Supramolecular Inclusion Complexes of Biodegradable Cholesteryl-(ε-caprolactone)$\overline{n}$ Functionalized Polymer with α-Cyclodextrin

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Received 31 October 2006; accepted 27 February 2007
DOI 10.1002/app.26382
Published online 25 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The biodegradable cholesteryl-(ε-caprolactone)$\overline{10}$ (Chol-(CL)$\overline{10}$) functionalized polymer was synthesized and then investigated for inclusion complexation with α-cyclodextrin (α-CD). The supramolecular inclusion complexes (ICs) were in detail characterized by fourier transform infrared (FTIR), ^{1}H-nuclear magnetic resonance, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X-ray diffraction (WAXD), and ^{13}C-NMR, respectively. All analyses indicated that oligo(ε-caprolactone)$\overline{10}$ chains of the Chol-(CL)$\overline{10}$ were included into the hydrophobic α-CD cavities and their original crystalline properties were completely suppressed. Moreover, the ICs of biodegradable Chol-(CL)$\overline{10}$ functionalized polymer with α-CD had a channel-type crystalline structure similar to that formed between the poly(ε-caprolactone) and α-CD. Further more, The TGA analysis revealed that the ICs had better thermal stability than their free components due to the inclusion complexation, suggesting that the complexation stabilized the polymer included in the CD chan-nels. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1700–1706, 2007

Key words: inclusion chemistry; cholesteryl-(ε-caprolactone)$\overline{10}$; supramolecular structures; crystallization; thermal properties

INTRODUCTION

In recent years, supramolecular inclusion complexes (ICs) formed between cyclodextrins (CDs) and polymers have gained considerable interest because of their multiple biomedical applications, such as drug delivery systems and tissue engineering.[1–5] CDs are a series of cyclic oligosaccharides consisting of six (α-CD), seven (β-CD), eight (γ-CD), and more glucose units linked by α-1, 4 bonds. Their shape is like a hollow truncated cone, and they have no hydroxyl groups inside their cavity. Therefore, the hydrophobicity of their cavity gives an ability to include hydrophobic molecules inside their cavity, leading to the formation of ICs. Since Harada and Kamachi[6] first reported the formation of ICs of α-CDs with poly(ethylene glycol) (PEG) in 1990, various kinds of polymer ICs with CDs have been reported, and not only hydrophilic polymers but also hydrophobic polymers formed stoichiometric ICs with corresponding CDs.[6–19] For examples, Yui and coworkers[17] made the polymer IC between poly(ε-lysine) (PL) and α-cyclodextrin (α-CD) by simple mixing of two aqueous solutions of PL and α-CD with initial stirring. Harada et al.[13–15] reported the crystalline ICs of CDs with hydrophilic polymers such as PEG, poly(propylene glycol), poly(tetrahydrofuran), and poly(methyl vinyl ether). Biodegradable aliphatic polyesters and their copolymers constitute a very important class of biomaterials of growing interest in the field of biomedical application, especially, as matrices for controlled drug delivery systems.[20] Many research groups have extensively investigated the ICs of biodegradable polyesters and their copolymers with CDs. For instance, Tonelli and coworkers thoroughly investigated the ICs of poly(ε-caprolactone) PCL, poly(L-lactide) (PLLA), PCL/PLLA blend, PCL-*b*-PLLA, PCL-*b*-PEO-*b*-PCL, and PCL-*b*-PPO-*b*-PCL with CDs, respectively.[21–25]

As is well known, cholesterol is natural product and frequently appears as a building block in molecular assemblies due to its structural characteristics and biological speciality. Recently, functionalized biodegradable polyesters by cholesteryl moiety hold promise as scaffold materials for drug release and tissue engineering. Klok et al.[26] reported that cholesteryl-oligo(L-lactic acid)$\overline{n}$ obviously promoted cell adhesion and proliferation compared with poly (L-lactic acid). Later, Cheng and coworkers[27–29]

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Contract grant sponsor: Ministry of Education of the People's Republic of China; contract grant number: 104187.

described the use of cholesteryl end-capped polycarbonates and cholesteryl-(ε-caprolactone)$\overline{n}$ as drug release carrier. In our investigation, we have studied for the first time the ICs between the functionalized biodegradable polyesters by cholesteryl moiety and α-CD, the polymer selected for guest part of ICs is cholesteryl-(ε-caprolactone)$\overline{10}$ (Chol-(CL)$\overline{10}$, a low molecular weight (Chol-(CL) $\overline{10}$ functionalized polymer. There exists block-selective molecular recognition and results in special block structure of great interest. On the other hand, the most attractive characteristic of such ICs involves the control of drug release utilizing the dissociation of supramolecular structure. This article describes the preparation and characterization of ICs of CDs with Chol-(CL)$\overline{10}$ and the properties of the complexes was discussed in detail.

