



Polymer Communication

A novel supramolecular shape memory material based on partial α -CD-PEG inclusion complex

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ABSTRACT

A novel supramolecular shape memory material was prepared based on partial α -CD-PEG inclusion complex, which contains α -CD-PEG inclusion crystallites as a fixing phase and naked PEG crystallites as a reversible phase. The recovery ratio of these materials could reach 97%. The characteristics of the material were investigated and a mechanism for the shape memory behavior was proposed.

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1. Introduction

Shape memory refers to the ability of certain materials to remember their original shape even after rather severe deformations. In recent years, shape memory polymers, especially thermally stimulated shape memory polymers, have received increasing attention because of their wide availability and broad possible applications [1–3]. In principle, thermally induced shape memory polymers should have two phases on the molecular level: a thermally reversible phase and a fixed phase. The thermally reversible phase serves as a “switch” and exhibits a lower transition temperature (T_{trans}). The fixed phase shows a higher thermal transition temperature which is responsible for determining the permanent shape. Most current shape memory polymers have been introduced two phases' structure by covalent linking method [3–5]. Only more recently, shape memory materials based on noncovalent self-assembly have been developed, which open the way to give classic general polymers' shape memory function through supramolecular assembly. However, the relative reports are few and the polymer complexes are limited to polyelectrolyte complexes and hydrogen-bonded polymer–poly(ethylene glycol) (PEG) complexes [6,7]. Here we report a novel shape memory inclusion complex, which is based on the inclusion of polymer chain and cyclodextrins (CDs). It is well known that the CD inclusion complex guests range from nonpolar to polar and from hydrophilic to hydrophobic polymers [8]. So this

method is expected to give much more general polymers' shape memory function compared with other supramolecular shape memory systems. Up to now, to the best of our knowledge, no similar research has been reported.

Last decade, CD–polymer inclusion complexes (ICs) with necklace-like supramolecular structures formed by cyclodextrins (CDs) and polymers have attracted special interest. A lot of polymers such as polyether, polyester, polyalkene, polyaniline, polysiloxane have been found to be able to form inclusion complexes with different types of CDs [9–12]. CD–polymer ICs are known having a thermally stable crystalline structure due to the strong hydrogen-bonding formation between adjacent CDs on the polymer chains. Generally the complete CD–polymer ICs have no melting behavior, but only decompose above 300 °C [13,14]. This particular thermal property serves as a great source of inspiration to us: if designed a kind of partial CD–polymer IC containing both thermally stable CD–polymer inclusion segment and thermal sensitive naked polymer segment, does it exhibit shape memory effect?

In this study, we select poly(ethylene glycol) (PEG) as a model for the construction of our supramolecular system, because the low melting temperature of PEG ($T_m = 50\text{--}70$ °C) is suitable as T_{trans} for the real application of shape memory materials.

2. Experimental section

2.1. Preparation of partial α -CD-PEG inclusion complexes

α -CD (from Sigma) and PEG ($M_w = 6000, 35,000, 100,000, 200,000, 300,000$) (from Aldrich Chemical Co.) were used

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Table 1
Composition of partial α -CD-PEG inclusion complex films

Notation	Average M_w of PEG	Mass ratio of inclusion segments/exclusion segments	
		Theoretical	Actual ^1H NMR analysis ^a
P2060	200,000	60/40	59.3/40.7
P2050	200,000	50/50	49.0/51.0
P2040	200,000	40/60	39.5/59.5
P2030	200,000	30/70	27.6/72.4
P3050	300,000	50/50	49.8/50.2
P1050	100,000	50/50	51.2/48.8
P3550	35,000	50/50	13.0/87.0
P06050	6000	50/50	13.6/86.4

^a ^1H NMR analysis result is the average value of three measurements. Mass ratio of inclusion segments/exclusion segments = $(nM_w(\alpha\text{-CD}) + 2nM_w(\text{EO})) / (M_w(\text{PEG}) - 2nM_w(\text{EO}))$ (n = the number of α -CD in a single PEG chain).

