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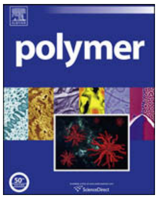

Polymer Communication

Novel moisture-sensitive shape memory polyurethanes containing pyridine moieties

Shaojun Chen, Jinlian Hu*, Chun-wah Yuen, Laikuen Chan

Institute of Textiles and Clothing, Hong Kong Polytechnic University, Hung Hom, Hong Kong, China

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ABSTRACT

In this communication, novel moisture-sensitive shape memory polyurethane (SMPU) was synthesized from 1,6-hexamethylene diisocyanate (HDI) and *N*,*N*-bis(2-hydroxylethyl) isonicotinamide (BINA) and 1,4-butanediol (BDO). Results show that the BINA based SMPUs have excellent moisture absorption properties which are not only influenced by the temperature, but also by the relative humidity (RH). As a result, high strain recovery with fast recovery speed is obtained after immersion in the moisture condition for a short time. FT-IR spectra provide a proof to the mechanism of moisture-sensitive SME which is based on the dissociation or disrupt of hydrogen bonding in the pyridine ring induced by moisture absorption. Thus, the strain recovery is achieved in the moisture-sensitive SMPUs by decreasing the glass transition temperature (T_g) below ambient temperature without external heating.

1. Introduction

Shape memory polymers (SMPs), which are known to have the ability of memorizing temporary shapes and recovering their permanent shapes upon external stimulation [1], are elastic networks equipped with suitable stimuli-sensitive switches; and their shape memory effect (SME) may be induced by temperature, light, pH, etc. [2]. For example, in the thermal-induced SMPs, thermal reversible phase serving as a “switch” is either a glass transition or a melting transition [3]. In the light-induced SMPs, stimulation has been realized by incorporation of reversibly reacting molecular switches [4]. In addition, SMEs are also observed in the polymer blends consists of immiscible elastomer and switch polymer [5]. Therefore, various SMEs including moisture-sensitive SME are expected to be achieved in elastic networks by incorporating suitable switches including molecular switches, switch segment and switch polymer.

Now, the most attractive SMPs are still thermal-induced SMPs due to their wide availability and broad possible applications [5]. The shape memory behavior of thermal-induced SMPs is generally triggered by heating the specimen above the melting point (T_m) of the crystalline soft segment or glass transition temperature (T_g) of amorphous soft segment [6,7]. However, sometimes, the application temperature is limited to a low temperature range, e.g. in the biomedical applications. Thus, the prestored strains are expected to be recovered without external heating. Recently, water-driven SMPU programmable shape memory behavior was observed in the shape memory polyurethane (SMPUs) since the T_g of SMPU was found to reduce dramatically after immersing in water. Further investigation shows that the hydrogen bonding is the key player behind the water-driven SME in SMPUs; and water or moisture absorbed in the polymer plays a main role in the shape recovery process [8–10]. However, their shape recovery is limited to water; and the strain recovery could not be triggered by moisture due to their very low moisture absorption.

In an earlier communication [11], we reported that hydrogen-bonded supramolecular polyurethane networks containing pyridine moieties could be used as shape memory materials. It was confirmed that the movement of polymer chain of pyridine containing polyurethane (PUPy) was influenced greatly by the hydrogen bonding; and the dissociation of hydrogen bonding in the pyridine ring resulted in the strain recovery in the PUPys. In addition, the humidity absorption of poly(vinyl pyridine) was observed to be a few times high during the investigation of humidity and solvent effects of polythiophene and poly(vinyl pyridine) by Jaczewska et al. [12]. It was suggested that the pyridine unit was responsive to the moisture absorption. Thus, the moisture-sensitive SME should be expected in the SMPU containing pyridine moieties since the pyridine based molecular “switches” shows response to the moisture. In the present study, the novel moisture-sensitive SMPUs based on pyridine derivative: *N*,*N*-bis(2-hydroxylethyl) isonicotinamide (BINA) was synthesized for the first time.

