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Introduction

Shape memory polymers (SMPs) possess the capability of changing their shape upon application of an external stimulus, among which the thermally induced SMPs have focused most of the attentions.¹⁻¹⁰ The classical SMPs, changing their shape in a predefined way from a single temporary shape (B) to another permanent shape (A), are called as dual shape polymers (DSPs). DSPs usually include two domains, one is the fixing domain to hold the permanent shape and the other is the switching domain to determine the temporary shape. Currently another type of emerging multiphase polymers, named as triple-shape polymers (TSPs), can change from the first (B) and second (C) temporary shape to their permanent shape (A) consecutively during heating in recovery process. The property is very important for their applications in controlled drug release, intelligent medical devices, textile and assembling systems.¹¹

To date TSPs have been reported as the following types: a network with two different covalently linking polymer,¹²⁻¹⁴ composites,^{15,16} bilayer epoxy polymer,¹⁷ side-chain liquid crystalline networks,¹⁸ nafion with a single but very broad T_{g} ,^{19,20} even a V-shaped gradient copolymer with broad T_{g} range.²¹ The general concept of the triple-shape capability is

Use of intermolecular hydrogen bonding to synthesize triple-shape memory supermolecular composites[†]

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We have developed a simple and controllable strategy to synthesize a triple-shape memory supermolecular composite (SMPU-INCh-*n*) through H-bonding interactions between a polymer and mesogenic units. The polymer is shape memory polyurethane (SMPU) with carboxyl groups; the mesogenic unit, named as cholesteryl isonicotinate (INCh), is a liquid crystal compound with an electron-rich pyridine ring. The H-bonding interactions between carboxyl and pyridine ring are proved by FT-IR spectroscopic analysis and ¹H solid-state NMR. The introducing of INChs promotes the bonded PU segments to change into glassy form by restraining the movement of polymer chains, which is responsible for the triple-shape memory property. Therefore, the composite presents excellent triple-shape effect, and may be of great potential for applications in the biomedical field.

> based on materials with at least two distinct switching domains or a broad thermal-transition range. As well-known DSPs have one switching domains, addition of a second type of switching domain in a DSP can endow it a triple-shape memory property. Forming the second switching domain includes two approaches. One is the chemical synthesis such as covalently linking two polymer,^{12,22} or a multiblock copolymer.²³ The another is physical incorporation such as incorporated fibers into a SMP matrix,¹⁵ or fabricated bilayer epoxy polymer.¹⁷ For the former approach, it is very complex due to the conjugation of a polymer segment or a block into DSPs by chemically covalent synthesis. For the physical incorporation, it has been recognized that molecular recognition processes between different molecular species through non-covalent interactions are advantageous for the design of functional molecular aggregates.²⁴ Hydrogen bonds (H-bonds) as an ideal non-covalent interaction have often been used to construct supermolecular architectures for its high selectivity and direction.^{25,26} It offers a simple and controllable way to constitute a desired block in DSP by H-bonds interaction. Since Kato and coworkers first exploited H-bonding between carboxylic acids and pyridine to induce liquid crystallinity, the carboxylic acid and pyridine complex has been widely investigated.27-29

> Inspired by it, we developed a new strategy to prepare a triple-shape memory polymer with mesogen units bonded to polymer through H-bonding interactions. Here, a new shape memory polyurethane (SMPU30) with carboxyl groups was synthesized by using 30 mmol 2,2-dimethylol propionic acid (DMPA) instead of the traditional butanediol as the chain extender as shown in Scheme 1.³⁰ The content of carboxyl groups in SMPU30 was measured according to the colorimetric

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[†] Electronic supplementary information (ESI) available: Table S1–S2, Fig. S1–S4, Movie 1. See DOI: 10.1039/c3ra00091e

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Scheme 1 Synthesis route of composites in this paper.

method with Toluidine Blue O staining as previously reported.³¹ Simultaneously, a liquid crystal compound with an electron-rich pyridine ring was synthesized, named as cholesteryl isonicotinate (INCh). INCh was selected for its excellent biocompatibility and good self-assembly as a liquid

crystal molecule. The supermolecular composite (SMPU30-INCh-*n*) was obtained by introducing INChs into the SMPU30 *via* the stronger H-bonding interactions between carboxyl groups of PU segments and pyridine rings of INChs. *n* stands for the molar ratio of INChs to the resultant carboxyl groups of SMPU30. In SMPU30, the PCL segments act as the switching domain and the PU segments with carboxyl groups are as the fixing domain. Based on the dual shape memory effect of SMPU30, we anticipate that the triple-shape memory property can be generated by the formation of the new mesogen pendant PU segments as a second fixing domain via adding INChs into the PU segments attached by the H-bonding