as-received. Films of partial CD-PEG were prepared by casting. As an example, the preparation of P2060 (see Table 1 for notation) is described: bulk PEGs ($M_w = 200,000$) (380 mg) were added to a predetermined amount of α -CD aqueous solution (500 mg, 0.04 g/mL). The feed ratio of PEG/ α -CD was made for maintaining the mass ratio of inclusion/exclusion segments in film to 60:40. After stirring for 60 min, the film was prepared by casting under atmospheric conditions at room temperature. Slow evaporation of solvent took over 48 h. The resulting film was washed with water several times to remove the free PEG and uncomplexed CD, and then was dried under vacuum at 40 °C. The complete α -CD-PEG ($M_w = 1000$) was prepared as described by Harada et al. [14].

2.2. Measurements

The ^1H NMR spectra were recorded on an Advance Bruker 600 NMR spectrometer at 600 MHz at room temperature. The crystalline changes in the partial CD-PEG inclusion complex formation were confirmed by X-ray diffraction measurements, which were performed by using Cu-K α irradiation with PHILIP X'Pert MPD (50 kV; 35 mA; 2°/min). Thermal analyses were performed using NETZSCH DSC 204 at a heating rate 10 °C/min. Thermogravimetric analyses were undertaken using a TA instrument Q500. Samples were heated at 10 °C/min from room temperature to 500 °C in a dynamic nitrogen atmosphere at a rate 70 mL/min. Atomic force microscopy (AFM) measurements were performed on Nanoscope Multimode SPM with NanoScope IIIa controller, Veeco Instruments (USA.). The images were taken with the tapping mode. Structural changes of P2060 with heating were observed and photographed through a polarized optical microscope (LEITZ LABORUX 12POL) equipped with a digital camera and a heating stage. Dynamic mechanical analysis was performed using a DMA Q800V7.1 in the strain mode at a fixed frequency of 10 Hz and under nitrogen gas purging. The measured specimen was heated from 30 °C to 80 °C.

2.3. Shape memory behavior test

The method of evaluating the shape memory effect was according to Liu et al. [7]. The specimen was deformed to an angle θ_i at 90 °C and then quenched to room temperature to maintain the deformation. The deformed sample was then heated to the test temperature (48–90 °C) rapidly and the change of the angle θ_f was recorded. The ratio of the recovery was defined as $(\theta_i - \theta_f)/\theta_i$.