EXPERIMENTAL

Materials

Cholesterol (Beijing chemical reagent, China) was purified by recrystallization from ethanol. ε-caprolactone (CL, Aldrich) and toluene were distilled from CaH_2, respectively. Stannous octanoate ($Sn(Oct)_2$, Aldrich) was purified by distillation under reduced pressure and then dissolved in dry toluene prior to use. α-CD were purchased from Aldrich and then dried *in vacuo* for 24 h at 100°C. PCL (M_n = 10,000, M_w/M_n = 1.4) was purchased from Aldrich. The other reagents and solvents were local commercial products and used without further purification.

Preparation of Chol-(CL)$\overline{10}$ functionalized polymer

The synthesis of Chol-(CL) $\overline{n}$ functionalized polymer followed the route described by a previous article.[29] Here, to synthesize the Chol-(CL)$\overline{10}$, the cholesterol (3.86 g, 0.01 mol), ε-caprolactone (11.4 g, 0.10 mol), and stannous octoate (17 μL, 0.05 mmol) were added into well-dried three-neck flask with a magnetic stirring bar. The reaction mixtures were stirred at 140°C for 8 h. After the polymerization, the product was dissolved in tetrahydrofuran (THF) and precipitated in methanol. The precipitated polymer was then isolated by filtration and dried under vacuum for 24 h.

The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker DMX-300 spectrometer. For Chol-(CL)$\overline{10}$, the typical signals from cholesteryl moiety and CL repeating units can be observed. ^{1}H-NMR ($CDCl_3$): 0.67, 0.85, 0.87, 0.98 (cholesteryl moiety: CH_3), 5.34 (cholesteryl moiety: CH = C), 4.58 (cholesteryl moiety: CHOCO), 1.38 (CL repeating unit: $CH_2CH_2CH_2CH_2CH_2$), 1.65 (CL repeating unit: $CH_2CH_2CH_2CH_2CH_2$), 2.30 (CL repeating unit: $COCH_2$), 4.05 (CL repeating unit: CH_2OCO), 3.64 (CL repeating unit: CH_2OH).

Preparation of ICs

The IC of Chol-(CL)$\overline{10}$ with α-CD was prepared as follows. Chol-(CL)$\overline{10}$ functionalized polymer 0.5 g was dissolved in 30 mL of acetone and α-CD 7.25 g was dissolved in 50 mL of distilled water. Then the Chol-(CL)$\overline{10}$ solution was added dropwise to the α-CD solution at 60°C with vigorous stirring. After stirring at 60°C for 3 h, the mixture was cooled to room temperature while continuously stirring overnight. The precipitated products were collected by filtration, twice washed with acetone (25 mL) to remove free polymers (stirred with a magnetic stirring bar at room temperature for 0.5 h), and then twice washed with distilled water (45 mL) to remove uncomplexed α-CD. The white powder was then dried overnight in vacuo at 45°C until a constant weight was obtained. The yield (wt %) for ICs was 70%. At the same time, the IC of PCL with α-CD was also prepared according to literature.[24]

Preparation of the physical blend of Chol-(CL)$\overline{10}$ and α-CD

A physical mixture consisting of Chol-(CL)$\overline{10}$ and α-CD in the same weight ratio as the contrast complex was prepared. The Chol-(CL)$\overline{10}$ and α-CD were admixed together in a mortar and pestle for 5 min to obtain a homogeneous blend.

