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ARTICLE

Thermo- and pH-sensitive Shape Memory Polyurethane Containing Carboxyl Groups

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A type of polyurethane with thermo-induce triple shape memory effect and pH-sensitive dual shape memory effect was delevoped. Firstly, a series of polyurethanes were successfully synthesized through solution polymerisation of polyethylene glycol (PEG, M_n=4000 kg mol^{-1}), dimethylol propionic acid (DMPA) and 4, 4'-diphenylmethane diisocyanate (MDI). These polymers named as PEG-i-MDI-DMPA, (i=20%, 30%, 40%), i represents the weight contents of PEG in the polymer. The results of shape memory testing showed that the PEG-30%-MDI-DMPA display both the triple-shape memory and pH sensitive dual-shape memory effect. In PEG-30%-MDI-DMPA, the glass transition of PEG chains and the association and disassociation of carboxylic dimer are as two switches to control triple-shape memory, while the carboxylic dimer affected by pH values to associate in acid (at pH 2) and dissociate in alkaline (at pH 9) to induce the pH-sensitive shape memory.The carboxylic dimers play an important role in construction of shape memory properties in this polyurethane.

Introduction

Hydrogen bonds as an noncovalent interaction have been widely used in molecular recognition, self-assembly and supramolecular chemistry for its orientation and reversibility.[1] Hydrogen bonds are applied to prepare shape memory polymers (SMPs) for easily tuning of the binding strength and a straightforward design of multifunctional materials.[2] The design of shape memory polymers based on hydrogen bonds relies mostly on pyridine moiety, ureidopyrimidine unit and carboxylic acid. Pyridine moiety can form reversible hydrogen bonds with urethane group to obtain temperature and humidity sensitive SMPs.[3-5] Hydrogen bonds between pyridine and carboxylic acid developed polymer with both shape memory and liquid crystalline properties.[6] Ureidopyrimidine unit, formed the strong quadruple-hydrogen-bonded dimer, is well-suitable for the design of SMPs with reversible network structure[7, 8] or end group functionalized interpenetrating structure.[9, 10] The hydrogen bonds between carboxylic acid can obtain stabilized shape memory complex,[11-13] and develop high modulus ratio SMPs with excellent shape memory effects.[14]

Dual-shape polymers (DSPs), as the most common SMPs, usually have two different domains, one not affected by external stimulus as the fixing domain to hold the permanent shape, and another sensitive to external stimulus as switch to induce shape change.[15-19] If there are two or more domains sensitive to external stimulus, the material may have multiple shape memory effect. [20] The multiple shape effects require at least two segregated domains associated with two distinct thermal transitions for fixing each temporary shape by the corresponding domain.[21-23] Recent progress reported polymers with only one broad phase transitions temperature range achieve the multiple shape effects.[24, 25] Our group reported one type of shape memory polyurethane, which bonded with mesogenic units exhibit triple-shape memory effects.[26] This polyurethane contained carboxyl groups in main chains forming strong hydrogen bonding interaction with mesogenic units. In fact, the carboxyl groups can bind cooperatively together, since both units act as proton donor and acceptor, forming a large eight-membered ring containing two hydrogen bonds.[27] The carboxylic dimers can be affected by temperature to dissociate and associate as the temperature rise and down, which likes a switch sensitive to temperature. So we consider to utilize carboxylic dimers as additional switch domain in polymer to induce triple shape memory.

It also considered that carboxylic acid is sensitive to pH, which in acid formed dimers while in alkaline transform from acid to carboxylate to disrupt the dimers. This property also can be used as a switch in shape memory procedure. Recently, pH stimulus became a good choice for the design of new shape memory polymers. Since Lendlein and Langer reported a PCL-based SMP with potential application in medicine, the SMPs exhibit tremendous applications in medical areas.[28-30] But the thermo-sensitive SMPs, studied most widely, are restricted in some medical application for probable tissue damage caused by heating. It is well known that physiological body is varied pH

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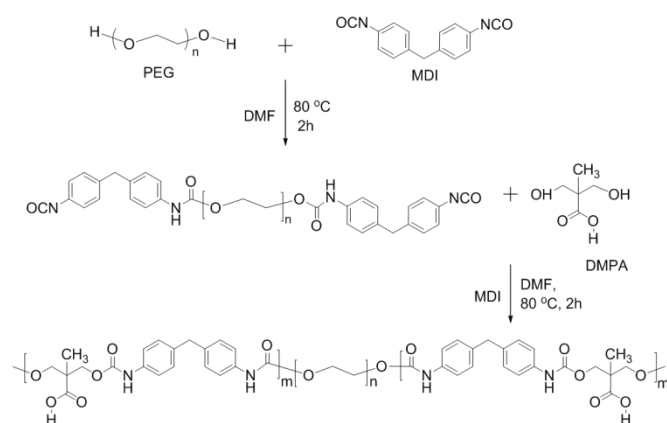
Scheme 1. Synthetic routes of PEG-*i*-MDI-DMPA