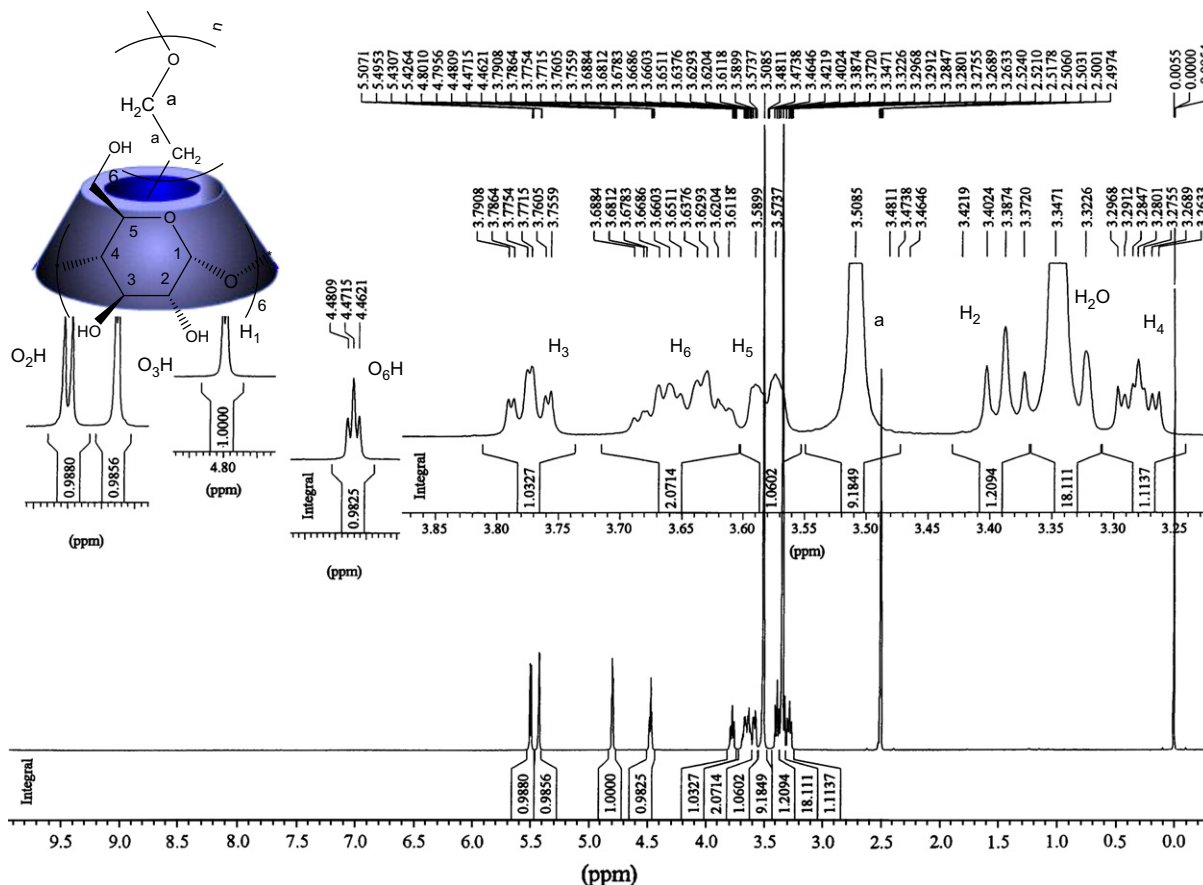


Fig. 1. ^1H NMR (600 MHz) of partial CD-PEG inclusion complex (P2060) in $\text{DMSO-}d_6$ at 25 °C.

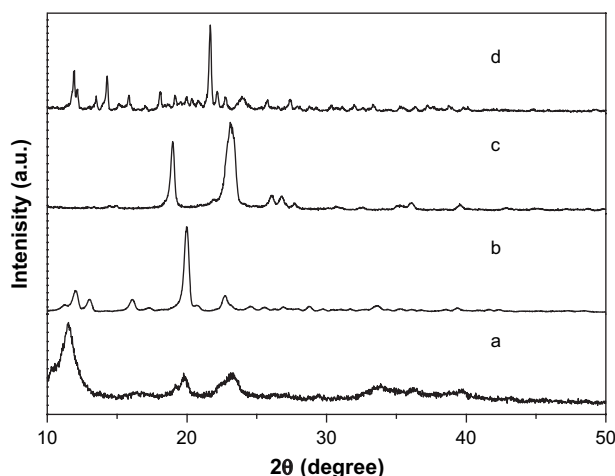


Fig. 2. X-ray diffraction patterns of (a) partial α -CD-PEG inclusion complex (P2060); (b) complete α -CD-PEG ($M_w = 1000$) inclusion complex; (c) homoPEG ($M_w = 200,000$); (d) α -CD.

3. Results and discussion

It is known that the crystalline complete α -CD-PEG inclusion complexes are usually formed by adding PEG ($M_w = 400$ – $100,000$) to a saturated aqueous solution of α -CD [13,15]. However, we have found that if the molecular weight of PEG is high enough and the ratio of CD/PEG is controlled, then the partial α -CD-PEG inclusion complex films could be obtained by casting solution at room temperature. Fig. 1 is the typical ^1H NMR spectrum of α -CD-PEG partial complex (P2060). (The ^1H NMR chemical shift data for α -CD-PEG partial complexes were shown in Supplementary data.) A comparison between the integral intensities of peaks for α -CD and those for PEG gave the compositions of α -CD-CD partial complex. Composition of the films calculated from ^1H NMR showed that the composition of α -CD-PEG partial complex film was almost consistent with the feed ratio when the molecular weight of PEG was over 100,000. However, the actual α -CD inclusion proportion of the complex films was much less than the theoretical ratio for low molecular weight PEG ($M_w = 6000$ and $M_w = 35,000$) (Table 1). This may be due to the dissociation behavior between the α -CDs and the PEG chains being more active than the inclusion behavior when the molecular weights and entanglements of PEG chains were not high enough. It should be noted that the partial α -CD-PEG inclusion complex films will dissolve in water completely when the theoretical proportion of the inclusion segment is less than 30% and hence the purification of low inclusion samples will be difficult.