 ϵ -Caprolactone (CL), Stannous octoate [Sn(Oct)₂, 95%] were purchased from Aldrich. CL was purified by drying over CaH₂ and distilled under reduced pressure. 4,4-Diphenylmethane diisocyanate (MDI), was purchased from Tokyo Chemical industry Co. LTD. 2,2-Bis(hydroxymethyl) propionic acid (DMPA, 99%) was purchased from Acros Organics, USA. Ethylene glycol (EG), pentaerythritol (PER), N,N-dimethyl formamide (DMF), isonicotinic acid, cholesterol were purchased from Kelong chemical reagent factory in Chengdu. EG was distilled under a reduced pressure. DMF was dried over CaH₂ for 2 days at room temperature, distilled under vacuum, and stored in the presence of 4 Å molecular sieves. Unless otherwise noted, all chemical reagents were obtained from commercial suppliers and used without further purification.

Preparation of PCL diols (HO-PCL-OH). CL (360 mmol), EG (10 mmol) and $Sn(Oct)_2$ (0.1 mmol) were added into a single neck flask with stirring and vacuum for 4 h at room temperature. Then the flask was put into an oven for reacting for 6 h at 150 °C. After cooling, the polymer was dissolved in a small amount of CHCl₃ and was precipitated into cold methanol. Finally the polymer was dried in vacuum for 48 h. Molecular weight of PCL diols is about 4100 Da measured by ¹H NMR.

Synthesis of SMPU30. PCL diols (4 mmol), MDI (8 mmol), $Sn(Oct)_2$ (0.02 mmol) and 50 mL of DMF were charged into a dried flask and reacted for about 1 h at 80 °C. Then, DMPA (30 mmol) and MDI (30 mmol) were successively added, with the reaction being maintained at the same temperature for 2 h, after that pentaerythritol (2 mmol) was added. Reacted at the same temperature for another 1 h, the solution was poured out and evaporated at 80 °C for 8 h; then obtained films were further dried under vacuum at room temperature for another 48 h.

Synthesis of INCh. Isonicotinic acid (16 mmol) and SOCl₂ (20 mmol) react at 70 °C for 4 h, then distilled the excessive SOCl₂ under reduced pressure. Later, 16 mmol of cholesterol in 40 mL of CH₂Cl₂ containing 1 mL of pyridine was dropped in the reaction bottle soaked in ice bath for 0.5 h. After stirring at room temperature for 1 h, the solution was refluxed for another 8 h. After it was finished and cooled to room temperature, the reaction solution was washed by distilled water two times and collected the organic solution. After removing the solvent, the solid was purified by column chromatography and recrystallized from ethanol, dried under vacuum for 24 h. Finally the INCh white powder was acquired. IR (KBr): v = 2952(s), 2892(s), 2867(s), 1724 (vs.; vs.(C=O)), 1560, 1469 (m; aromatic C=C), 1281(s; vas(C-O-C)), 1123 cm⁻¹ (s; *vs.*(C–O–C)). ¹H NMR (CDCl3): *δ* = 8.78 (s, 2H, Ar*H*), 7.88 (s, 2H, ArH), 5.43 (m, 1H, CH=C), 4.88 (m, 1H, C(O)OCHCH₂), 2.48 (m, 2H, C(O)OCHCH₂), 2.01-0.69 (41H, CH, CH₂, CH₃). Synthesis of SMPU30-INCh-n. SMPU30 and INCh were

dissolved in appropriate amount of DMF and CHCl₃ respectively. The two solutions were mixed and stirred for 1 h at 70 °C. Then the solution was poured out and evaporated to remove the DMF at 80 $^{\circ}$ C for 8 h to form a film. To remove the organic solvent completely, the film was dried under vacuum at room temperature for 48 h.