environment, which are adaptive application of pH sensitive shape memory polymers. Some studies on this type of shape memory polymer are under exploring. Zhang and his co-workers prepared a pH-sensitive shape memory polymer, which can process into different temporary shapes at pH 11.5 and recover to its permanent shape at pH 7.[31] Our group prepared a polyurethane with pyridine ring, which can fix temporary shape at pH 10 and recovery its permanent shape at pH 1.3, and the drug delivery also be tested. [32] In our report, pyridine ring sensitive to pH variation act as a switch to control shape memory and drug release. For carboxylic acid, it demonstrates an opposite pH sensitive value compared to pyridine ring. Carboxylic acid form dimers in acid and be disrupted in alkaline, while pyridine ring form hydrogen bonded interaction in alkaline and be disrupted in acid. So polymer containing carboxyl groups is possible to exhibit pH-sensitive property.

Based on the above consideration, we aim to prepare polymer containing carboxyl groups, which probably be a multi-functional material presenting both the triple-shape memory and pH sensitive dual-shape memory effect. Polethylene glcol (PEG) as a kind of amphiphilic and good biocompatibility materials was chose as the soft segments in polymer. Then 4, 4'-diphenylmethane diisocyanate (MDI) and dimethylol propionic acid (DMPA) reacted with PEG through solution polymerisation as Scheme 1 shown. A series of polyurethanes named as PEG-*i*-MDI-DMPA (*i*=20%, 30%, 40%) were synthesized, *i* represents the weight contents of PEG in the polymers.

Experimental

Materials

Unless otherwise noted, all chemical reagents were obtained from commercial suppliers and used without further purification. Polyethylene glycol (PEG) purchased from Johnson Matthey Company, with M_n=4000 g mol^{-1}. Dimethylform amide (DMF) was purchased from Kelong Chemical Reagent Factory in Chengdu. 4,4-Diphenylmethane

diisocyanate (MDI) and dimethylolpropionic acid (DMPA) were purchased from Enery Chemical.

PEG was purified by precipitation from methylene chloride into diethyl ether and was used after drying under vacuum for 24h. DMF was dried over CaH_2 for 2 days at room temperature, distilled under vacuum, and stored with 4 Å molecular sieve.

Synthesis of PEG-*i*-MDI-DMPA

A typical synthesize route of PEG-30%-MDI-DMPA: PEG (0.25mmol), MDI (1.3mmol) and 50ml of DMF were added into a dried flask and reacted around 80◦C for 2h. Then, DMPA (6mmol) and MDI (5mmol) were successively added, with the reaction being maintained at the same temperature for 2h. After the reaction finish, the solution was poured into a mould, evaporating at 80◦C for 12h to obtain the film and further dried under vacuum for another 12h. ^{1}H NMR (400 MHz, DMSO-d_6). 9.55 (δ H$_a$, 2 H, s, -NH- in urethane), 8.58(δ H$_b$, 1 H, s, -OH in carboxylic acid), 7.32 (δ H$_c$, 4 H, s, -CH= in benzene ring), 7.08 (δ H$_c$, 4 H, s, -CH= in benzene ring), 4.19 (δ H$_f$, 4 H, s, -OCH$_2$-).

The synthesized procedure of PEG-20%-MDI-DMPA and PEG-40%-MDI-DMPA are the same as PEG-30%-MDI-DMPA mentioned above.

Characterizations

FT-IR spectroscopic analysis was carried out with a Nicolet 5700 FT-IR spectrometer (Thermo Electron, U.S.A) by the ATR method. ^{1}H-NMR experiments were performed on a Varian 400 NMR spectrometer. Thermal analysis was conducted using a TA Instruments DSC-Q100 at heating and cooling rates of 10 ◦C min^{-1}. Static tensile test was accomplished at the cross-head speed of 2 mm min^{-1} at room temperature using a universal testing machine Instron 5567 (Instron Co., Massachusetts). Dynamic mechanical thermal analysis experiments were performed using a TA Instruments DMAQ800, in the tensile resonant mode, under N$_2$ and at a heating rate of 3◦C min^{-1} and 1 Hz.

Investigation of the Triple Shape-Memory Effect (TSME)

TSME was tested by the bending test according literature [33], as Figure S1 shown in electronic supplementary information (ESI). Polymer was cut into rectangular strips with dimension of 25.0mm × 5.0mm × 0.5 mm (length × width × thickness). First, the straight sample (shape A) was heated to T_{high} (80◦C, T_{high} > T_g) for 5 min, and was bended to an angle θ$_1$ (θ$_1$=90°). Then the sample was quickly cool to T_{mid} (T_{mid} = 40◦C) under force and kept the force for 10 min. After releasing the force, the temporary shape B was fixed and the angle marked as θ$_{f1}$. After that, shape B was further deformed at 180° under force and cooled to T_{low} (T_{low} =0◦C) to keep the shape for 10 mins. After releasing the force, temporary shape C was obtained and angle marked as θ$_{f2}$. For recovery, shape C was heated to T_{mid} to yield the recovered shape B' and recovering angle marked as θ$_{r1}$. When the temperature further increased to T_{high}, shape A was obtained and the recovering angle marked as θ$_{r2}$. The triple-shape memory cycle was repeated three times using the

