/p.p.m.): 17.16, 18.94, 23.91, 33.43, 62.41, 62.70, 106.90, 117.01, 126.45, 131.06, 135.09, 136.47, 148.68, 151.85, 153.09, 154.58, 172.86, and 173.01.

Synthesis of poly(ethylene adipate)diol [PEA-diol]

PEA-diol was synthesized using two-step polycondensation as follows. A mixture of adipic acid and ethylene glycol, with the molar ratio of adipic acid to ethylene glycol = 1:1.1, was melted and stirred at 170 °C for 2 h with exclusion of water. The reaction mixture was then stirred at 170 °C under a reduced pressure (<2 mm Hg) for 4 h. After cooling to room temperature, the product was dissolved in chloroform, precipitated with methanol at 0 °C and dried under vacuum. GPC: $M_n^{GPC} = 2.0 \times 10^3$ and $M_w/M_n = 2.3$. ^{1}H NMR [$CDCl_3$] (δ/p.p.m.): 1.67 (br, CH_2), 2.37 (br, CH_2), 3.83 (t, CH_2), 4.22 (t, CH_2), and 4.27 (br, CH_2). $M_n^{NMR} = 4.5 \times 10^3$.

Synthesis of UPy-hexamethylene-telechelic poly(ethylene adipate) [PEA-Hex-UPy]

The PEA-Hex-UPy synthesis was based on the procedure for UPy-hexamethylene-telechelic polymers used in a previous paper.[16] Under an N_2 atmosphere, PEA-diol (1.625 g) and 2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (595 mg per excess) were dissolved in 15 ml of dehydrated chloroform. The reaction mixture was stirred for 2 days under reflux and then cooled to room temperature. The product was filtered, precipitated with excess methanol at 0 °C and dried under vacuum at room temperature to obtain PEA-Hex-UPy. Yield: 792 mg. ATR-IR (cm^{-1}): 3391, 2953, 1732, 1663, 1586, 1385, 1279, 1253, and 1138. ^{1}H NMR [$CDCl_3$] (δ/p.p.m.): 1.36 (m, CH_2), 1.50 (m, CH_2), 1.68 (br, CH_2), 2.24 (s, CH_3), 2.37 (br, CH_2), 3.15-3.25 (m, CH_2), 4.25 (m, CH_2), 5.12 (br, NH), 5.84 (s, CH), 10.14 (br, CH), 11.85(br, NH), and 13.12 (br, NH). $M_n^{NMR} = 5.1 \times 10^3$. ^{13}C NMR ($\delta$/p.p.m.): 18.94, 24.19, 25.07, 26.15, 29.33, 29.67, 33.44, 36.22, 39.68, 40.82, 62.08, 106.60, 148.35, 154.64, 156.06, 156.48, and 172.94.

Analytical procedures

^{1}H NMR spectroscopy was performed on a JNM-EC S400 NMR system (JEOL, Tokyo, Japan). Gel permeation chromatography (GPC) was conducted using a HLC-8220 GPC system (Tosoh, Tokyo, Japan) equipped with TSK-Gel GMH_{HR}-N columns (40 °C, 1 mg ml^{-1}). DMF containing 0.01 mol l^{-1} of LiCl or $CHCl_3$ was used as an eluent. Polystyrene standards with low polydispersity were used to obtain a calibration curve. Viscosity measurements were conducted using an viscometer SV-1A (A&D, Tokyo, Japan). Chloroform solutions of PEA-Toly-UPy (40 mg ml^{-1}) and of a mixture of PEA-Toly-UPy (40 mg ml^{-1}) and Hex-UPy (2.9 mg ml^{-1}, molar ratio of UPy in PEA-Toly-UPy to that in Hex-UPy = 1:1) were analyzed at 28.0 and 26.5 °C, respectively. The results from at least three samples were averaged. Dynamic mechanical spectroscopy was conducted with a AR2000ex (TA Instrument, New Castle, DE, USA) at a frequency of 1 Hz and a heating rate of 5 °C min^{-1}. Samples 10 mm × 10 mm × 0.36 mm in size were measured. Differential scanning calorimetry (DSC) was conducted with a Pyris 1 (Perkin-Elmer, Waltham, MA, USA) at a heating rate of 10 °C min^{-1} under a N_2 atmosphere. The melting temperature, T_m, and heat of fusion, ΔH_f, were taken to be the location of the peak maximum and the area under the melting endotherm, respectively. The crystallinity of PEA-UPy polymers was calculated by dividing the ΔH_f of the sample with the hypothetical ΔH_f of PEA with 100% crystallinity. The mechanical properties of film samples were evaluated using a tensile testing machine, EZ test (Shimadzu, Kyoto, Japan), with a cross-head speed of 50 mm min^{-1} at room temperature. Rectangular sample specimens (5–5.5 mm wide, 7.0 mm long and 1.65–1.81 mm thick) were used. Values of the Young modulus, stress at yield, and elongation at break from at least three specimens were averaged. Attenuated total reflection infrared (ATR-IR) spectroscopy was performed using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific, Walthem, MA, USA) equipped with a Smart iTR accessory