A phase-separated structure was suggested as the internal structure for the partial α -CD-PEG ICs. The X-ray diffraction pattern of the P2060 showed both typical α -CD-polymer inclusion channel crystalline peak ($2\theta = 19.9^\circ$) and homoPEG crystalline peaks ($2\theta = 19.2^\circ$ and 23.3°); the α -CD crystalline peak ($2\theta = 21.5^\circ$) was absent [13,14]. This indicates that this complex was not a blend of

Table 2
Thermal properties of partial α -CD-PEG inclusion complex films

Sample	T_m ($^\circ\text{C}$)	ΔH_m (J/g)	χ_c^a (%)
HomoPEG ($M_w = 200,000$)	70.4	176.8	83.0
P2030	62.2	91.8	61.6
P2040	64.2	70.54	55.2
P2050	61.3	54.47	51.1
P2060	63.2	33.3	37.9

ΔH_0 for PEG = 213 J/g [16].

^a $\chi_c = (\Delta H_m/\text{naked PEG segments content})/\Delta H_0$.

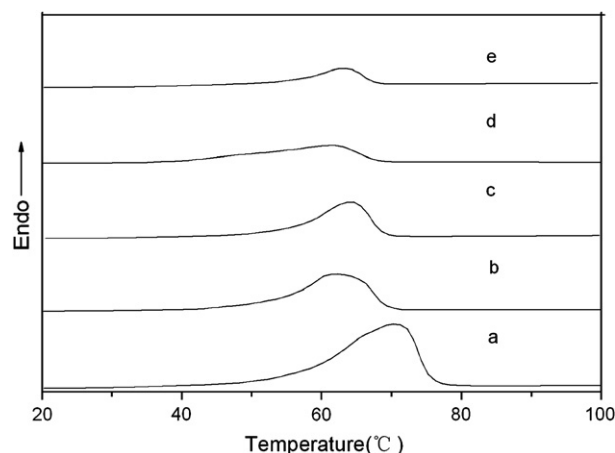


Fig. 3. DSC thermograms of (a) homoPEG ($M_w = 200,000$); (b) P2030; (c) P2040; (d) P2050; (e) P2060.

α -CDs and PEGs, but rather a partial α -CD-PEG inclusion complex simultaneously containing channel-type supramolecular crystallite (α -CD-PEG) and homoPEG crystallite (Fig. 2). The patterns of P2060 were little broad compared to those of crystalline α -CD-PEG inclusion complex and pure. This was in accordance with the fact that the P2060 contained large amorphous domains of PEG chains in the complex (As shown in Table 2).

Differential scanning calorimetry (DSC) was carried out to get the thermal information for partial α -CD-PEG ICs. As shown in Fig. 3, all of the partial α -CD-PEG ICs had a clear endothermic peak which is due to the melting of PEG crystallites. It should be noted that complete α -CD-PEG ICs studied previously present no thermal transitions before decomposition because every single polymer chain is closely included in the channels formed by α -CDs [15]. It indicated that some of the PEG segments in partial α -CD-PEG ICs were uncovered by α -CDs and formed PEG crystallite. The melting temperature (T_m) and crystallinity (χ_c) calculated from fusion enthalpy (ΔH_m) are listed in Table 2. All partial α -CD-PEG ICs exhibited lower T_m and lower χ_c than the corresponding homoPEGs. These results likely resulted from two facts: (1) the regular chain structure of PEG should be destroyed by the inclusion; (2) the crystallization of the naked PEG segments should be restricted because their mobility decreasing by its interior part residing in the CD cavity, although the inclusion parts also leading to the nucleation of the polymer [16].

