Polymers with Multishape Memory Controlled by Local Glass Transition Temperature

Chao Zeng,[†,‡] Hidetake Seino,[†,⊥] Jie Ren,*[,‡] and Naoko Yoshie*[,†]

[†]Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

[‡]Institute of Nano and Bio-Polymeric Materials, School of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China

Ⓢ Supporting Information

ABSTRACT: A multishape memory polymer with flexible design capabilities is fabricated by a very simple method. Local glass transition temperatures of a loosely cross-linked polymer film are changed by immersing sections of the film in a cross-linker solution with a different concentration. Each section memorizes a temporary shape, which recovers its permanent shape at a different recovery temperature depending on the local glass transition temperature. As a base polymer, we chose a network polymer prepared by a Diels−Alder reaction between poly(2,5-furandimethylene succinate) (PFS) and 1,8-bis-maleimidotriethyleneglycol (M_2). Quintuple shape memory behavior was demonstrated by a PFS/M film with four sections with distinct glass transition temperatures. The number of temporary shapes was determined by the number of different M_2 solutions. Furthermore, owing to the reversibility of the Diels−Alder reaction, the permanent shape was rewritable.

KEYWORDS: multishape memory polymer, Diels−Alder reaction, local glass transition temperature control, biobased polymer
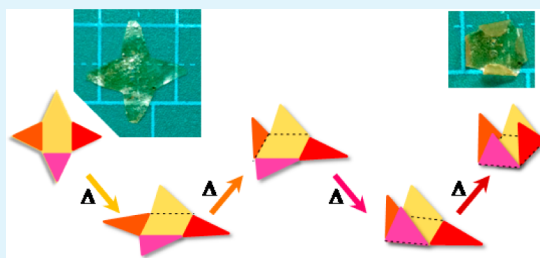
■ INTRODUCTION

Shape memory polymers (SMPs) are materials that can memorize one or more temporary shapes and recover their permanent shape upon exposure to an external stimulus. The most extensively studied SMPs are thermoresponsive SMPs; their phase transitions at the glass transition temperature, T_g, and the melting temperature, T_m, are used to preserve a temporary shape and to trigger shape recovery.[1−3] Many SMPs memorize only one temporary shape, but a few carefully designed SMPs can memorize two or more. For example, triple-shape memory polymers have been realized with network polymers containing two kinds of polymer segments[4,5] and with polymeric composites.[6] In these multiphase polymer materials, the ability to memorize two temporary shapes arises from the distinctive transition temperatures (T_g or T_m) of the phases. Polyfluorosulphonic acid, which does not have a multiphase structure and has one broad glass transition, exhibits multishape memory behavior; the broad transition can be regarded as the collective contribution of many transitions, each of which is a shape memory element.[7] Up to quadruple-shape memory behavior was experimentally demonstrated by this SMP. Light-induced reactions such as dimerization and monomerization of cinnamic acid can also be used as a phase transition for shape fixation and recovery.[8]

Indirect heating by various stimuli offers another attractive trigger for certain SMPs. SMPs triggered by various stimuli have been obtained by incorporating carbon nanotubes (CNTs) into a simple dual-shape memory polymer. CNTs generate heat upon activation by IR light,[9,10] current,[9] and radiofrequency,[11] and exposure of composite SMPs to these stimuli results in shape recovery. Embedding Fe_3O_4 into a SMP has a similar effect.[12,13] Indirect heating with light is advantageous for selective irradiation of a small area, which allows localized shape memory response.[10,14,15] By this method, shape recovery with a specific number of intermediate temporary shapes can be achieved. Recently, similar multistep shape recovery was realized by localized heating with selective current.[16] When SMPs susceptible to different stimuli are combined, other types of multishape memory materials can be obtained. For example, a multicomposite was prepared by embedding Fe_3O_4 nanoparticles and CNTs into different parts of a simple thermoresponsive SMP,[11] and exposure of this multicomposite to the characteristic radiofrequency of Fe_3O_4 or CNT resulted in selective heating of the corresponding section and local shape recovery.