having a ZnSe crystal. The IR spectra were recorded over the spectral range 650–4000 cm^{-1} with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Characterization of supramolecular PEA-UPy polymers

PEA-Toly-UPy was obtained from the condensation of tolylene-2,4-diisocyanate-terminated PEA with 2-amino-4-hydroxy-6-methylpyrimidine. The terminal modification was confirmed by ^1H and ^{13}C NMR spectra and by IR spectra. The number average molecular weight, M_n^{NMR}, of PEA-Toly-UPy was determined by comparing the peak area at 2.28 p.p.m. (CH_3 of tolylene) with that at 4.27–4.33 p.p.m. (main chain CH_2 of PEA) in the ^1H NMR spectrum measured in a $CDCl_3$ solution. The terminal modification rate, R_{tm}, of PEA-Toly-UPy polymers was evaluated using the peak areas at 2.23 p.p.m. (CH_3 of UPy) and at 2.18 p.p.m. (CH_3 of tolylene) in the ^1H NMR spectrum measured in a DMSO-d_6 solution. PEA-Toly-UPy with $M_n^{NMR} = 5.9 \times 10^3$ and $R_{tm} = 74\%$ was synthesized from PEA-Toly with $M_n^{NMR} = 5.7 \times 10^3$ ($M_n^{GPC} = 5.3 \times 10^3$ and $M_w^{GPC} = 1.0 \times 10^4$). Note that the GPC measurements (eluent = 0.01 mol l^{-1} LiCl in DMF) of this PEA-Toly-UPy gave $M_n^{GPC} = 1.3 \times 10^4$ and $M_w^{GPC} = 2.8 \times 10^4$. The large difference between M_n^{NMR} and M_n^{GPC} is most likely due to the aggregation or supramolecular formation of PEA-Toly-UPy in the GPC apparatus. The NMR spectra of PEA-Toly-UPy also showed that the terminals other than UPy were primarily amines, which were generated by the hydrolysis of the isocyanate group. Two more PEA-Toly-UPy polymers were synthesized using a similar procedure. PEA-Toly-UPy with $M_n^{NMR} = 5.7 \times 10^3$ and $R_{tm} = 82\%$, which was synthesized from PEA-Toly with $M_n^{NMR} = 5.5 \times 10^3$, was used for the viscosity measurement and dynamic mechanical spectroscopy. PEA-Toly-UPy with $M_n^{NMR} = 3.3 \times 10^3$ and $R_{tm} = 84\%$, which was synthesized from PEA-Toly with $M_n^{NMR} = 3.3 \times 10^3$, was used for the healing analysis of the amorphous sample. All of the other experiments were conducted using PEA-Toly-UPy with $M_n^{NMR} = 5.9 \times 10^3$. PEA-diol ($M_n^{NMR} = 4.5 \times 10^3$), PEA-Hex-UPy ($M_n^{NMR} = 5.1 \times 10^3$, $R_{tm} = 94\%$), and Hex-UPy polymers were also prepared as comparative samples and as an inhibitor for supramolecular chain extension.