The thermal stability of partial α -CD-PEG ICs, homoPEG ($M_w = 200,000$) and α -CD was investigated by thermogravimetric analysis (TGA), and the results are shown in Fig. 4. The partial

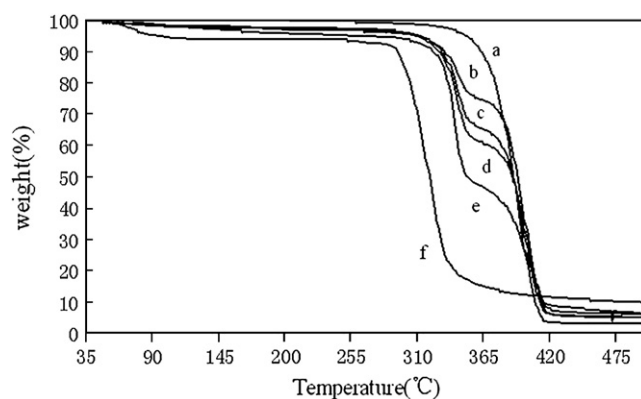


Fig. 4. TGA thermograms of (a) homoPEG ($M_w = 200,000$); (b) P2030; (c) P2040; (d) P2050; (e) P2060; (f) α -CD.

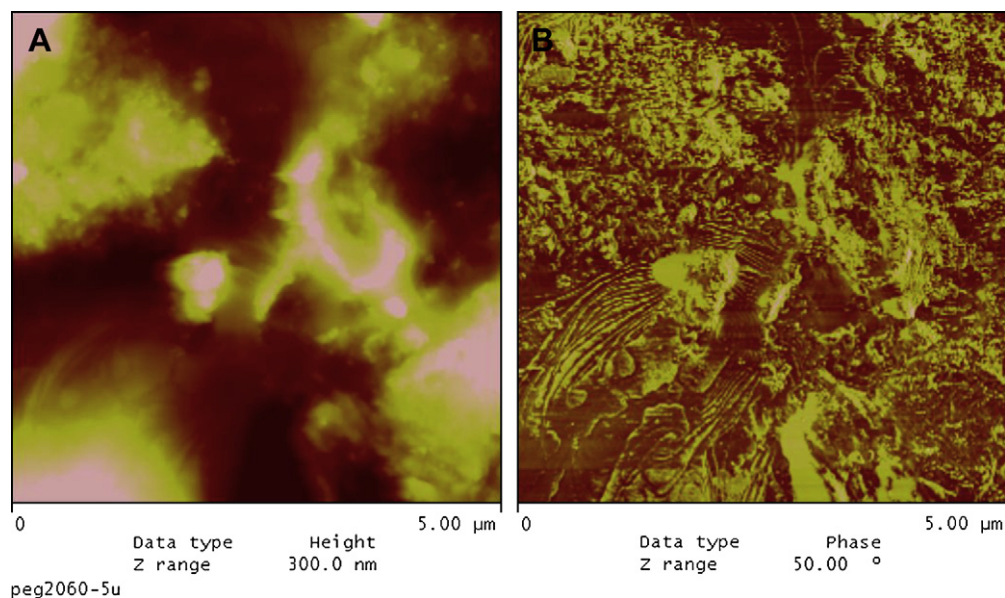


Fig. 5. AFM topographic (A) and phase (B) images of the P2060 film.

α -CD-PEG ICs showed two-step thermal degradation. The first step mainly attributed to the decomposition of α -CD, while the second one to naked PEG component mainly. The decomposition points of α -CD in partial CD-PEG ICs were all higher than free α -CD (increased 26–28 °C) and those for PEG in the partial α -CD-PEG ICs were also slightly higher than homoPEG (increased 13–16 °C). Therefore, two phases existed in partial α -CD-PEG ICs

and they were stabilized by the formation of α -CD-PEG inclusion.

The AFM image of P2060 film proved the microphase separation (Fig. 5). It was supposed that the minor component (naked semi-crystalline PEG) formed the dark regions in the image and the major component (α -CD-PEG inclusion crystallites) formed brighter patches.