Polymers with reversible dynamic bonds, such as Diels−Alder (DA) adducts between furan and maleimide, have attracted interest as high-performance materials. Their structural changeability in response to external stimuli makes them applicable for healing polymers,[17−20] recycling polymers,[21] and SMPs.[22−24] Recently, we prepared a biobased healing polymer by a DA reaction between poly(2,5-furandimethylene succinate) (PFS) and a bismaleimide.[25,26] This material, designated PFS/M, displays excellent self-healing

behavior at room temperature without an external stimulus. Because the molar ratio of furan in PFS to maleimide in the bismaleimide (F/M ratio) was kept >1, healing efficiency was improved by activation with a bismaleimide solution. We also found that T_g of PFS/M depends strongly on F/M, which inspired us to develop a novel strategy for fabricating the multishape memory polymer.

In this paper, we describe a multishape memory behavior of PFS/M controlled by local glass transition temperature. A piece of PFS/M film (F/M > 1) is divided into sections, and each section is immersed in a 1,8-bis-maleimidotriethyleneglycol (M_2) solution with a different concentration (Figure 1a). This
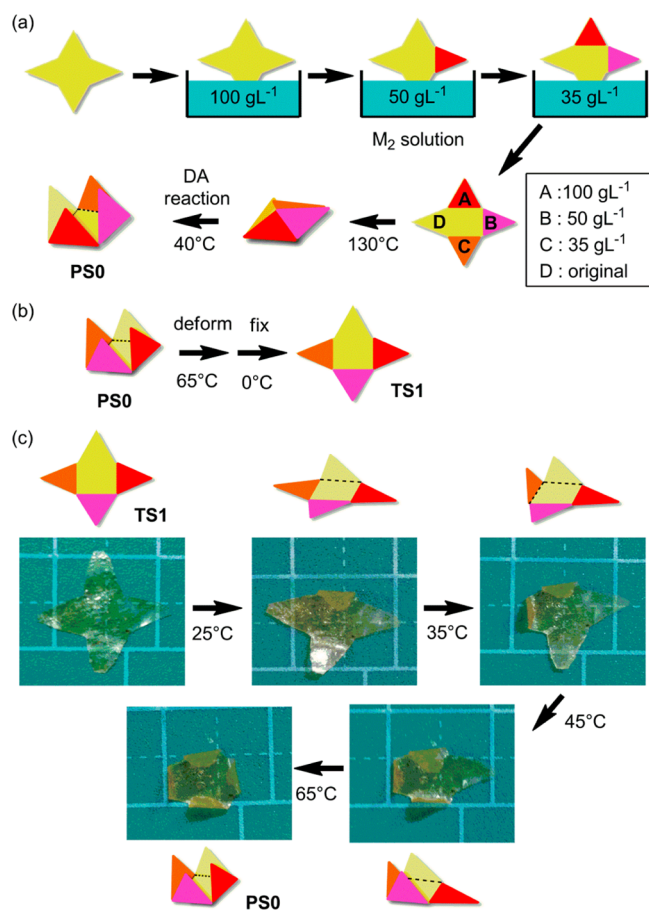

Figure 1. (a) Preparation, (b) shape memory, and (c) shape recovery of quintuple-shape memory PFS/M film.

process results in a PFS/M film with multisections each of which has a different T_g and, therefore, can memorize an individual temporary shape with a different recovery temperature. The number of temporary shapes and the recovery

temperature of each temporary shape can be designed simply by changing the number of sections and the M_2 concentration, respectively. Therefore, this method provides a very simple way to fabricate a multishape memory polymer with a highly flexible design capability.