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* Corresponding author. Tel.: +86 852 2766 6437; fax: +86 852 2775 1432.
E-mail address: tchujl@inet.polyu.edu.hk (J. Hu).

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2. Experimental part

2.1. Materials

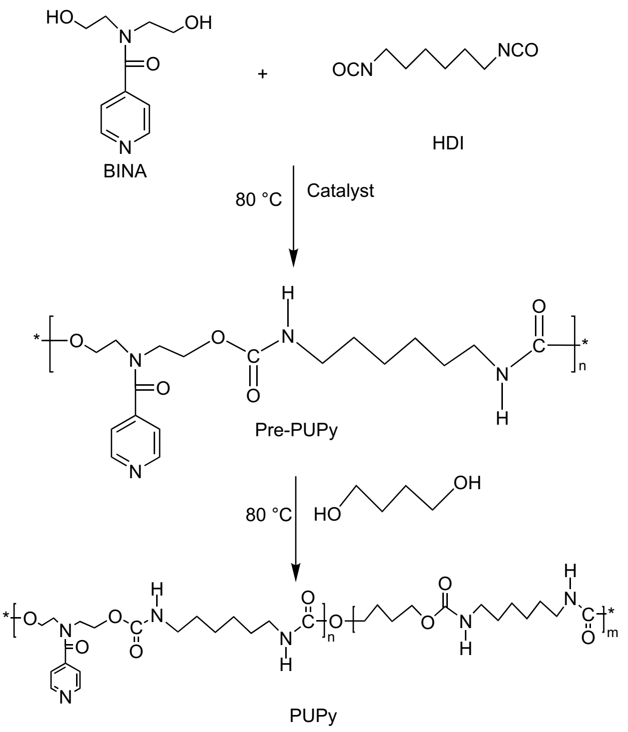
Extra-pure-grade 1,6-hexamethylene diisocyanate (HDI), 1,4-butanediol (BDO) and BINA (all from Sigma–Aldrich Chemical Co., St. Louis, MO) were used directly; and dimethylformamide (DMF) (from Ajax Finechem Ltd., Auckland, New Zealand) was dehydrated with 4-Å molecular sieves for several days before its use as a solvent.

2.2. Synthesis of PUPy

The synthesis routine of PUPy is presented in Scheme 1. The composition in each sample is designed with the NCO/OH molar ratio of 1.02. The reaction was carried out in a 500-ml flask filled with nitrogen and equipped with a mechanical stirrer, a thermal meter, and a condenser. A constant temperature was kept to about 80 °C in the whole reaction process. Firstly, BINA powder and 10 ml DMF was added to the flask; After the BINA was dissolved completely under the mechanical stirring, HDI and 0.02 wt% catalyst (Dibutyltin dilaurate) was added to the flask. Then the reaction started immediately, and the viscosity was observed to increase significantly. After 2 h, BDO was added to the reaction. The reaction was kept for another 4 h. To control the viscosity of solution, 10 ml DMF each was added into the reaction occasionally during the reaction process. Finally, 10 wt% PUPy/DMF solution was obtained. After casting on the PTFE mould and putting on the 100 °C oven for 12 h, film of PUPy with various BINA content was prepared. In this study, sample is coded as PUPy**, where the "**" delegates the BINA content, e.g. PUPy45.

2.3. Characterization

Thermal analysis was carried out by using Perkin–Elmer DSC-7 at a scan rate of 20.0 °C/min. Moisture absorption was tested after 0.5 mm thickness specimens was dried at 100 °C for 12 h, the specimens were put on the standard temperature humidity chamber. Weight percentage of specimen was weighted after each 5 min firstly, and the moisturizing time increased gradually when its absorption speed was slow [13]. Finally, the dependency of moisture absorption on time could be obtained. For moisture-sensitive strain recovery measurement, dried specimens with 5 mm width and 40 mm length were elongated to 100% strain at 70 °C by instron 4466, and fixed at room temperature for 10 min under load. Thereafter, they were also put on the standard temperature humidity chamber. The length percentage of specimen was measured after each 10 min. Finally, the strain recovery could be calculated according to the method in literature [14], and the dependency of strain recovery on time could be obtained. Infrared spectra at various times were recorded on a Nicolet 760 FT-IR spectrometer.