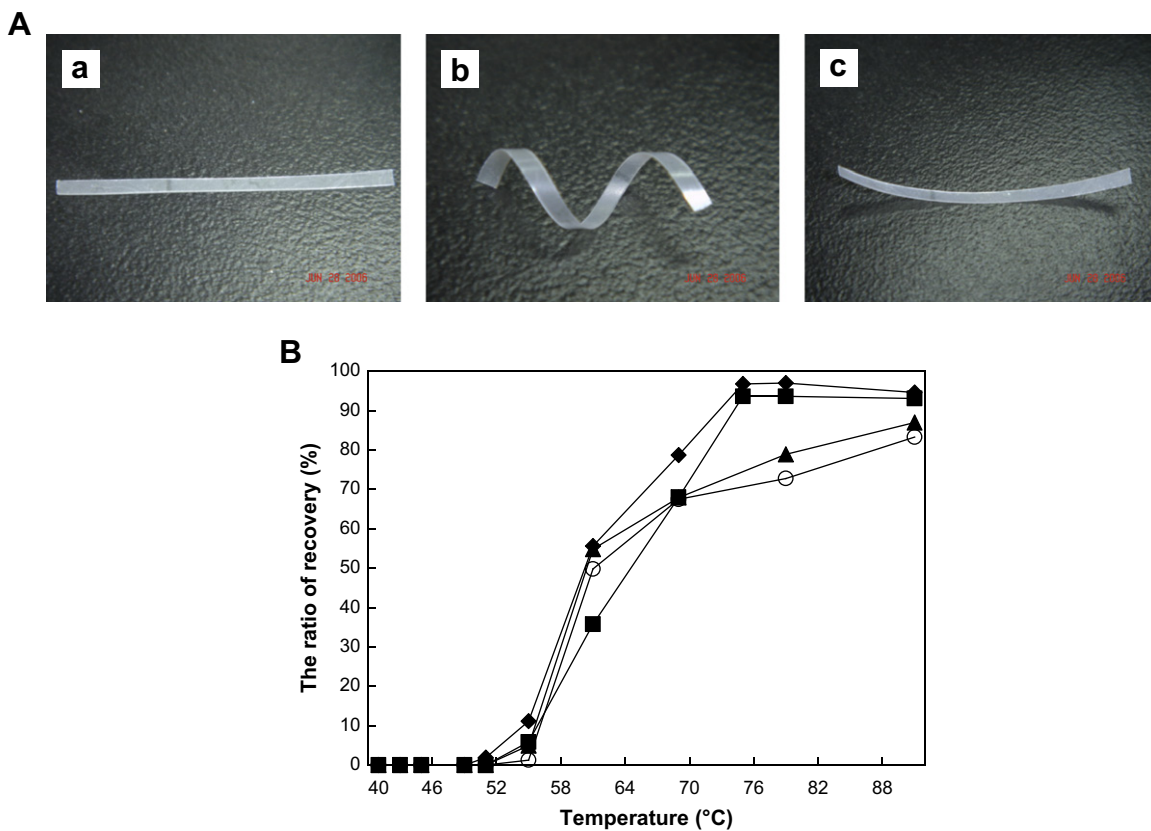


Fig. 6. (A) Photographs demonstrate the macroscopic shape memory effect for P2060. (a) Original shape; (b) spiral temporary shape; (c) recovered shape obtained by heating to 75 °C; (B) shape memory behaviors of partial α -CD-PEG inclusion complexes as a function of temperature. (P2060, filled diamonds; P2050, filled squares; P2040, filled triangles; P2030, open circles.)

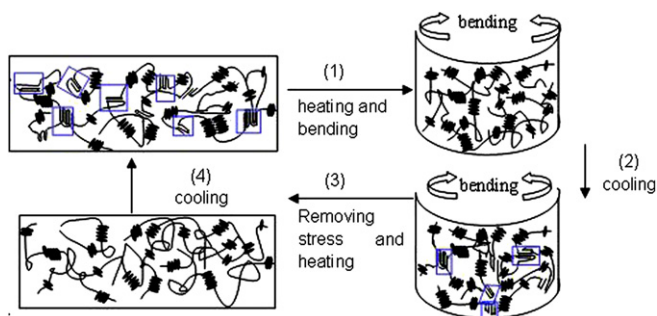


Fig. 7. Molecular mechanism of shape memory effect of partial α -CD-PEG inclusion complex: α -CD-PEG inclusion crystallites (filled oval) as fix phase and PEG crystallites (ordered lines in rectangles) as reversible phase.