■ MATERIALS AND METHODS

Preparation of PFS/M Shape Memory Polymer Films. PFS (M_n = 5.7 × 10³, M_w = 9.3 × 10³)[25] and M_2[27] were synthesized as previously reported. A film of a mixture of PFS and M_2 (F/M = 4/1) was cast from chloroform solution at room temperature and compression-molded between two Teflon sheets with an aluminum spacer (0.16 mm) at 130 °C for 5 min under a pressure of 5 MPa. For attenuated total reflection infrared (ATR-IR) spectroscopy, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), the film immediately after the molding was immersed in an M_2 solution (35, 50, or 100 g L⁻¹) for about 1 s and held at 130 °C for 5 min. After the solution and thermal treatments were repeated, the film was heated at 40 °C for 3 h and then at room temperature for 3 days to complete the DA reaction between PFS and M_2. For quintuple-shape memory experiments, a sample shaped like a four-rayed star was cut from the PFS/M film immediately after molding. Each triangular section of the film was immersed in an M_2 solution of a different concentration (100, 50, or 35 g L⁻¹), and the whole film was then heated at 130 °C for 5 min. After the solution and thermal treatments were repeated, the triangular sections were folded to form a small square, which was heated at 40 °C for 3 h and then held at room temperature for 3 days. A three-dimensional four-sided pyramid was obtained.

Characterization. ATR-IR spectra were obtained with a Thermo Scientific Nicolet iS10 Fourier transform IR spectrometer equipped with a ZnSe crystal and a Smart iTR sampling accessory. Spectra were recorded over a wavenumber range of 600−3800 cm⁻¹ with 2 cm⁻¹ resolution. Absorption peak intensities were calculated with the Fit Multiple Peak tool of OriginPro 8 software (OriginLab Corporation). DSC was carried out on a SII DSC6220N equipped with an EXSTAR6000. Samples (2−5 mg) in an aluminum pan were analyzed from −60 to 200 °C at a heating rate of 10 °C min⁻¹ under N_2. The tensile properties of the samples were evaluated with a Shimadzu EZ Test at a cross-head speed of 5 mm min⁻¹ at room temperature. No. 2 (1/5) dumbbell-shaped specimens described in JIS K 7113 (active region: 7.0 mm × 1.4 mm × 0.3−0.4 mm) were used for tensile testing. To ensure data reproducibility, we repeated each measurement at least four times, and we report average values. DMA was conducted on a SII DMS6100 equipped with an EXSTAR6000 in controlled-force mode. A rectangular film (20 mm × 9 mm × 0.16 mm) was stretched at 65 °C (= deformation temperature, T_d) by applying stress at 0.1−1 N min⁻¹ to approximately 12% strain. To fix the temporary shape, the sample was cooled to 0 °C (= fixation temperature, T_f) while the stress was maintained. Then, the sample was unloaded and equilibrated at T_f for 10−20 min. Finally, the sample was heated to a recovery temperature, T_r, which is 2−13 °C higher than T_g (see Table 1) and kept isothermal for 30 min to restore the permanent shape. The shape memory effect was quantified in terms of the shape fixity, R_f, and the shape recovery, R_r:

Table 1. Effect of Treatment with M_2 Solutions on PFS/M Film Properties

M_2 concentration/g L⁻¹	$F_{M\text{-}add}{}^a$/%	$F_{M\text{-}ur}{}^b$/%	Young's modulus/MPa	T_g/°C	$T_r{}^c$/°C	$R_f{}^d$/%	$R_r{}^e$/%
0^f		2	23.3 ± 3.1	16.8	25	97.7	95.8
35	47	3	857 ± 53	29.2	35	97.2	98.4
50	87	7	1880 ± 220	43.0	45	100	97.2
100	190	23	2067 ± 282	52.7	65	99.1	96.2

^{a}Fraction of M_2 added by dipping PFS/M film in M_2 solution (experimental error was estimated to be ±2%). ^{b}Fraction of unreacted maleimide (experimental error was estimated to be ±2%). ^{c}Shape recovery temperature selected for R_f and R_r estimation. ^{d}Calculated with eq 1. ^{e}Calculated with eq 2. ^{f}Original PFS/M film.

$$R_f = [\varepsilon_1/\varepsilon_L] \times 100\% \qquad (1)$$

$$R_r = [(\varepsilon_1 - \varepsilon_R)/\varepsilon_L] \times 100\% \qquad (2)$$

where ε_L is the maximum strain under load at T_f, ε_1 is the fixed strain after unloading the applied force at T_f, and ε_R is the strain after the completion of the shape recovery at T_r.