The supramolecular chain extension of PEA-Toly-UPy was confirmed by viscosity measurements. The viscosity coefficient, η, of 40 mg ml^{-1} of a PEA-Toly-UPy solution in chloroform was 21.7 ± 0.3 mPa s at 28.0 °C. When a supramolecular chain extension inhibitor, Hex-UPy, was added to the PEA-Toly-UPy solution (molar ratio of UPy in the inhibitor to UPy in the polymer = 1:1), η was 2.94 ± 0.07 mPa s at 26.5 °C. The high viscosity of the PEA-Toly-UPy solution indicates a supramolecular formation that arises from the quadruple hydrogen bonding between UPy units. The supramolecular structure had a clear effect on the film strength. PEA-Hex-UPy and PEA-Toly-UPy produced flexible, free-standing films, whereas PEA-diol formed a brittle solid. The dynamic mechanical spectroscopy data (Figure 2) show that the glass transition temperature of PEA-Toly-UPy is −33 °C. The storage modulus at the rubbery plateau is 4×10^6 Pa, which gradually decreases above room temperature with increasing temperature and intersects with the loss modulus at 49 °C.

Crystallization of PEA-UPy polymers

The progress of crystallization in PEA-Toly-UPy, PEA-Hex-UPy and PEA-diol at room temperature was analyzed by DSC. The time evolution of the exothermic peak during isothermal crystallization was observed for melt samples at room temperature using DSC. For PEA-diol, the endpoint of the peak at 40 min indicates that the crystallization equilibrium had been reached in 40 min. The crystallinity at equilibrium was 47%, which was determined by X-ray diffraction analysis. No crystallization exotherm was observed using the same procedure for PEA-Toly-UPy and PEA-Hex-UPy because of their slow crystallization. For these polymers, the time evolution of the enthalpy of fusion was analyzed.

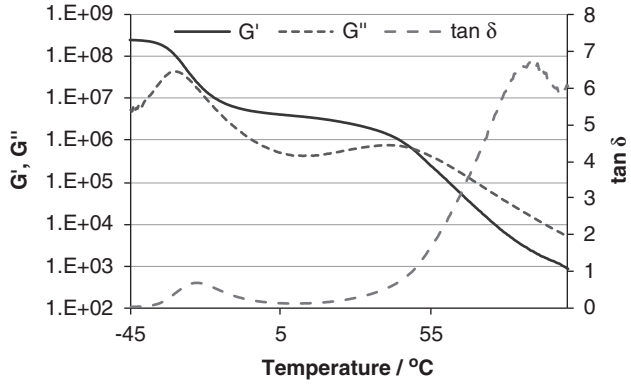

Figure 2 Storage modulus (G'), loss modulus (G") and tan δ as a function of temperature for PEA-Toly-UPy (degree of crystallinity = 1%).

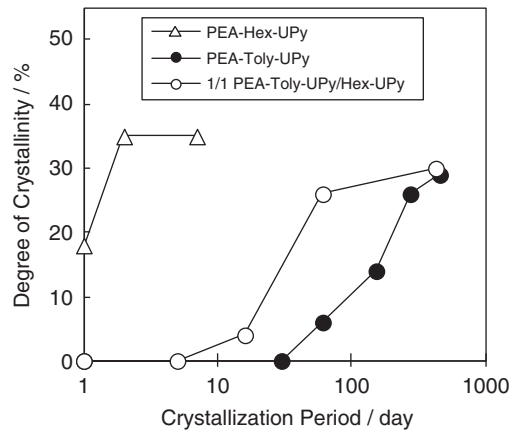

Figure 3 Time evolution of the crystallinity of PEA-Hex-UPy, PEA-Toly-UPy and a 1/1 mixture of PEA-Toly-UPy/Hex-UPy.

Melt samples of PEA-Toly-UPy and PEA-Hex-UPy were kept at room temperature for predetermined crystallization periods, and thermal profiles of the samples during melting were then recorded using DSC heating scans. The crystallinity was estimated as the ratio of the area under the endothermic peak at 40–55 °C to the heat of fusion of hypothetical PEA with 100% crystallinity, ΔH_f^0. By dividing the heat of fusion of PEA-diol with the equilibrium crystallinity (= 47%), ΔH_f^0 was estimated as 128 J g^{-1}.