Characterizations

The structure of INCh and molecular weights of the PCL diols were determined by ¹H NMR (Bruker Unity-400, Mn). FT-IR spectroscopic analysis was carried out with a Nicolet 5700 FTIR spectroscope (Thermo Electron, USA). Each sample for infrared analysis was prepared by scraping powder to press a pellet with KBr. Samples were heated from 20 °C to 180 °C. After reaching each desired temperature and isothermy for 1 min to record, the infrared spectra were recorded between 4000 and 400 cm⁻¹ with the resolution of 4 cm⁻¹. ¹H solidstate NMR experiments were performed on a Bruker Avance III spectrometer with frequencies of 400 kHz, Hahnecho MAS measurements, a 1.3 mm MAS probe and spinning of 60 kHz. Thermal analysis was conducted by using a differential scanning calorimeter (DSC-Q100, TA, USA) at heating and cooling rates of 10 °C min⁻¹. All runs were carried out with samples of ca. 2-5 mg. 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 properties were determined with a dynamic mechanical thermal analyzer (DMA-Q800, TA, USA), in the tensile resonant mode, at a heating rate of 3 $^{\circ}$ C min⁻¹ and 1 Hz.

Results and discussion

The confirmation of hydrogen bonded interaction

H-bonding interactions between the NH groups and C=O groups in single polyurethane polymer have been studied.³²⁻³⁴ In general, the mechanism of H-bonding interaction is very complex, especially for polymers. In SMPU30, there are several kinds of H-bonding pairs, such as H-bonding interaction between COOH dimer, COOH and C=O (C=O in urethane and PCL), NH and C=O (C=O in urethane, PCL and COOH). After introducing INCh, both the electron-rich pyridine ring and ester group of INCh compete with the original C=O of SMPU30 to form new H-bonding pairs. To confirm it, we selected polyethyleneimine (PEI) without C=O and with NH to replace SMPU30 to investigate whether there exists H-bonding interactions between PEI and INCh. From the FT-IR spectrum in Fig. S1, ESI[†], it can be clearly seen that there are no H-bonding interactions between C=O in ester group of INCh and NH of PEI because the C=O stretching does not change. In addition, no H-bonding interaction can be found between pyridine ring

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Fig. 1 (a) FTIR spectra of (A) INCh, (B) SMPU30 and (C) SMPU30-INCh-0.7; (b) magnification of the circle part of (a); (c) temperature-programmed IR of SMPU30; (d) temperature-programmed IR of SMPU30-INCh-0.7; (e) ¹H solid-state NMR of INCh, SMPU30 and SMPU30-INCh-1.0.

of INCh and NH of PEI due to the absence of red-shifting of the NH stretching. Therefore, INChs can form H-bonding pairs only with COOH groups in SMPU30-INCh-*n* composites.

In Fig. 1a, the stretching peak of NH at 3317 cm⁻¹ and C=O at 1724 cm⁻¹ have no shift after introducing INChs into SMPU30 but during the region from 2800 to 1800 cm^{-1} , the OH stretching is obviously changed. Compared with the OH stretching peaks of carboxylic acid dimer at 2645 and 2535 cm⁻¹ in SMPU30 (Fig. 1b), in the SMPU30-INCh-0.7 they become weaker and a new peak at 1905 cm⁻¹ appears due to the strong interaction between COOH and pyridine ring according to ref. 35. It suggests that the pyridine ring prefers to form the interaction with COOH, resulting in a decrease of amount of the COOH dimers. The bond energy between the nitrogen of pyridine ring with lone pair electrons and the proton of COOH is as strong as 45 kJ mol⁻¹ to form the stable H-bonding system.²⁵ Fig. 1c, 1d show temperature-programmed IR spectra of SMPU30 and SMPU30-INCh-0.7, further confirming the formation of hydrogen bonding pairs. In SMPU30, the OH stretching peaks of carboxylic acid dimers at 2645 and 2535 cm⁻¹ gradually weakened as the temperature increased, and they disappeared above 60 °C. In SMPU30-INCh-0.7, the peak at 1905 cm^{-1} for the typical H-bonding interaction between COOH and pyridine ring also gradually weakened as the temperature increased but it still existed

obviously after 100 °C. The results indicate that the H-bonding interaction between COOH and pyridine ring is stronger than that between carboxylic acid dimer.