■ RESULTS AND DISCUSSION

Before analyzing the multishape recovery of the PFS/M film, we investigated the effect of treating PFS/M films with M_2 solutions of different concentrations. Films (thickness = 0.16 mm) cast from a mixture of PFS and M_2 (F/M = 4/1) were dipped in 35, 50, or 100 g L^{-1} M_2 solution for about 1 s and heated to 130 °C to erase their thermal history. To ensure making the clear T_g difference between films, the solution and thermal treatments were repeated. The very short immersion time is chosen because deep swelling by longer immersion time often results in the undulation of the film surface. Then, DA cross-linking was conducted at 40 °C. The chemical structures of the films treated with M_2 were compared with the structure of the original film by means of attenuated total reflection infrared (ATR-IR) spectroscopy. In the spectrum of the original film, the M_2 carbonyl peak (1700 cm^{-1}) was obviously smaller than the PFS carbonyl peak (1730 cm^{-1}, Figure 2a),
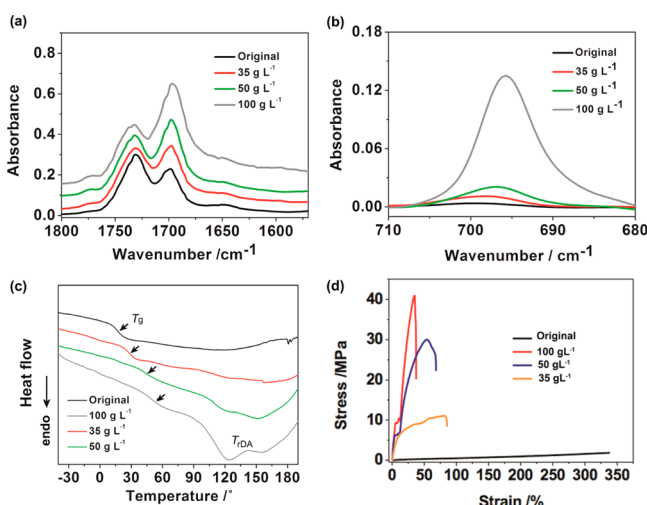

Figure 2. (a) Carbonyl and (b) imide peak regions of ATR-IR spectra, (c) DSC thermograms, and (d) stress−strain curves of PFS/M films treated with M_2 solutions.

which is consistent with the F/M ratio of 4/1 in this sample. Treatment with M_2 enlarged the M_2 carbonyl peak relative to the PFS carbonyl peak. The fraction of maleimide added to the PFS/M film by M_2 treatment, F_{M-add}, was calculated from[25]

$$F_{M-add} = [I_{C=O}{}^{st} - I_{C=O}{}^{or}]/I_{C=O}{}^{or} \qquad (3)$$

where $I_{C=O}$ is the M_2 carbonyl peak intensity relative to that of the PFS carbonyl peak, and the superscripts "or" and "st" indicate the original film and the films treated with M_2, respectively. As expected, F_{M-add} increased with increasing M_2 concentration (Table 1). Treatment with 100 g L^{-1} M_2 increased the amount of M_2 by a factor of 3 relative to the amount in the original PFS/M.