Figure 3 shows the time evolution of the crystallinity of the samples. PEA-Hex-UPy required 2 days to reach equilibrium (31%), whereas the crystallization of PEA-Toly-UPy proceeded much slower. Although the crystallinity of PEA-Toly-UPy after 15 month of crystallization at room temperature was 29%, it was still not clear if this degree of crystallinity was the equilibrium value. The crystallization of PEA-Toly-UPy proceeded on a time scale of years. When the inhibitor, Hex-UPy, was added to PEA-Toly-UPy (molar ratio of UPy in the inhibitor to UPy in the polymer = 1:1), the crystallization of PEA was accelerated. The degree of crystallinity reached 27% in 2 months. These results indicate that the polymer chain extension due

to the hydrogen bonding of UPy units slows the crystallization of PEA-UPy polymers and that the bulky tolylene unit between PEA and UPy further reduces the crystallization rate.

Healing capability of PEA-UPy polymers

As mentioned in the introduction, a supramolecular polymer with a high molecular mobility is expected to have a healing capability. Thus, a healing analysis of PEA-Toly-UPy was first conducted using an amorphous sample. A film of PEA-Toly-UPy was melted at 100 °C and then kept at room temperature. After 1 month, the PEA-Toly-UPy sheet (degree of crystallinity still ~0%) was torn into two pieces. Shortly afterward, the torn surfaces were brought into contact. After 5 min at room temperature, a new boundary face was generated between the cut surfaces, as expected (Figure 4). This result indicates the quick healing capability of amorphous PEA-Toly-UPy.

The healing capability of amorphous PEA-Toly-UPy was further analyzed using tensile tests. Films of PEA-Toly-UPy were prepared by casting them from a chloroform solution. Before crystallization (degree of crystallinity <1%), the film was torn into two pieces, which were brought into contact. After 2 days, a tensile test was performed. Figure 5 shows the stress–strain curve of healed PEA-Toly-UPy with that of the original uncut film. Table 1 summarizes the results of this tensile test. The healed samples initially traced the tensile profile of the original sample. Although the healed sample broke at the repaired tear position before reaching the yield point, the stress at the break ($=0.73\pm0.05$ MPa) was 85% of the maximum stress of the uncut sample ($=0.87\pm0.04$ MPa).

When the torn surfaces of the amorphous PEA-Toly-UPy film were kept separate at room temperature for 2 days, the surfaces lost their healing ability. Even when the surfaces were pressed against each other with an external force, no sign of healing was observed. Similarly, a longstanding surface, such as the one present since film preparation, did not have a healing capability. This longstanding surface did not attach to another longstanding surface or to a freshly torn surface. The healing of PEA-Toly-UPy is surface-selective, and the surface only has the healing capability right after tear formation. This type of time dependence is commonly observed in healing polymers.[10,11,14] The surface selectivity can be attributed to the reformation of hydrogen bonds within the torn surface, which results in a decrease in the number of free UPy units available for healing.

The healing capabilities of crystalline PEA-Toly-UPy and PEA-Hex-UPy were also examined. PEA-Toly-UPy with a degree of crystallinity ~26% and PEA-Hex-UPy with equilibrium crystallinity (31%) were prepared by melt crystallization at room temperature. Freshly cut surfaces of the sample specimens were brought into contact with each other and kept at room temperature without any external stress. After two days, the cut surfaces of PEA-Hex-UPy were still separate. Conversely, the PEA-Toly-UPy surfaces were healed at room temperature. The healed sample withstood a strain of 20 kPa (Figure 6). As it was not heat-treated, PEA-Toly-UPy retained the bulk crystallinity during the tearing and healing process. Similar to the amorphous sample, the healing property of crystalline PEA-Toly-UPy was surface-selective. A longstanding surface did not attach to another longstanding surface or to a freshly torn surface. Furthermore, PEA-Toly-UPy could be healed repeatedly at the same position.

The presence of the crystalline phase usually significantly reduces the molecular mobility and inhibits the reformation of hydrogen bonds. The inability of PEA-Hex-UPy to heal at room temperature is expected as it is a crystalline polymer, although PEA-Hex-UPy can be healed at temperatures higher than T_m (Figure 7). Then, why was crystalline PEA-Toly-UPy able to heal at room temperature? The surface crystallinity was analyzed to answer this question.