Scheme 1. Synthesis routine of PUPy.

3. Results and discussions

Fig. 1 presents the DSC heating curves of PUPy with various BINA contents after annealing at 100 °C for 12 h. In Fig. 1, it can be found that an obvious glass transition appears at the temperature range of 38–60 °C when the BINA content is beyond 30 wt%. As the BINA content decreases from 53 wt% to 30 wt%, the T_g moves to lower temperature; and the change in heat capacity (ΔC_p) also decreases gradually. When the BINA content decreases to less than 25 wt%, the T_g tends to disappear. In addition, crystals are measured at the temperature range of above 110 °C when the BINA content is below 40 wt%; moreover, the crystal melting temperature (T_m) and the change in enthalpy (ΔH_m) increases with the decreasing of BINA content. It implies that the phase separation consisting of soft phase and hard phase occurs in the PUPy. Similar to the micro-structures changing in the SBS/PCL blends [5], as the BINA content decreases from 53 wt% to 15 wt%, the soft phase tends to change gradually from continuous amorphous phase at above 30 wt% to droplet-like dispersion phase at below 15 wt%; while the hard phase grows up from droplet-like dispersion amorphous phase at above 40 wt% to continuous crystalline phase at below 30 wt%. Thus, it implies that the soft phase is determined by the BINA unit, while the hard phase is influenced by the HDI-BDO unit. It indicates that the hydrogen bonding between the urethane groups serves as the physical netpoint due to its relative higher association temperature, whereas the thermal reversible hydrogen bonding in the pyridine ring act as the molecular "switches". Accordingly, if the

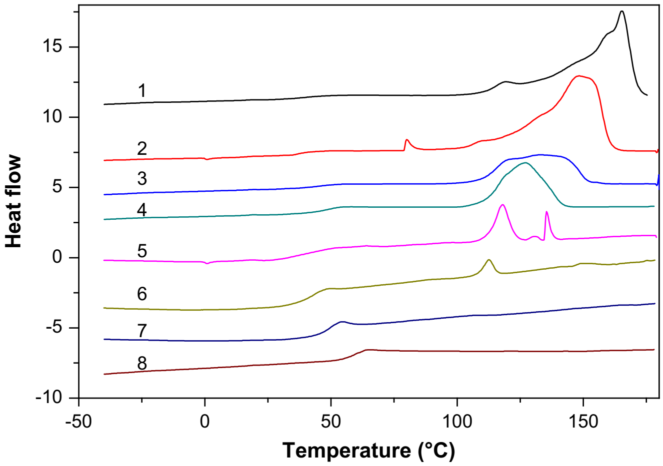


Fig. 1. DSC curves of PUPy with various BINA contents (1–15 wt%; 2–20 wt%; 3–25 wt%; 4–30 wt%; 5–35 wt%; 6–40 wt%; 7–45 wt%; 8–53 wt%).