In the spectrum of the original PFS/M film, no imide peak for unreacted maleimide in M_2 was observed near 700 cm^{-1} (Figure 2b), indicating that almost all the maleimide groups

were cross-linked with furan groups. Although the imide peak remained small even after M_2 treatment, a closer look at the spectra revealed that the number of unreacted maleimide groups in the PFS/M film increased with increasing M_2 concentration. The fraction of the unreacted maleimide, F_{M-ur}, was estimated as[25]

$$F_{M-ur} = I_{C=C}I_{C=O}{}^{M2}/I_{C=O}I_{C=C}{}^{M2} \qquad (4)$$

where $I_{C=C}$ is the imide peak intensity and the superscript "M2" indicates pure M_2 (Table 1). At the surface of the PFS/M film treated with 100 g L^{-1} M_2 solution, 23% of maleimide remained unreacted. At high M_2 concentration, denser cross-links would limit the molecular mobility of PFS and hinder the reaction between furan and maleimide.

Differential scanning calorimetry (DSC) thermograms of the PFS/M films treated with M_2 showed a single glass transition and an endothermal peak for the retro DA reaction (Figure 2c). The peak was enlarged by M_2 treatment, clearly indicating that additional cross-links were formed by the DA reaction between the added M_2 and the residual free furan groups in the PFS/M film. The cross-link density enhancement drastically increased T_g (Table 1); treatment with the 35, 50, and 100 g L^{-1} M_2 solutions increased the T_g of the films by 12.4, 26.2, and 35.9 °C, respectively. The T_g increase coincided with increases in the Young's modulus and tensile strength of the films (Figure 2d, Table 1). The increase in Young's modulus can be attributed to the increase of cross-linking density after M_2 solution treatment. These data indicate that the cross-link density and T_g of PFS/M could be controlled by changing the concentration of the M_2 solution.

We used dynamic mechanical analysis (DMA) to investigate the shape memory of PFS/M films treated with M_2. Films were first deformed at 65 °C (= deformation temperature, T_d) to approximately 12% strain, and then, the temporary shape was fixed at 0 °C . The film was then heated to a recovery temperature, T_r, higher than T_g (see Table 1). At T_r, all the PFS/Ms films treated with M_2 recovered their permanent shapes (Figure 3). The shape memory effect was quantified in terms of shape fixity, R_f, and shape recovery, R_r, calculated with eqs 1 and 2, respectively (Table 1). All the films demonstrated good shape memory, with R_f and R_r values exceeding 97.2% and 95.8%, respectively.