same sample, and the results represent the averages of three times. The shape memory fixity ratio (R_f) and recovery ratio (R_r) were calculated according to the following equations:

$$R_f(A \rightarrow B) = \frac{180 - \theta_{f1}}{\theta_1} \times 100\% \quad (1)$$

$$R_f(B \rightarrow C) = \frac{\theta_{f1} - \theta_{f2}}{\theta_{f1}} \times 100\% \quad (2)$$

$$R_r(C \rightarrow B') = \frac{\theta_{r1} - \theta_{f2}}{\theta_{f1} - \theta_{f2}} \times 100\% \quad (3)$$

$$R_r(B' \rightarrow A') = \frac{\theta_{r2} - \theta_{r1}}{180 - \theta_{r1}} \times 100\% \quad (4)$$

Investigation of the pH-sensitive shape memory effect

The pH-sensitive shape memory effect was tested as Figure S2 shown in ESI. A dimension of 25 mm × 5 mm× 0.5 mm (length × width × thickness) straight specimen film was immersed in base at pH 9 for 120 min and then deformed at angle 180° and immersed in acid at pH 2 to fix this shape. After 10 minutes, this shape was fixed and obtained a fixing angle marked as θ_f. Then, this specimen was returned to alkaline at pH 9 recovery to the initial shape and the angle marked as θ_r. The above procedures were repeated three times, and the experimental temperature kept at 25°C. The shape memory fixity ratio $R_{f\ (pH)}$ and recovery ratio $R_{r\ (pH)}$ were calculated according to the following equations:

$$R_{f\ (pH)} = \frac{180 - \theta_f}{180} \times 100\% \quad (5)$$

$$R_{r\ (pH)} = \frac{\theta_r - \theta_f}{180 - \theta_f} \times 100\% \quad (6)$$

Water-Absorption Measurements.

Samples were dried at 60 °C under vacuum before the water absorption testing, and the weight marked as m_0. Then the samples were placed in water with different pH value at room temperature (25 °C). The specimens were weighed at different time intervals, and the weight marked as m_i. The water content, W, was defined as the weight ratio of the water to the dry sample [W = (m_i - m_0)/m_0].

Results and discussion

Synthesize and characterization

The PEG-*i*-MDI-DMPA (*i*=20%, 30%, 40%) were synthesized through solution polymerisation using poly-(ethylene glycol) (PEG) with the molecular weight of 4000 g mol^{-1}, diphenyl-methanediisocyanate (MDI) and dimethylolpropionic acid (DMPA). The chemical structures of the polymers were confirmed by FT-IR and ^{1}H-NMR analysis.

FT-IR spectra in Figure 1 clearly showed that the designed polymers were successfully synthesized. There is no isocyanate (-N=C=O) peaks occurred at 2270 cm^{-1}, indicating all the MDI completely reacted. Two obvious bands appeared around 3300

and 1724 cm^{-1} assign to the stretching vibrations of N-H and C=O in urethane, respectively, demonstrating the formation of the urethane group (-NHCOO-). ^{1}H-NMR spectra further
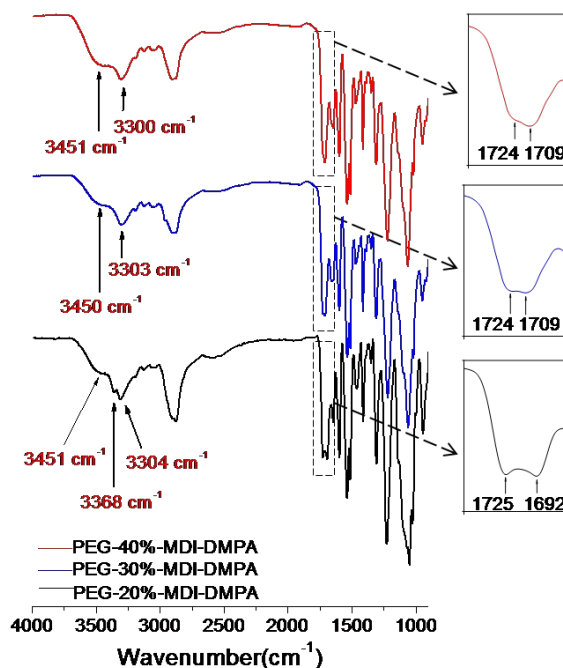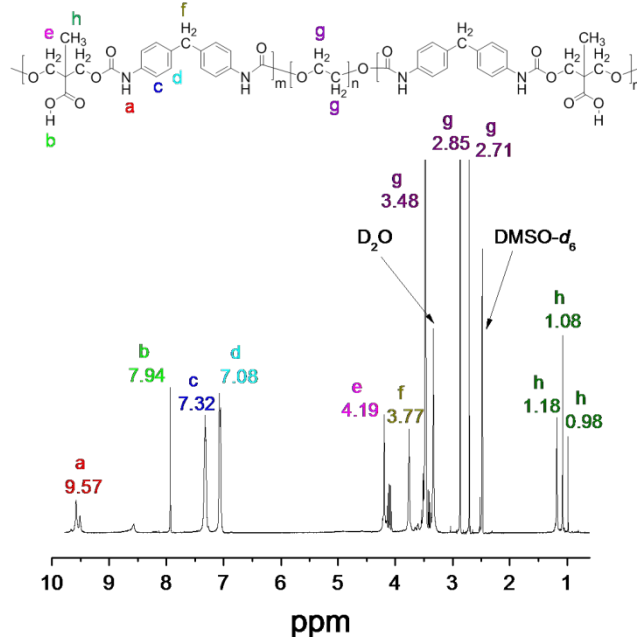