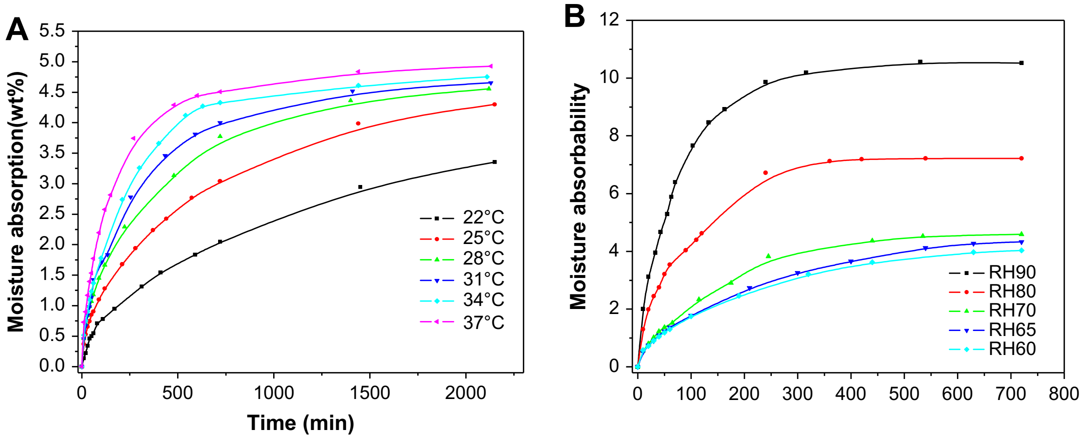


Fig. 2. Dependencies of moisture absorption on time: (A) at various temperatures by fixing RH = 80%; (B) at different RH conditions by fixing $T = 34$ °C.

molecular “switches” shows response to the other external stimulus like moisture, the moisture-sensitive SME should be achieved.

Fig. 2(A) and (B) presents the dependencies of moisture absorption for sample PUPy45 on time at different immersion temperature by fixing relative humidity (RH) of 80%, and at different RH condition by fixing temperature of 34 °C, respectively. In Fig. 2(A), it can be observed that the sample PUPy45 absorbs moisture very quickly within the first 90 min. Then it slows down and tends to reach its saturated state after 1500 min at the temperatures range of 22–37 °C. That is, this moisture absorption process matches with Fick’s second law in the initial stage [13]. In addition, it was known from the Shen–Springer equation that the diffusion coefficient increased with increasing of immersion temperature [15]. Thus, it is observed in Fig. 2(A) that the moisture content of polymer at any time increases with the increasing of immersion temperature. For example, within 90 min, the moisture absorption at 22 °C is only 0.7%, while it reaches 2.1% at 37 °C. Finally, it is observed that the maximum moisture absorption also increases with increasing of immersion temperature. However, it should be pointed out that maximum moisture absorption increases a little when the temperature is raised to above 28 °C, because the moisture absorption is mainly determined by the moisture content between immersion environment and materials [13]. In addition, it is observed that the slope of moisture absorption at 37 °C is much higher than that at 22 °C. That is, the moisture absorption speed is higher in the high temperature.

Similarly, in Fig. 2(B), it is also observed that before the sample PUPy45 is saturated with the moisture after it has been exposed to moisture condition for a certain time (e.g. 300 min at RH = 90%, above 450 min at RH = 70%, and above 700 min at RH = 60%), the moisture absorption kept increasing with time. Finally, it is found that the maximum moisture absorption increases with the RH, and it reaches 7.23% at RH = 80%, and 10.51% at RH = 90%. It is confirmed that the moisture absorption at equilibrium is dependent on the RH; and the higher RH results in a higher moisture absorption speed. It indicates that the BINA based SMPU is sensitive to the moisture. The temperature as well as RH influences the moisture absorption speed and the maximum moisture absorption greatly. Thus, high moisture absorption can be obtained by controlling the RH and temperature.