The H-bonding interaction between COOH and INCh was further confirmed by ¹H solid-state NMR (Fig. 1e). In compound INCh, the chemical shifts of 6.931, 7.976, 9.048 and 9.858 ppm are attributed to four types of protons in pyridine ring, respectively. In SMPU30, the chemical shifts of 7.087 and 7.420 ppm are ascribed to the benzene protons of isocyanate groups, 8.021 ppm for the protons of NH groups. The protons of COOH groups in SMPU30 don't appear due to the fact that they cannot be detected by 1H solid-state NMR. After adding INCh into SMPU30, a new chemical shift of 10.024 ppm appeared, which was attributed to the protons of COOH groups bonded to the pyridine ring of INCh, further demonstrating the formation of the H-bonding.

In SMPU30-INCh-*n*, the amount of COOH bonded to INCh were estimated by curve fitting of IR spectra in the C=O stretching region ($1800-1640 \text{ cm}^{-1}$) at room temperature (Fig. 2a), and the results are summarized in Table S1, ESI.[†] The procedures afford a best fit of the original curve, and the resulting correlation factors for all the fittings are over 0.998. From the curve fitting results, the total COOH divided into three peaks. The peak during 1709–1704 cm⁻¹ attributed to the COOH bonded to the C=O in ester of PCL and urethane of

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Fig. 2 (a) Curve fitting results for IR spectra in the C=O stretching region ($1800-1640 \text{ cm}^{-1}$) at room temperature. (b) Proportions of the total COOH for each composite, including COOH dimers, COOH hydrogen bonded to INCh and COOH hydrogen bonded to C=O in ester of PCL and urethane of PU segments, obtained from curve fitting the IR spectra recorded at room temperature.

PU segments, 1703–1696 cm⁻¹ attributed to the COOH bonded to C=O of INCh and 1692–1685 cm⁻¹ attributed to the COOH in dimers. Proportions of total COOH in SMPU30-INCh-*n* are demonstrated in Fig. 2b. For SMPU30-INCh-0.7, the amount of COOH dimers deceased obviously compared to SMPU30 and a new amount of COOH bonded to INCh appeared, which

responding to the results of IR spectra (Fig. 1b) shows that INCh disturbed the COOH dimers interaction and formed the new hydrogen bonding between COOH and INCh. For SMPU30-INCh-1.0, the amount of COOH bonded to INCh is nearly the same as SMPU30-INCh-0.7. It means that more INCh don't prefer to form more hydrogen bonds between



Fig. 3 Polarization microscope (POM) photographs of INCh (a) 150 °C, (b) 110 °C; SMPU30 (c) 20 °C; SMPU30-INCh-0.7 (d) 110 °C, (e) 20 °C; SMPU30-INCh-01.0 (f) 110 °C, (g) 20 °C; SMPU30-INCh-1.5 (h) 110 °C, (i) 20 °C.

COOH and INCh. As the ratio of introduced INCh increased to 1.5, the amount of COOH bonded to INCh decreased. The results clearly showed that SMPU30-INCh-0.7 has the most suitable amount of INCh for these composites. The over added INCh in composites, such as SMPU30-INCh-1.0 and SMPU30-INCh-1.5, prefer to form the mesogen domain, which will disturb the hydrogen bond interaction for the amount of COOH bonded to INCh.

Thermal properties

Fig. S2, ESI[†] displays the DSC curves of these compounds, and the data is also summarized in Table S2, ESI[†]. In DSC curve of INCh, there is only a melting point (T_{mH}) at 173 °C during heating while there are two peaks on cooling, one appeared at 167 °C called clearing point ($T_{\rm cp}$) and the other appeared at 133 $^{\circ}$ C called crystalline point (T_{cH}). Observed from polarization microscopy (POM), the typical fan-like texture of cholesteric phase (N* phase) was appeared on cooling during 167-133 °C (Fig. 3a). Further cooling, INCh presented the colourful texture due to the crystallization as shown in Fig. 3b. SMPU30 shows one melting point (T_{mL}) and one crystalline point (T_{cL}) , which are ascribed to the melting and crystallization of PCL soft segments, while the phase transition of PU segments are not observed in DSC curves as previously reported.³⁶ After INCh introduction, SMPU30-INCh-n exhibited two melting points $(T_{\rm mL} \text{ and } T_{\rm mH})$ and two crystallization points $(T_{\rm cL} \text{ and } T_{\rm cH})$. However, the T_{cp} of INCh from isotropic phase to the mesophase was not observed, indicating that the INCh attached to COOH of SMPU30 could not form the mesophase.