Figure 1 FT-IR spectra of PEG-i-MDI-DMPA

Figure 2 ^{1}H-NMR spectra of PEG-30%-MDI-DMPA

confirmed the structures of PEG-*i*-MDI-DMPA series. The polymer PEG-30%-MDI-DMPA as an example, ^{1}H-NMR spectra of that was showed in Figure 2. The chemical shifts of 9.55 ppm are attributed to the protons of NH groups and the 8.58 ppm for the protons of hydroxyl in carboxylic acid. The

chemical shifts of 7.32and 7.08 ppm are ascribed to the benzene protons of isocyanate groups, respectively. Both the FT-IR and ^{1}H-NMR results showed that PEG-*i*-MDI-DMPA series are successfully synthesized.
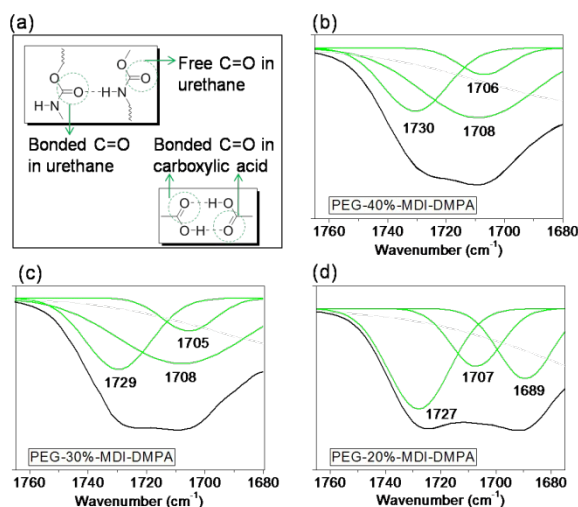

Figure 3 (a) Three types of C=O in polymer; Curve fitting results for IR spectra in the C=O stretching region (b)PEG-40%-MDI-DMPA, (c) PEG-30%-MDI-DMPA and (d) PEG-20%-MDI-DMPA;.

Prove the formation of carboxylic dimers. The peak at 1724 cm^{-1} attributed to the free C=O in urethane, growing bigger and more obviously with decrease of the PEG soft segment as Figure 1 showed. When the urethane formed hydrogen bonding, as shown in figure 3(a), the stretching vibrations of C=O in urethane will shift to lower frequency at 1700 cm^{-1}. And the vibration of carbonyl in carboxylic dimers also appeared at 1700cm^{-1} according to the literature.[11] The two types bonded carbonyls overlapped at 1700 cm^{-1} to demonstrate a wide vibration as the amplification part shown in Figure 1. Curve fitting was used to distinguish the two types C=O vibration, as shown in Figure 3(b) to 3(d). From the results of curve fitting range from 1770 to 1670 cm^{-1}, the vibrations of C=O in urethane are around 1708 cm^{-1}, while that of C=O in carboxylic acid are around 1705 and 1689 cm^{-1}. As the increasing of the MDI-DMPA content, the vibration intensity of bonded C=O in carboxylic acid increased, and gradually shift to the lower frequency. It is known that C=O stretching of monomeric carboxylic acid at 1750 cm^{-1}. For the PEG-*i*-MDI-DMPA, the C=O stretching absorption of carboxylic acids appeared at 1700 cm^{-1} rather than 1750 cm^{-1}, indicating that there is no monomeric state for carboxylic acids and that the carboxylic acid groups may have a dimeric structure resulting from hydrogen bonding interaction by themselves. A carboxylic acid of monomeric form is known to give a sharp band at ~3600 cm^{-1}.[34] But there is no peak appeared at that band in the PEG-*i*-MDI-DMPA series. The peaks at 3450cm^{-1} are responsible for the vibration of hydroxyl in carboxylic acid, which implies a hydrogen bond between hydroxyl and carbonyl specific interactions according the literature.[13] It also indicated the formation of carboxylic dimers.
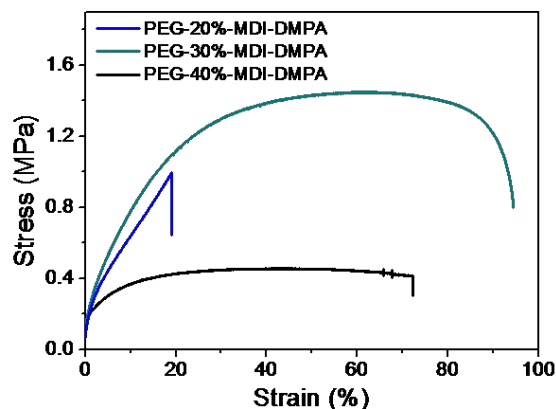