Analysis of cut surfaces of PEA-UPy polymers

Figure 8 shows part of the ATR-IR spectra of PEA-Toly-UPy and PEA-Hex-UPy, which were measured at a longstanding surface, a freshly

Table 1 Mechanical Properties of Original and Healed PEA-Toly-UPy

Sample	*Young modulus/MPa*	*Maximum stress/MPa*	*Elongation at break/%*
Original	1.4 ± 0.06	0.87 ± 0.04	785 ± 260
Healed	1.2 ± 0.39	0.73 ± 0.05	112 ± 12

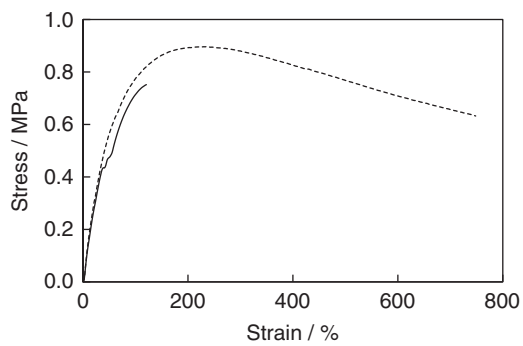

Figure 5 Stress-strain curves of original (broken line) and healed (solid line) PEA-Toly-UPy.

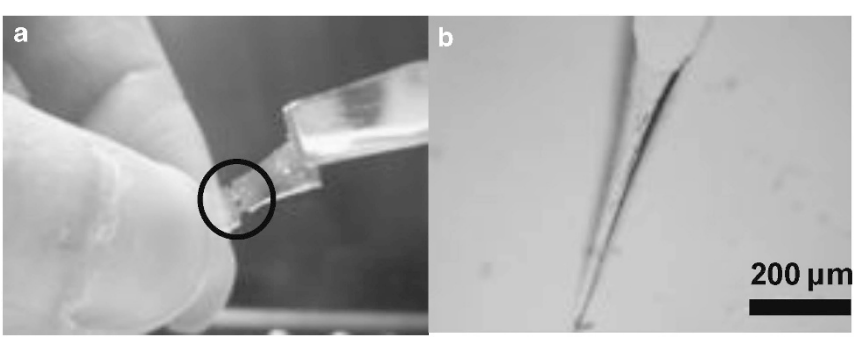

Figure 4 Amorphous PEA-Toly-UPy after healing for 5 min at room temperature. (**a**) Photograph of healed PEA-Toly-UPy during drawing. The healed position is circled. (**b**) Optical microscopic image of a new boundary face generated between cut surfaces.

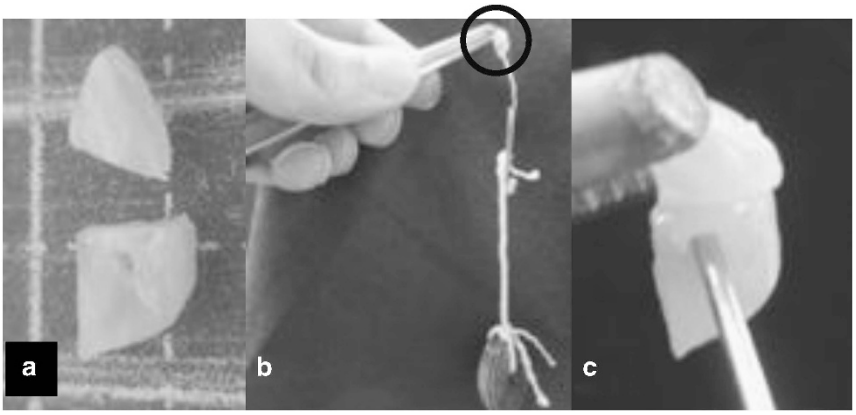

Figure 6 Healing behavior of crystalline PEA-Toly-UPy (degree of crystallinity = 26%) at room temperature. Photographs of (**a**) a freshly cut specimen of PEA-Toly-UPy and (**b**) the same specimen after healing for two days. The specimen is healed enough to stand a 20 kPa strain. Photograph (**c**) is an enlarged view of (**b**).