To demonstrate quintuple-shape memory behavior, we prepared a PFS/M film with four-rayed-star shape and immersed each triangular section (A, B, and C) in an M_2 solution of a different concentration (100, 50, or 35 g L^{-1}; Figure 1a). After the whole film was heated to 130 °C to erase its thermal history, the triangular sections were folded and the sample was heated at 40 °C to make a three-dimensional four-sided pyramidal permanent shape (PS0). Then, a temporary open four-rayed star (TS1) was deformed at 65 °C, which is higher than the highest T_g of the sample, and fixed at 0 °C, which is lower than the lowest T_g (Figure 1b). When the temperature was increased stepwise from 0 °C to 25, 35, 45, and 65 °C, the four sections of TS1 recovered their permanent shapes one by one as their respective T_g values were reached. That is, section D recovered its permanent shape at 25 °C, and sections C, B, and A recovered theirs at 35, 45, and 65 °C, respectively (Figure 1c). The recovery process of the sections initially proceeded fast followed by gradual slowdown. At 65 °C, the section D showed 90% shape recovery in ≈4 s while the full recovery required ≈30s. The 90% recovery in sections C, B, and A took ≈1 min at 35 °C, 3 min at 45 °C, and 3 min at 65
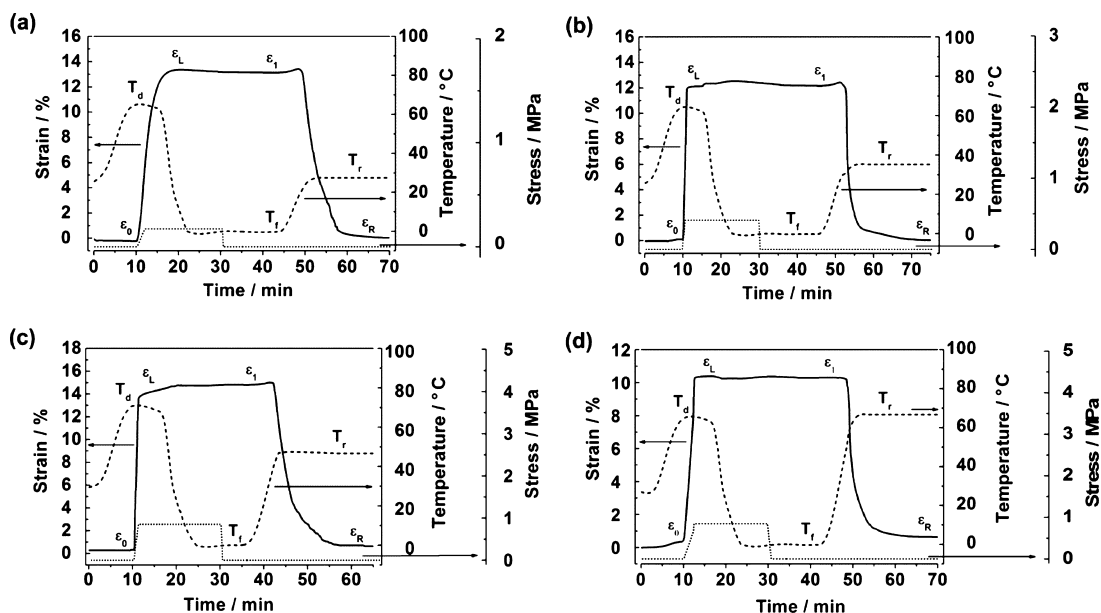
Figure 3. Shape memory properties of (a) original PFS/M film ($T_r = 25$ °C) and PFS/M films treated with (b) 35 g L^{-1} M_2 ($T_d = 65$ °C, $T_f = 0$ °C, and $T_r = 35$ °C), (c) 50 g L^{-1} M_2 solution ($T_r = 45$ °C), and (d) 100 g L^{-1} M_2 solution ($T_r = 65$ °C). All the samples were deformed at $T_d = 65$ °C and fixed at $T_f = 0$ °C.

°C, respectively, while the full recovery in the sections required 5, 10, and 10 min, respectively. Higher cross-linking density results in faster recovery rates due to the higher content of cross-link points that drive shape recovery.

The shape memory effect was repeatable at least 10 times. Further, the recovery temperature can be controlled fairly well by careful selection of the concentration of bismaleimide solution and dipping time. However, the difference in recovery temperature between sections can hardly be decreased from 10 to 5 °C.

Instead of being heated stepwise, TS1 was placed directly on a hot stage at 65 °C, which exceeds the highest T_g of the quintuple-shape memory PFS/M film, and the sections with different T_g values recovered their permanent shapes at different rates (Figure 4 and the movie in the Supporting Information). Section D, which had the lowest T_g, recovered first, followed by C, B, and A in that order. The large difference in the recovery rates can be attributed to differences in variation
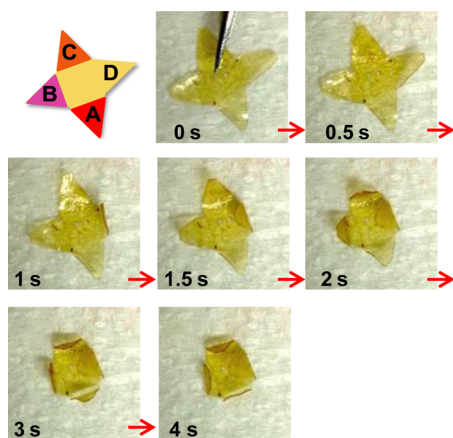
of $\Delta T = T - T_g$ ($T = 65$ °C). The region with a large ΔT exhibits higher molecular mobility and faster shape recovery.