Fig. 3(A) and (B) presents the dependencies of strain recovery on time at various temperatures and at various RH conditions, respectively. In Fig. 3, it can be found that similar to the thermal-induced SME, the shape tends to keep stable before the moisture absorption reaches a critical value. For example, the deformed strain in the PUPy53 starts to recover after 50 min immersion in the moisture condition of $T = 26$ °C and RH = 80%; while it starts to recover after 250 min immersion in the moisture condition of $T = 30$ °C and RH = 60% in the PUPy45. Then a significant strain recovery is followed in both PUPy53 and PUPy45. Finally, more than 95% strain recovery is achieved in PUPy53. It means that the BINA based polyurethane

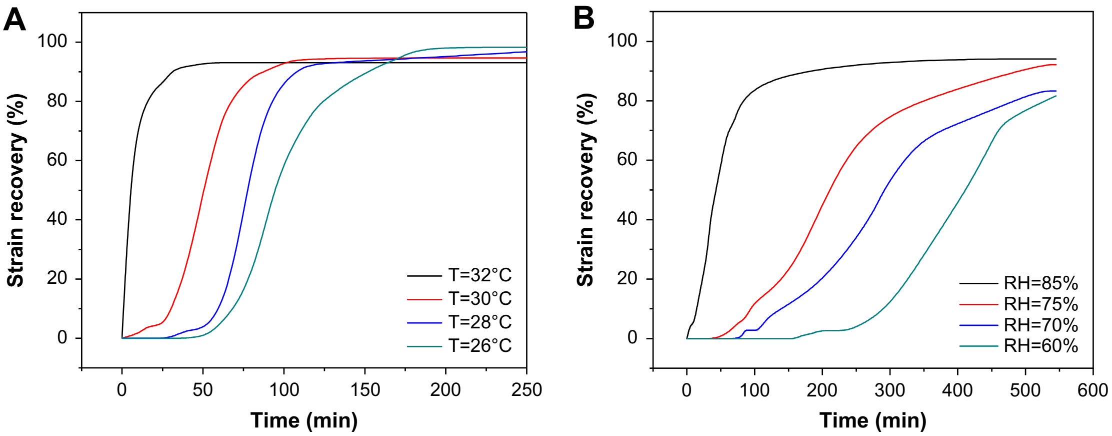
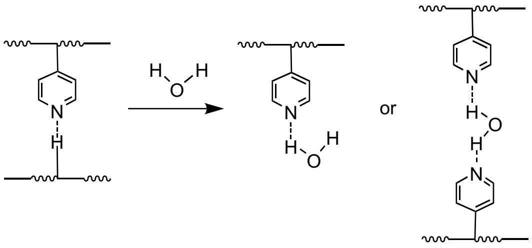


Fig. 3. Dependencies of strain recovery on time (A) at various temperatures by fixing RH = 80% for PUPy53; (B) at various RH by fixing $T = 34$ °C for PUPy45.

shows typical strain recovery properties; and the strain recovery is induced by the moisture.

In addition, it can be observed in Fig. 3(A) that the temperature influences the strain recovery significantly. As the temperature increases, the strain recovery curves depending on time moves to short time range, e.g. PUPy53 recover its 95% strain within 10 min at 32 °C under the RH = 80%. Because the moisture absorption is very quick at the higher temperature due to their higher diffusion coefficient as mentioned above. Furthermore, it is also observed in Fig. 3(B) that the RH also influences the strain recovery greatly. PUPy45 recovers its close 90% strain within 50 min under the RH = 85%; whereas under the RH = 65%, the strain recovers little within the first 250 min; and the final maximum strain recovery is less than 80%. This strain recovery tendency is consistent with the tendency of moisture absorption as described above: higher temperature shows a high moisture absorption speed as well as a short strain recovery time; higher RH results in higher maximum moisture absorption as well as higher strain recovery. Thus, it is confirmed that the strain recovery is induced by the moisture in the PUPy.