All samples were firstly heated to 180 °C for all component melting, and then cooled to 10 °C to observe the crystalline procedure. Crystallization of SMPU30 was only observed on cooling to 20 °C (Fig. 3c) according to the $T_{\rm cL}$ in the DSC curve, which is attributed to the crystallization of PCL segments. For SMPU30-INCh-0.7, the crystallization appeared when first cooling down to $T_{\rm cH}$ (Fig. 3d), which is ascribed to INChs attached to PU segments. The crystallization texture is

different from that of free INCh monomers. Go on cooling to 20 °C, the crystallization of the bonded INChs was disturbed due to the fact that the PCL segments crystallized (Fig. 3e). For SMPU30-INCh-1.0 and SMPU30-INCh-1.5, the crystallizations were also observed after cooling down to $T_{\rm cH}$ (Fig. 3f, 3g) and $T_{\rm cL}$ (Fig. 3h, 3i), respectively. For SMPU30-INCh-1.5 with the most INCh content, the crystalline texture looks more like that of free INCh monomers because the content of INCh is beyond the amount of COOH hydrogen bonded to it, responding to the results in Fig. 2b.

Tensile testing

Tensile stress, strain and Young's modulus of SMPU30 and the composites are presented in Fig. S3, ESI.[†] The maximum tensile stress increased with the introduction of INCh with suitable content. When the content of INChs is more than that of bonded carboxyl groups, such as the SMPU30-INCh-1.5, the tensile stress decreased. Therefore, the H-bonding interactions in the supermolecular composite are helpful to improve its properties when the amount of INChs is matched with carboxyl groups. The Young's modulus of all the composites was enhanced compared with SMPU30, and the Young's modulus of SMPU30-INCh-0.7 was the highest with 131 MPa.

Dynamic mechanical analysis (DMA)

DMA was performed to evaluate the shape memory properties of the composite. Fig. 4a, 4b show the tensile storage modulus and tan delta (tan δ) as a function of temperature for SMPU30 with different INCh contents. DMA was tested from -70 °C to 100 °C, but heating above 80 °C the tan δ values of the materials still increased, suggesting that the polymers became viscous and were not suitable for assessing the shape memory effect. Therefore, the temperature ranging from 20 to 80 °C was employed to investigate the shape memory effect.

Upon heating from 20 to 80 °C, both the SMPU30 and SMPU30-INCh-n composites exhibit two thermal transitions and three plateaus as shown in Fig. 4a. All of the second step transition of PU segments from glassy to rubbery state was not observed in DSC curves but appeared in DMA curves. The first step transition from plateau 1 to 2 was corresponding to the thermal transition of $T_{\rm mL}$ in DSC. In the plateau 1, the PCL segments were semi-crystallized and PU segments were glassy; while in the plateaus 2, the PCL segments melted and PU segments were still glassy. Go on heating, the second step transition from plateau 2 to 3 appeared. For SMPU30, the second step transition corresponded to the all PU segments from glassy to rubbery. After the second transition above 60 °C, the tan δ of SMPU30 turned bigger. As the tan δ corresponds to the strain energy dissipated by viscous friction, a large tan δ implies that the material is more likely viscous than elastic. Therefore, SMPU30 are viscous rather than rubbery and thus it loses the capacity of holding the shape in plateau 3, which are also in line with the result of temperature-programmed IR that the H-bonding interactions between COOH dimers were disturbed when the temperature was above 60 °C (Fig. 1c). For SMPU30-INCh-n, the second transition is corresponding to the thermal transition of PU segments unbonded with INChs from glassy to rubbery. In plateau 3, the PU segments bonded with INCh are still glassy as the hard domain to hold the



Fig. 4 Storage modulus (a) and tan δ (b) vs. temperature for the SMPU30 and SMPU30-INCh-n; (c) and (d) shape fixing and recovery of SMPU30-INCh-n. A is original shape, B is the first temporary shape, and C is the second temporary shape.

shape. The storage modulus of SMPU30-INCh-*n* was bigger than that of SMPU30 after the first step transition. The reason may be that the crystalline domains formed by the attached INChs restrain the movement of PU segments like rivets. The PU segments bonded with INCh have higher stiffness than the unbonded ones, resulting in the increase of the storage modulus of SMPU30-INCh-*n*.