Figure 4 Stress–strain curves of PEG-*i*-MDI-DMPA

Mechanical properties

The stress–strain curves of the PEG-*i*-MDI-DMPA are showed in Figure 4. PEG-30%-MDI-DMPA showed the highest stress and strain, with the maximum tensile strength (ε_m) of 1.49 MPa and the elongation at break of 90%. Although the elongation at break of PEG-40%-MDI-DMPA can reach 70%, but the ε_m only 0.5 MPa, while PEG-20%-MDI-DMPA can obtain ε_m as 1.0 MPa, but the elongation at break only 20%. It means PEG segments determined the elasticity of the polymers and the MDI and DMPA determined the hardness of the polymers. Appropriate content of the above mentioned components play an important role in the mechanical properties of polymers. As the results of tensile testing, PEG-30%-MDI-DMPA showed the best mechanical properties during these series.

Thermal properties

Differential scanning calorimetry (DSC). Figure 5(a) shows typical DSC curves of PEG-*i*-MDI-DMPA. The specimens were heated from -50 to 100 °C at the rates of 10°C /min under N$_2$. The T_g of PEG-20%-MDI-DMPA, PEG-30%-MDI-DMPA and PEG-40%-MDI-DMPA are -7.2 °C, 13.0°C and 26.6°C, respectively. It is obviously that the T_g of polymer increased as the increasing of PEG content. We also find that these polymers do not show any melting endotherms at all. It may because that the PEG, as the soft segment of polyurethane, cannot crystallize for the restraint from the hard segments and only have glass transition. It means the T_g can attribute to the phase transition of PEG from glass state to rubber state.

Dynamic Mechanical Analysis (DMA). Thermal transitions of the polymer also can be detected by DMA. Figure S3 showed the DMA results of PEG-20%-MDI-DMPA and PEG-40%-MDI-DMPA, in which the two polymer demonstrate only one tan Delta peaks at 17.8 ℃ and 26.1 ℃ respectively. That means the two polymers may have dual-shape memory properties. Figures 5(b) showed the DMA results of PEG-30%-MDI-DMPA. From -20 °C to 80 °C, it is a wide temperatures transition range and the storage modulus reduced from 700MPa to 3MPa. Our

previous research indicated that polymer with a wide range transition temperatures may exhibit triple-shape memory effect.[35] From the curve of storage modulus, we can find polymer PEG-30%-MDI-DMPA possesses a wide transition temperature, suggesting a probable triple-shape memory effect of it. Here, it clearly showed that sample display two peaks tan Delta. In DSC curve, the glass transition at 13.0 °C is according to the peak of tan delta at 23.9 °C, but there is no obvious transition temperature according to the peak of tan delta at 56 °C. Many SMPs are phase-segregated polymers with hard and switching domains, where each domain is related to different transition temperature.[36] Although for our polymer PEG-30%-MDI-DMPA, there is only one transition temperature in DSC, but the two tan delta peaks means two phase transition temperature according to two shape memory procedure.[37] At the glass transition of 13.0 °C, the polymer network changes from the glassy state (700 MPa) at -20 °C to the rubbery state (40 MPa) at 40 °C. For the temperature of 56.2 °C, as we designed at the beginning, the polymer network may changes from the rubber state (40MPa) crosslinked by carboxylic dimers to the viscous state (3MPa) with dissociated carboxylic dimers according to our previous report of the carboxylic dimers damaged above 60 °C.[26]
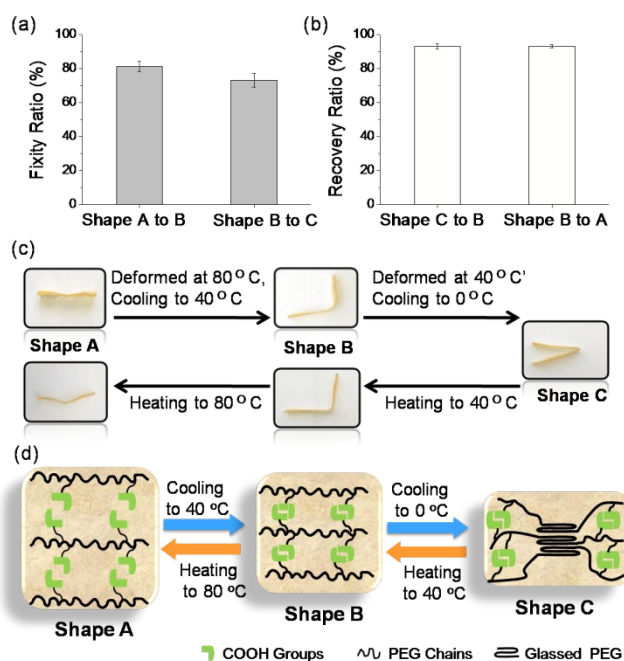