As expected, the partial inclusion complexes obtained in this study exhibited typical thermoresponsive shape memory function, which was very different from the homoPEG (melt above T_m) and complete α -CD-PEG IC (keep stable until decomposition above 300 °C). An example of the macroscopic shape memory effect of these partial ICs is demonstrated in Fig. 6(A). A band complex was changed into a spiral shape at 100 °C, and then cooled rapidly to room temperature (25 °C). On heating again to 75 °C, the complex recovered its original shape within 5 s. The shape memory behavior is detected in the temperature study (The method of evaluating the shape memory effect was according to Liu et al. [7]). As shown in Fig. 6(B), the partial α -CD-PEG inclusion complexes would keep deformation at the temperature which was lower than the T_m of PEG and recover to the original shape under the heating process. The complex with a higher inclusion ratio shows a higher recovery ratio. When the inclusion content was 60%, the final recovery rate reached 97%.

A mechanism of the shape memory effect found in partial α -CD-PEG IC was proposed as follows: when α -CD molecules were threaded on the long PEG chains according to the designed ratio, the α -CD-PEG inclusions and naked PEG units form α -CD-PEG crystallite (filled oval) and homoPEG crystallite (the ordered structure in the blue rectangles), respectively. By heating the sample to temperature above $T_{m(\text{PEG})}$, the material would have become soft and flexible and would have readily deformed because of the fusion of the naked PEG crystallites (Fig. 7, process 1.). When the deformed specimen was cooled, the deformation would be “frozen” due to the crystallization of naked PEG segments (Fig. 7, process 2). Once the specimen was heated up to $T_{m(\text{PEG})}$ again, the strength of the “frozen deformed specimen” would have disappeared. As a result of its entropy elasticity, the materials recovered its original shape (Fig. 7, process 3 and 4). This “switch function” of naked PEG segments is caused by their fusion and crystallization transition.

As shown in polarized light microscopy (POM) images (Fig. 8), some light crystallites disappeared due to the melting of the naked PEG segments at around 65 °C. In contrast, the other crystallites which were the α -CD-PEG inclusion still kept stable even at temperatures above 180 °C. That stable crystallites served to act as permanent entanglements to prevent the chains from slipping and to fix the original shape.

Difference in the modulus above and below the T_{trans} is a significant property to describe the materials' shape memory function. A high storage modulus ratio ($E'_{T_{\text{trans}}-20\text{ }^\circ\text{C}}/E'_{T_{\text{trans}}+20\text{ }^\circ\text{C}}$) implies that good shape fixity on cooling and large shape recovery upon heating [7]. As shown in Fig. 9, a pronounced drop in storage modulus (E') occurred for all the partial CD-PEG ICs, while E' values for pure PEG cannot be obtained because of melting. These results indicated that the naked PEG segments appearing large scale motion and the complex materials abruptly became soft and flexible because of the melting of crystallites above the transition temperature (60 °C). But