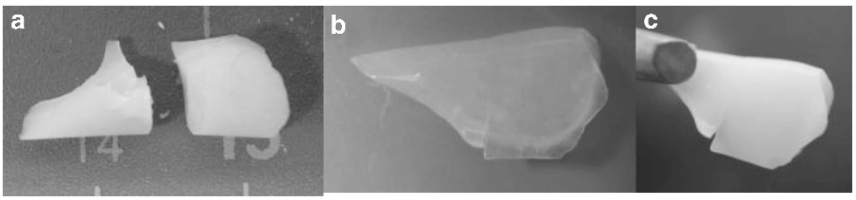

Figure 7 Healing behavior of PEA-Hex-UPy at 60 °C. Photograph of (**a**) a freshly cut specimen of PEA-Hex-UPy and (**b**,**c**) the same specimen after healing for 10 min at 60 °C. The specimen immediately after healing (**b**) is translucent because of its low crystallinity but soon became opaque because of crystallization (**c**).

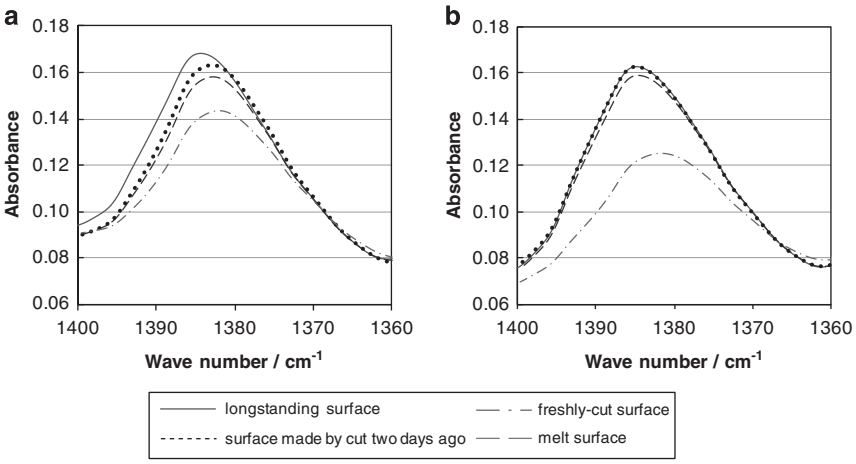

Figure 8 ATR-IR spectra near 1380 cm^{-1} for (**a**) PEA-Toly-UPy and (**b**) PEA-Hex-UPy. The spectra were measured at a longstanding surface (solid line), a freshly cut surface (dotted and dashed line), a surface made by cutting two days ago (dotted line) and a melt surface (dashed line). The intensities of the spectra are normalized by the absorbance at 1367 cm^{-1}, which is insensitive to the crystallinity.

cut surface, a surface made by cutting 2 days ago and a melt surface. The peak at 1385 cm^{-1} (from the asymmetrical wagging mode of CH_2) is sensitive to the crystallinity of PEA.[20] The comparison of the spectra measured at the longstanding surface with those measured at the melt surface shows that the crystalline phase has a larger peak at a higher wavenumber than the amorphous phase. For both PEA-Toly-UPy and PEA-Hex-UPy, the freshly cut surface exhibited a smaller peak at a lower wavenumber than the longstanding surface, indicating that the crystallinity at the cut front was diminished. When the cut sample was kept at room temperature for 2 days, the spectrum of PEA-Hex-UPy reverted to that of the longstanding surface, whereas the spectrum of PEA-Toly-UPy still had a smaller peak. Thus, PEA-Hex-UPy recovered the crystallinity at the cut surface within 2 days, whereas PEA-Toly-UPy retained a lower crystallinity for a longer period of time.

The fracture energy expended when a polymer material is cut includes three terms: the energy that reflects the intrinsic molecular strength, the energy dissipated because of the viscoelastic and plastic

processes of the polymer chains, and the frictional energy between the polymer and the cutting blade.[21] Whereas the frictional energy varies significantly based on the cutting conditions, the fracture energy under minimal friction[22] was estimated to be 1–4 kJ m^{-2} for crystalline polyethylenes[21] and approximately 0.2–1 kJ m^{-2} for organic elastomers.[23,24] As the intrinsic molecular strength of polymers is expected to be of the order of several tens of J m^{-2},[25,26] most of the fracture energy under minimal friction is expended through the dissipative processes. It is reasonable to assume that some of the dissipated energy (and the frictional energy, if any) melts the crystalline phase near the cut front.