Figure 6 Shape fixity ratio (a), shape recovery ratio (b), and triple-shape memory procedure (c) and mechanism (d) of PEG-30%-MDI-DMPA .
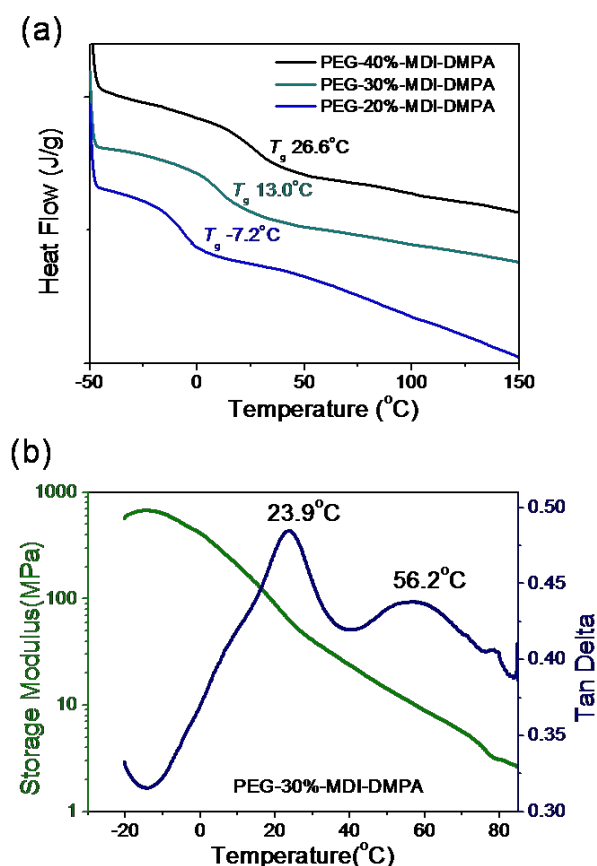

Figure 5. (a)DSC curves of PEG-*i*-MDI-DMPA (b)DMA curves of PEG-30%-MDI-DMPA

Triple Shape-Memory Effect (TSME)

Based on the DSC and DMA results, polymer PEG-30%-MDI-DMPA may possesses a triple-shape memory effect. The two temperatures, 40 °C and 80 °C, were selected as the two transition temperatures for the triple shape memory process. The bending test was employed to calculate the quantitative results of triple shape memory effect, and the shape fixity ratio (R_f) and shape recovery ratio (R_r) were calculated according to equations (1) to (4). Firstly, the sample with permanent shape A was heated to T_{high} = 80 °C and cooled to T_{mid} = 40 °C to deformed the shape B under a constant load. After 10 mins the stress was released, and the first temporary shape B was obtained. Next, the shape B was further deformed to shape C under stress and cooled to T_{low} = 0 °C; 10 mins later, the external stress was removed, and temporary shape C was fixed. Lastly, reheating to T_{mid} = 40 °C, the sample recover to shape B, and further heating to T_{high} = 80 °C, the sample recover to permanent shape A.

As Figure 6(a) and 6(b) showed, from shape A to shape B the $R_{f(A \to B)}$ can above 80%, while from shape B to shape C the $R_{f(B \to C)}$ around 75%. During the shape recovery procedure, the $R_{r(C \to B)}$ and $R_{r(B \to A)}$ could reach 93% and 95%, respectively. Figure 6(c) shows the shape deformation and recovery processes of the triple shape memory properties.

In PEG-30%-MDI-DMPA, there are two kinds of hydrogen bonding pairs, one is hydrogen bonding interaction between carboxylic dimer, and another is that between NH and C=O in urethane. From the view of the molecular design, the association and disassociation of carboxylic dimers and the glass transition of PEG chains are as two switches to control

triple-shape change. Figure 6(d) shows the proposed mechanism of triple-shape memory behaviour of PEG-30%-MDI-DMPA. In this polymer carboxylic dimers can be damaged by heating above 60 °C according to our previous research [26] and PEG segments will transform from glass state to rubber above 20 °C according to the DSC curve. When heating to 80 °C, only the hydrogen bonded PU segments are still stable to hold the permanent shape. Cooling to 40 °C, the carboxylic dimers formed again to hold the temporary shape B. Further cooling to 0 °C, PEG segments transform from rubber to glass to hold the temporary shape C. When sample reheating to 40 °C, PEG segments became rubber and carboxylic dimers still formed to recover shape B. When temperature reached 80 °C, carboxylic dimers disassociated to recover shape A.

pH-sensitive shape memory effect

The polymers PEG-*i*-MDI-DMPA containing the PEG segments are hydrophilic materials. And carboxylic groups are introduced into the main chains by the DMPA groups. It is well known that carboxylic acid prefer to form dimers and the carboxylic dimers can be damaged by heat or alkaline condition. Inspired by association and dissociation of carboxylic dimers in different pH condition, we further studied the pH-sensitive shape memory effect of PEG-*i*-MDI-DMPA. Theoretically, the more DMPA contents the better pH-sensitive properties of these series polymers are. PEG-20%-MDI-DMPA and PEG-30%-MDI-DMPA should be better than PEG-40%-MDI-DMPA in the pH-sensitive shape memory effect. But the PEG-20%-MDI-DMPA is poor in mechanical performance from the prior study, so we choose PEG-30%-MDI-DMPA for further study. And the next all experiments are performed at 25 °C, at which temperature the PEG segments are in rubber status and the carboxylic dimers as the switch to control the shape.