Aiming at investigating the molecular mechanism of moisture absorption as well as the influence of moisture on the structure, FT-IR spectra of sample PUPy53 at different times were recorded after it was dried completely. From the FT-IR spectra, it can be found that as the time increases, the density of frequency for water vibration increases quickly within the first 20 min. Finally, it reaches to a stable density. This result indicates that the PUPy53 reaches its equilibrium state within 20 min under the condition of RH = 80% and $T = 30$ °C. This moisture absorption time is very close to the strain recovery time for PUPy53. It is confirmed that the moisture absorption results in the strain recovery. At the same time, the frequencies for the vibration of pyridine ring are also observed to shift to higher frequency. FT-IR spectra of PUPy53 at different times at the frequency range of 1015–985 $\mathrm{cm^{-1}}$ under the condition of $T = 30$ °C and RH = 80% is presented in Fig. 4. It is observed that the moisture absorption results in the breathing vibration frequency of pyridine ring shifts from 994 $\mathrm{cm^{-1}}$ to 999 $\mathrm{cm^{-1}}$. At the equilibrium state, the frequencies for pyridine ring appear at 3060 $\mathrm{cm^{-1}}$, 1603 $\mathrm{cm^{-1}}$ and 999 $\mathrm{cm^{-1}}$. These frequencies are very close to the frequencies of pyridine ring observed at the high temperature in temperature-dependent FT-IR [11]. These results indicate that the hydrogen bond in the pyridine ring is free or very weak when it absorbs moisture. That is, the moisture results in the dissociation of hydrogen bonding between pyridine ring and N–H of urethane group.



Scheme 2. Illustration of moisture absorption at the pyridine ring.

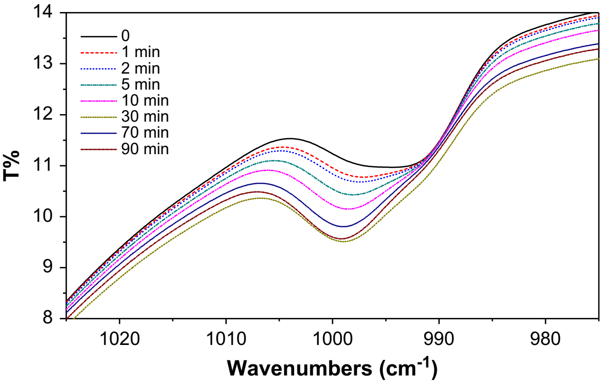


Fig. 4. FT-IR spectra for vibration of pyridine ring.

In the previous models for the interaction of water with hydrophilic polymers, it is generally hypothesized that water molecules are either bond to specific polymer chain sites or free to disperse them homogeneously throughout the amorphous polymer matrix [8]. However, in the PUPy, based on the FT-IR analysis, the moisture absorption mechanism can be explained with the theory of dynamic combinatorial chemistry or constitutional dynamic chemistry proposed by J.M. Lehn, which relies on the selection of the thermodynamically most stable product from an equilibrating mixture [16]. The illustration of moisture absorption mechanism in the pyridine ring is proposed in Scheme 2. Under the stimulus of H_2O, the pre-formed hydrogen bonding N–H···N–Py at dried state is replaced by a more adaptive hydrogen bonding. The resulted pyridine ring tends to be protonized by water (O–H···N–Py) or be linked via hydrogen bonding of the bridged water molecules (Py–N–H···O–H–O···H–N–Py), which shows a long bond distance [17]. As a result, the interaction gets weak, and the stiffness or modulus of polymer gets soft as the moisture absorption increases. Finally, similar to the dissociation of hydrogen bonding induced by temperature, the replacement of hydrogen bonding in the pyridine ring also results in the shape recovery. Therefore, the hydrogen bonding between pyridine ring and N–H of urethane group is used as the moisture-sensitive "switch", whereas the formed hard phase via hydrogen bonding between urethane groups are the physical netpoints in the moisture-sensitive SMPU.

4. Conclusions

In this communication, novel moisture-sensitive SMPU was synthesized from HDI, BDO and BINA. Results show that the BINA based SMPUs have excellent moisture absorption properties which are not only influenced by the temperature, but also by the RH. As a result, high strain recovery with fast recovery speed can be obtained. Finally, FT-IR spectra provide a proof to show the mechanism of moisture-sensitive SME which is based on the dissociation or disrupt of hydrogen bonding in the pyridine ring induced by moisture absorption.

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