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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.

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 ($T_m = 50$–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 ^{1}H 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] ^{1}H NMR analysis result is the average value of three measurements. Mass ratio of inclusion segments/exclusion segments $= (nM_{w(\alpha\text{-CD})} + 2nM_{w(EO)})/(M_{w(PEG)} - 2nM_{w(EO)})$ ($n =$ 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 ^{1}H 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-Kα irradiation with PHILP 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, Vecco 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 12POLS) 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 $(\theta_i - \theta_f)/\theta_i$.

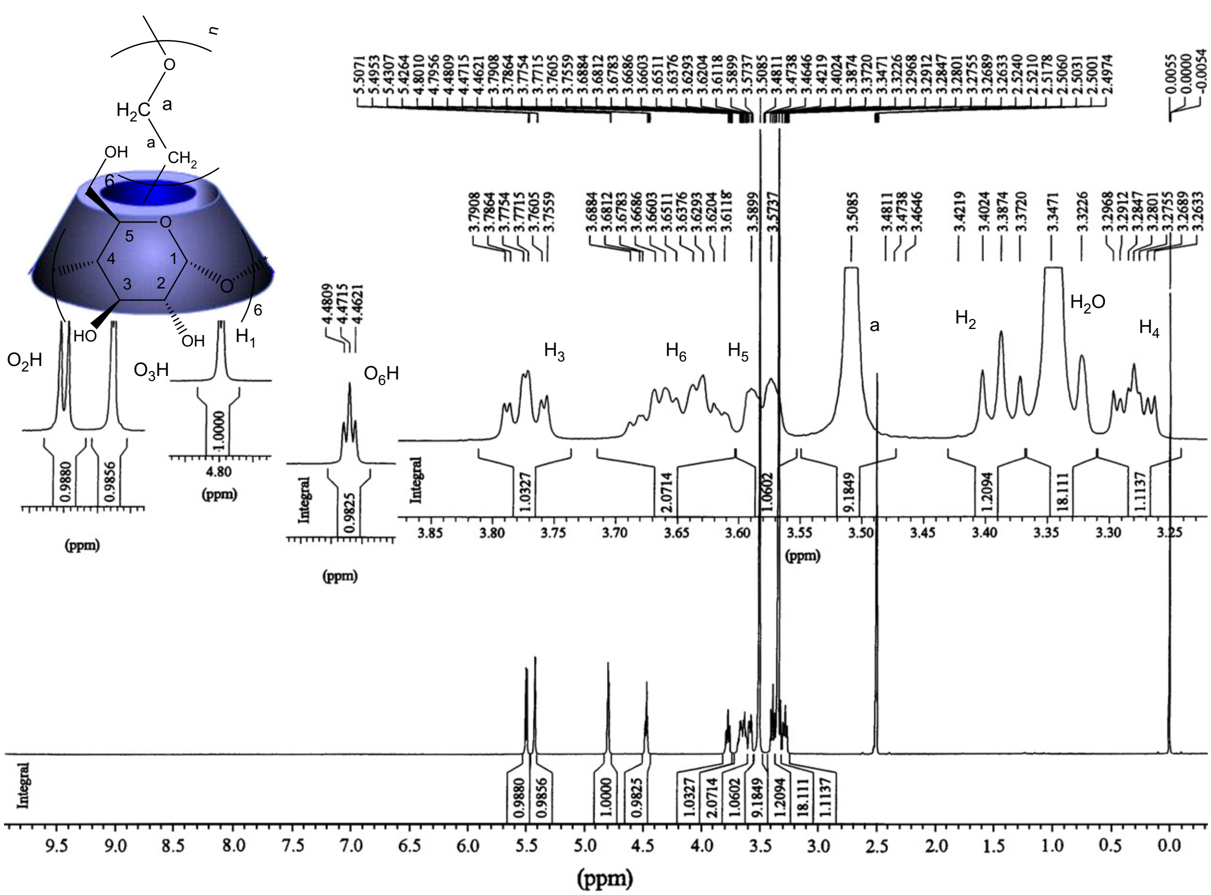

Fig. 1. ^{1}H NMR (600 MHz) of partial CD–PEG inclusion complex (P2060) in DMSO-d_6 at 25 °C.