In figure 7(a), water absorption testing of PEG-30%-MD-DMPA at three different condition showed that polymer at pH 9 have the higher water absorption than at pH 2 or in water, while in water or at pH 2 the polymer have the nearly same water absorption ratios, as half of the value at pH 9. At pH 9, water absorption increased sharply before 120 mins and the ratio can reach about 38%, then the increase became slowly and the ratio reached 42% after 480 mins. In water or at pH 2 condition, most of the water are also absorbed during the first 120 mins and the highest water absorption ratio only can reach 20%. It seems that the water and acid condition have the same effect on polymer. PEG-30%-MDI-DMPA immersed in different pH condition for 2h is enough for polymer to interact with solution.

In order to decide acid at which pH value are fit for shape fixity, PEG-30%-MDI-DMPA, after immersing at pH 9 for 2 h, was fixed shape at pH 1, pH 2, pH 3 and pH 4 respectively, and the fixity ratio are calculated according to equation (5). As Figure 7(b) shown, polymer at pH 1 and pH 2 performed the better shape fixed effect and both the fixity ratios are above
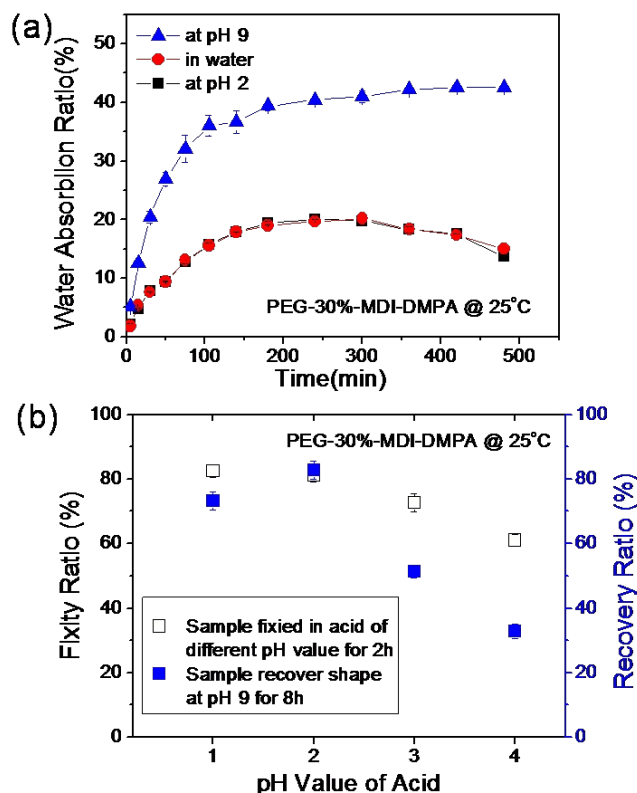

Figure 7 pH-sensitive memory effect (a) and schematic route of the pH sensitive (b) of PEG-30%-MDI-DMPA.

80%, while at pH 3 at pH 4 the fixity ratio are about 70% and 60% respectively. Considered the acid at pH 1 is too much to be fit for application, while the pH 2 seem be better as the shape fixed condition. Then the samples fixed shape in acid at different pH value, return to alkaline at pH 9 to recover the initial shapes, and the shape recovery ratios are calculated according to equation (6). In Figure 7(b), the shape recovery ratio for polymer fixed shape only at pH 2 can reach 80%, while for polymer fixed at pH 1, the recovery ratio is about 70%. At pH 3 and pH 4 the recovery ratio are even more lowered, below 50%. It also indicated the pH 2 is the better condition, so PEG-30%-MDI-DMPA fixed shape in acid at pH 2 in next studies.