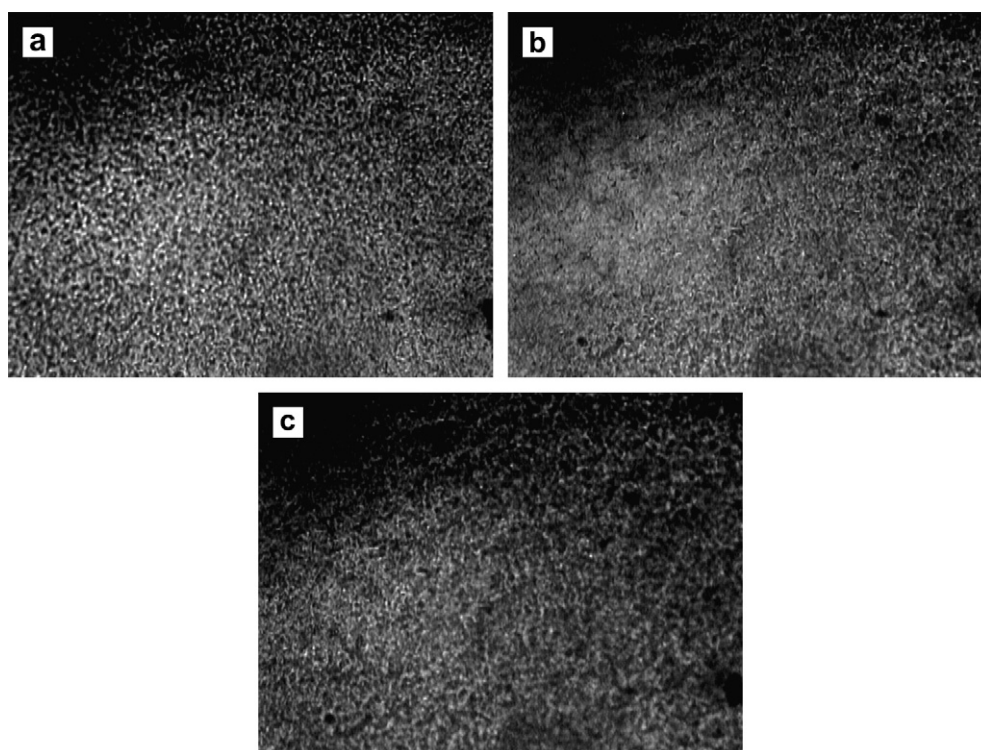


Fig. 8. Structural changes of a partial α -CD-PEG inclusion complex (P2060) sample with heating (obtained using polarizing optical microscopy). (a) 30 °C; (b) 65 °C; (c) 185 °C.

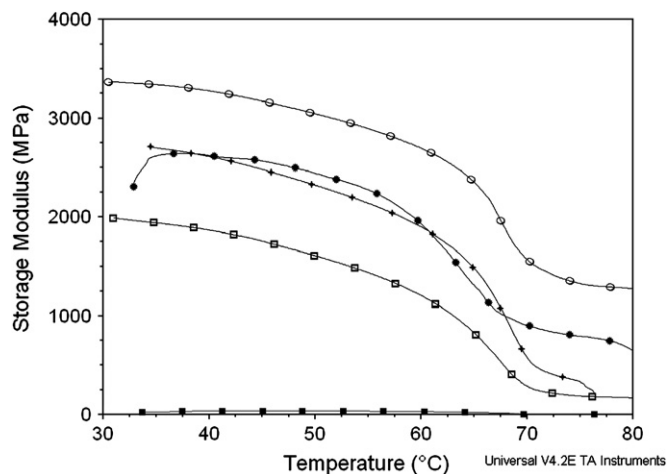


Fig. 9. Dynamic mechanical analysis of partial α -CD-PEG inclusion complexes. (Hom-PEG ($M_w = 200,000$), filled squares; P2030, open squares; P2040, filled circles; P2050, filled diamond; P2060, open circles.)

the complex didn't disintegrate because the thermal stable inclusion segments limit the slipping of chains. With the α -CD inclusion ratio increasing, the mechanical strength of partial α -CD-PEG ICs increases.

4. Conclusions

In conclusion, a novel supramolecular shape memory material based on partial α -CD-PEG inclusion, which contains CD-PEG inclusion crystallites as a fixing phase and naked PEG crystallites as a reversible phase, was successfully designed, prepared and characterized in this study. As highlighted earlier, a wide range of various polymers have been reported to be able to penetrate different sizes of cavity of CD to form inclusion. Therefore the self-assembly

inclusion method described in this study can be expected to provide shape memory function to several other classical polymers thereby widening the available pool of shape memory materials for various applications.

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Appendix. Supplementary data

^1H NMR chemical shift data for α -CD-PEG partial complexes. These materials available free of charge via the internet at <http://pubs.acs.org>. Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.polymer.2008.05.030](https://doi.org/10.1016/j.polymer.2008.05.030).

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