Because the DA reaction is reversible, the permanent shape of the PFS/M film was rewritable (Figure 5). PS0 was first heated to 130 °C to induce partial decross-linking by means of a retro DA reaction. Then, the sample shape was changed to another permanent shape (PS0′) and kept at room temperature for 3 days to complete recross-linking (Figure 5a). Three-
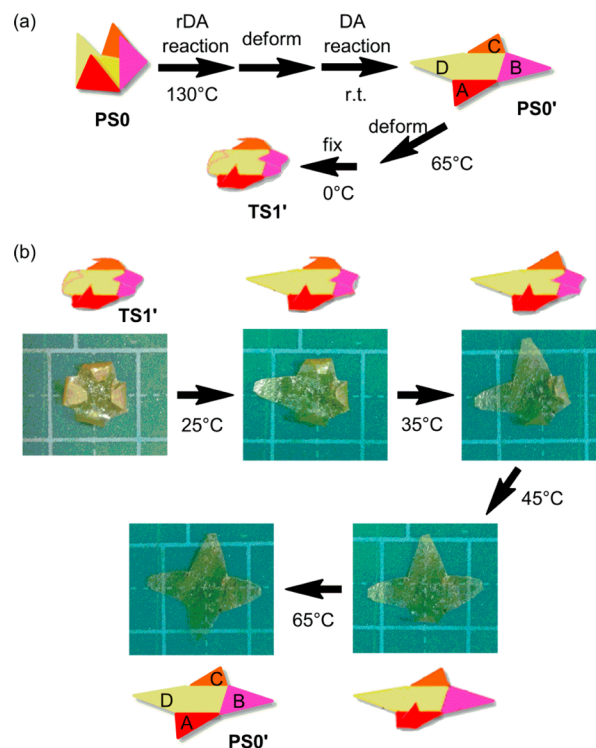

Figure 4. Sequential shape recovery of a quintuple-shape memory PFS/M film at 65 °C.

Figure 5. (a) Permanent shape rewriting and (b) shape recovery of quintuple-shape memory PFS/M.

dimensional temporary shape TS1′ was made from PS0′ at $T_d = 65\,°C$ and fixed at $T_f = 0\,°C$. Similar to TS1, TS1′ recovered its permanent shape (PS0′) stepwise; that is, the TS1′ sections recovered their permanent shapes in the order D → C → B → A upon stepwise heating to 25, 35, 45, and 65 °C (Figure 5b).

CONCLUSIONS

To summarize, a PFS/M film with four sections with distinct T_g values was fabricated by immersing each section in an M_2 solution with a different concentration. Depending on the concentration, the T_g values of the sections could be tuned in a wide range (17−53 °C). Each section memorized an individual temporary shape with a different recovery temperature. Therefore, when the film was heated from 0 to 65 °C stepwise, the four sections recovered their permanent shapes in order of their T_g values. That is, the recovery temperature could be controlled simply by changing the M_2 concentration. The number of temporary shapes that could be memorized was determined by the number of M_2 solutions. All the sections were able to memorize their respective temporary shapes when T_d exceeded the highest T_g and when T_f was below the lowest T_g of the PFS/M film treated with M_2. Further, because the DA reaction is reversible, the permanent shape was rewritable. The strategy described here offers a simple, versatile way to prepare multishape memory polymers with highly flexible design capabilities. No complicated molecular design and fabrication processes were required. With this strategy, any network polymer with controllable cross-link density can be made into a multishape memory polymer with a tunable number of temporary shapes and recovery temperatures.

ASSOCIATED CONTENT

Ⓢ Supporting Information

A movie showing sequential shape recovery of quintuple-shape memory PFS/M at 65 °C. This information is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: yoshie@iis.u-tokyo.ac.jp.
*E-mail: renjie65@163.com.
Present Address
[⊥]Faculty of Education and Human Studies, Akita University, 1-1 Tegata Gakuen-machi, Akita City, 010-8502, Japan.
Notes
The authors declare no competing financial interest.

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2758

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