Figure 8(a) showed the pH-sensitive shape memory procedure. Firstly, a strip of PEG-30%-MDI-DMPA was immersed in alkaline for 2h to damage the carboxylic dimers (Initial Shape). Then deformed a new shape and immersed in acid to reform the carboxylic dimers to fix this temporary shape (Fixed Shape). Next, the sample return to alkaline, the fixed shape gradually recover to initial shape, 2h later the recovery ratio only 32% and 8h later it reach 80%. As figure 8(b) shown, carboxylic dimers formed in acid condition to hold the temporary shape, while the carboxyl transform to be carboxylate radical in alkaline to damage the dimers and polymer recover to its initial shape.
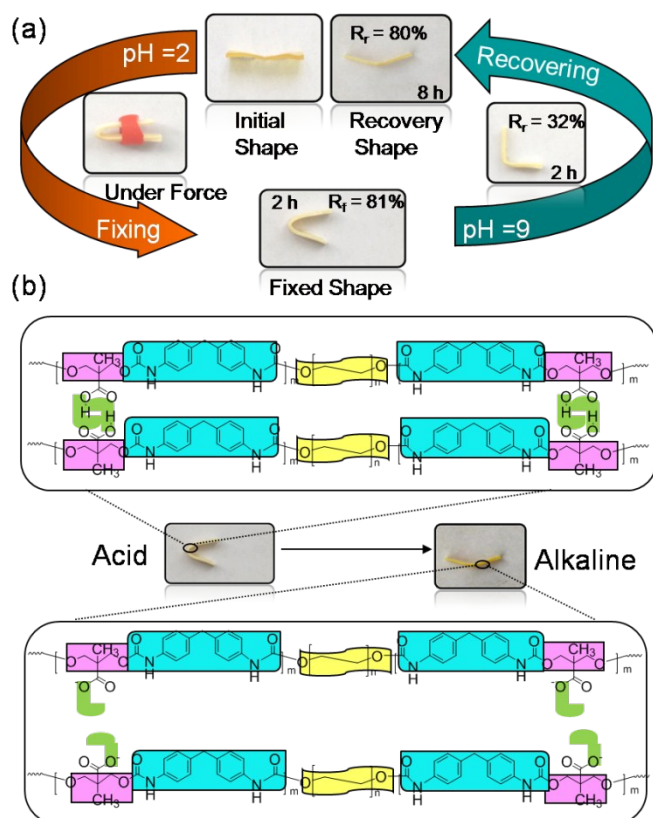
Figure 8 pH-sensitive memory effect (a) and schematic route of the pH sensitive (b) of PEG-30%-MDI-DMPA.

Figure 9 (a) FT-IR spectra of PEG-30%-MDI-DMPA initial materials, treated in alkaline at pH 9 and in acid at pH2 after treatment at pH 9; ^{1}H NMR spectra of PEG-30%-MDI-DMPA (b) initial material, (c) at pH 9 and (d) at pH 2 after treatment at pH=9.

Mechanism of pH-sensitive shape memory effect. To further confirm whether the carboxylic dimers associated and dissociated as we deduced in pH-sensitive shape memory procedure, the FT-IR spectra of PEG-30%-MDI-DMPA treated at pH 2, in water and at pH 9 are measured, respectively. As showed in Figure 9(a), the peak at 1709 cm^{-1}, assigned to the C=O stretching of the carboxylic dimers, disappeared at pH 9, and then appeared again when the polymer treated in acid at pH 2. ^{1}H-NMR also showed a reversible protonated and disprotonated procedure of carboxylic acid. As Figure 9(b) shown, the shift of proton from COOH, appeared at 8.58 in initial material, gradually disappeared as immersed in alkaline at pH 9, and appeared again at 8.52 when that materials transfer to acid at pH 2. The carboxylic dimer can be associated and disassociated by changing the pH value of the external environment.

The above results further confirm that carboxylic dimer are formed in acid and broken in alkaline. Thus, in the shape memory procedure, the carboxyl group sensitive to pH can be used as a switch to shift the polymer shape. Simply adjusting the pH value leads to a pH induced shape memory effect for this polymer containing carboxyl groups.
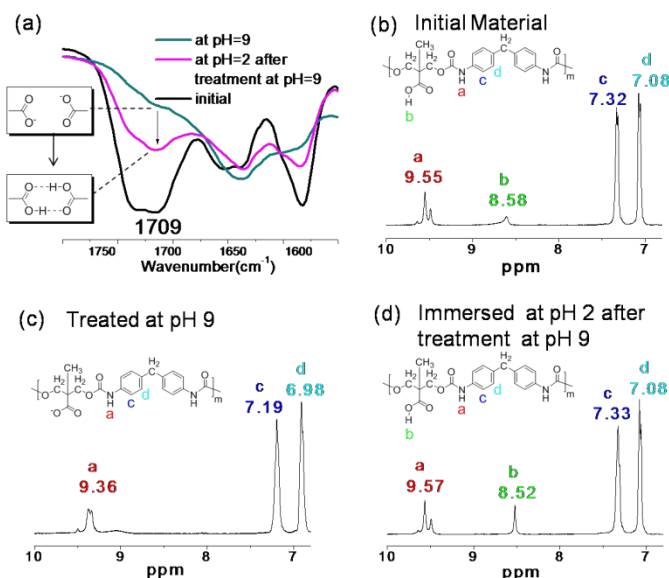
Conclusions

In conclusion, a series of polyurethane with different PEG weight ratio were synthesized successfully. The PEG-30%-MDI-DMPA displays both the triple-shape memory effect and pH-sensitive dual-shape memory effect. In PEG-30%-MDI-DMPA, the glass transition of PEG chains and the association and disassociation of carboxylic dimers are as two switches to control triple-shape memory property. And the carboxylic dimers can also be affected by pH values to association in acid (at pH 2) and dissociation in alkaline (at pH 9). However, polymers PEG-20%-MDI-DMPA and PEG-40%-MDI-DMPA exhibit no shape memory property for their too higher or lower carboxylic contents. The carboxylic contents play an important role in the construction of shape memory properties in these polyurethanes.

Acknowledgements

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