Shape memory effect

In shape memory process of SMPU30, PCL segments act as the reversible phase to change the shape and PU segments act as the stationary phase to fix the permanent shape. By introducing INChs into SMPU30 through H-bonding interactions, the unbonded PU segments of SMPU30 transform to the second switching domain above 60 °C. Thus, SMPU30-INCh-*n* composites possess two thermal transitions as we expected, which can be employed to trigger the potential triple-shape memory behavior. One is the first step transition around 55 °C for recovery of shape C to shape B, the other is the second step transition around 65 °C for recovery of shape A.

The shape fixing ratio (R_f) and shape recovery ratio (R_r) are tested as mentioned in Fig. S4, ESI[†] according to the literature.³⁷ R_f and R_r are listed in Fig. 4c, 4d, respectively. For all samples, the shape fixing ratio of shape A to shape B (<70%) is lower than that of shape B to shape C (>97%), and the shape recovery ratio of shape B to shape A (<80%) is also lower that of shape C to shape B (>80%). For SMPU30, there is only one shape memory procedure because the shape B hardly recovered to shape A, which is corresponding to the result in

DMA. From shape A to shape B, the fixing ratio rises with the content of INChs increasing. It suggests that the INChs play an important role in holding the shape B. However, the properties are almost the best when the content of INChs is matched with the amount of COOH groups of SMPU30. If the content of INChs is excessive, it will also disturb the recovery behavior of SMPU30 backbone, resulting in the recovery ratio of SMPU30-INCh-1.5 decreasing.

Sample SMPU30-INCh-0.7 was chosen to undergo further analysis of the shape memory behavior. The sample of SMPU30-INCh-0.7 was cut into a stripe with an I shape. The stripe was first immersed in a water bath at 70 °C for one minute and held the I shape. Then the sample was fixed to a U shape at 55 °C and the S shape at 20 °C. After immersing the stripe of S shape back into the water bath at 55 °C, it quickly recovered to U shape. When go on immersing into the water bath at 70 °C, the stripe recovered to its permanent I shape, as shown in Fig. 5a. Movie 1 (ESI†) also shows the dynamic tripleshape memory recovery process.

Fig. 5b shows the proposed mechanism of triple-shape memory behavior of SMPU30-INCh-*n*. PCL segments are melted around 55 °C while the PU segments become viscoelastic state above 65 °C. The H-bonded INCh crystalline domains are also melted above 120 °C, moreover the crystalline domains restrain the movement of PU segments bonded with them. When sample is heated to 70 °C, the PCL segments are melted and PU segments unbonded to INChs are still rubbery, while the PU segments bonded with INChs are glassy as the fixed domains to hold the shape A. After deformation,



Fig. 5 (a) Illustration of the triple-shape memory effect of SMPU30-INCh-0.7; (b) proposed mechanism of triple-shape memory behavior in SMPU30-INCh-*n*.

cooling to 55 °C, the unbonded PU segments become glassy and fix the shape B. Deformation again, cooling to 20 °C, the PCL segments are crystallized and fix the shape C. During heating, when the temperature is above 55 °C the PCL segments are melted but the PU segments are still glassy, thus the shape B is recovered. Go on heating to 70 °C, the PU segments unbonded to INChs are changed from glassy to rubbery, while the PU segments bonded to INChs are still in the glass state because of the inhibition of INCh crystalline domain, as a result the shape A is recovered.

Conclusions

In summary, the supermolecular composites with triple-shape memory properties were successfully synthesized by introducing INChs into SMPU30 polymer through a strong H-bonding interaction between COOH of SMPU30 and pyridine ring of INCh. The interaction is confirmed by FT-IR analysis and ¹H solid-state NMR. The H-bonding interaction in the composite is helpful to improve the mechanical properties. The introducing of INChs promotes the bonded PU segments to change into glassy state by restraining the movement of polymer chains, which is responsible for triple-shape memory property. To the best of our knowledge, it is the first time to synthesize supermolecular composites with triple-shape memory function based on the H-bonding interaction between PU and mesogen. This study has great potential for providing an effective and simple way to design and develop triple-shape memory polymers.

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