The energy, E_m, required to melt the surface of PEA up to a depth, d, is given by

$$E_m = \rho d[c_p(T_m - T) + x_c \Delta H_f] \quad (1)$$

where ρ c_p, T_m, and x_c are the mass density ($=1.2\,g\,cm^{-3}$),[27] the specific heat capacity at constant pressure, the melting temperature and the degree of crystallinity of PEA, respectively. ΔH_f^0 is the heat of fusion of hypothetical PEA with 100% crystallinity ($=128\,J\,g^{-1}$), and T is the experimental temperature ($=298$ K). For PEA-Toly-UPy, T_m and x_c are 324 K and 26%, respectively. The specific heat, c_p, of most polymers is between 1 and 2 J g^{-1}K. The c_p values of poly(caprolactone)[28] and poly(butylene adipate),[29] which are aliphatic polyesters, are 1.8 and 2.0 J g^{-1}K, respectively. By substituting these values into the above equation, E_m is estimated to be $5\times10^7 d$–$10\times10^7 d$ J m^{-2}. The surface melting of PEA-Toly-UPy up to a depth of 1 μm only requires an E_m of 50–100 J m^{-2}, which is less than the dissipated energy. Therefore, crystal melting up to a depth of 1 μm or more is highly likely to occur at the cut surfaces of PEA-Toly-UPy. This depth would be large enough to allow molecular motion.

The self-healing behavior of PEA-Toly-UPy can be ascribed to the retained low crystallinity at the cut surface and to the reversibility of the hydrogen bonding (Figure 9). Similar to the other UPy-based supramolecular polymers,[17,18] tearing a bulk sample of PEA-Toly-UPy induces the cleavage of the hydrogen bonds between the UPy units, which results in an increase in the number of free UPy units at the torn surfaces. At the same time, the crystallinity at the torn surface is supposedly reduced by the dissipated energy. Owing to the extremely slow crystallization of PEA-Toly-UPy, the molecular mobility near the cut surface is maintained for a long period of time, even at room temperature ($>T_g$). By keeping the cut surfaces in contact with each other, hydrogen bonds can be reformed between the free UPy units, thus rejoining the cut surfaces. In the case of PEA-Hex-UPy, the fast crystallization must inhibit the rejoining of the cut surfaces, even though a number of free UPy units might be generated at the broken front as a result of tearing. As tearing can only melt the crystals near the torn surfaces, the bulk crystallinity of PEA-Toly-UPy must be retained throughout the healing process. Therefore, except for the direct damage caused by tearing, no negative effects were introduced by this healing mechanism.

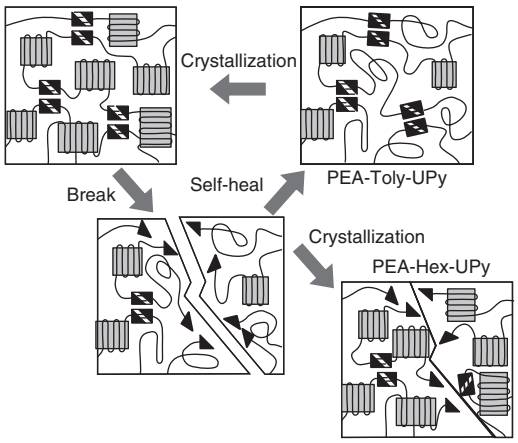

Figure 9 Schematic representation of the healing mechanism in PEA-Toly-UPy. Slow crystallization allows PEA-Toly-UPy to heal at room temperature, and fast crystallization inhibits PEA-Hex-UPy from healing.

CONCLUSION

We proposed a novel approach for obtaining crystalline polymers with self-healing capabilities. Dynamic bonds were introduced into a target crystalline polymer to enable the reversibility of the supramolecular structure. Bulky units were inserted between the polymer chain and dynamic bonds to reduce the crystallization rate. Tearing a sample of this supramolecular crystalline polymer causes dissociation of the dynamic bonds and reduction of the crystallinity at the torn surfaces. Owing to the slow crystallization, a high molecular mobility at the torn surfaces is maintained for a long period of time, which allows reformation of dynamic bonds between the broken surfaces and thus repair of the sample. Owing to the the reversibility of the dynamic bonds and the melt/crystallization, this healing mechanism works repeatedly for the same tear position.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

This work was supported in part by the Grant-in-Aid for Scientific Research (No. 21350083) and the Global COE Program for Chemistry Innovation through the Cooperation of Science and Engineering from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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