Methods

Molecular weights and molecular weight distributions of the polymer were determined on a Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector, THF as the eluent (1.0 mL/min). The differential scanning calorimetry (DSC) analysis was carried out using a Mettler DSC822e instrument under nitrogen flow (50 mL/min). All samples were first heated from 0 to 100°C at 10°C/min and held for 2 min to erase the thermal history, then cooled to 0°C at 10°C/min. Thermogravimetric analysis (TGA) was performed from room temperature to 600°C at a heating rate of 10°C/min under nitrogen flow (20 mL/min), using a PerkinElmer Pyris 1 instrument. Wide angle X-ray diffraction (WAXD) patterns of powder samples were obtained at room temperature on a Rigaku D_{max}-RB X-ray diffractometer with a Cu Kα radiation source (wavelength 0.154 nm). The supplied voltage and current were set to 40 kV and 150 mA, respectively. Samples were exposed at a scan rate of $2\theta = 2^\circ$/min between $2\theta = 5^\circ$ and 40°. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet-510P spectrometer at frequencies ranging from 400 to 4000 cm^{-1}. Samples were thoroughly mixed with KBr and pressed into pellet form. The ^{1}H-NMR and ^{13}C-NMR

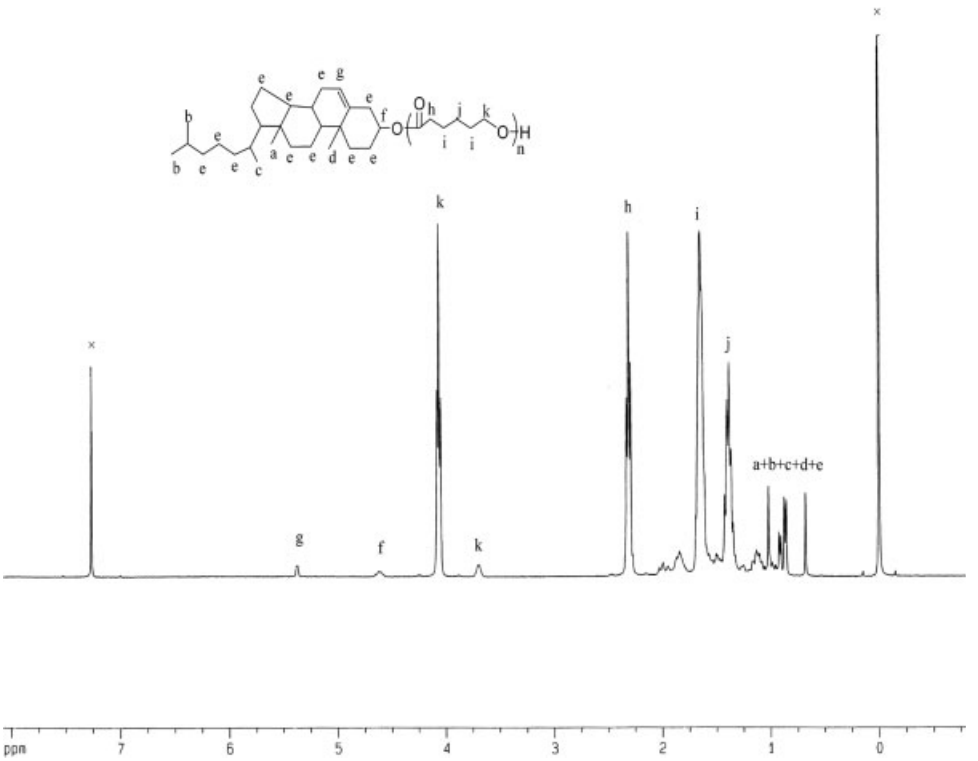


Figure 1 The 400-MHz ^{1}H-NMR spectrum of the Chol-(CL)$\overline{10}$ functionalized polymer in $CDCl_3$.

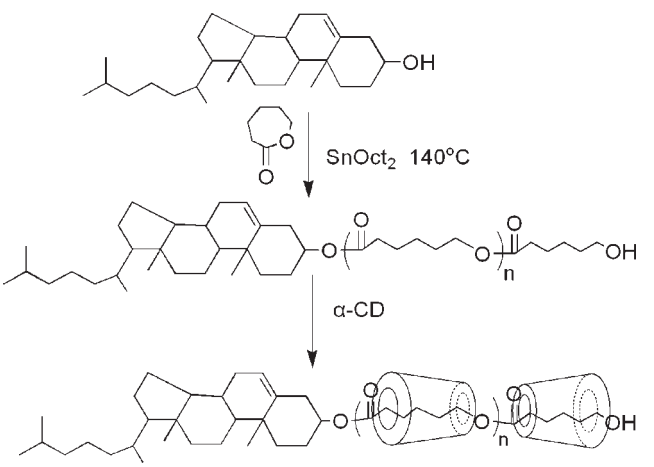
experiments were performed at 400.1 and 100.6 MHz, respectively, on a Bruker DMX-300 spectrometer. $CDCl_3$ and DMSO-d_6 were used as the deuterated solvents for the polymers and the ICs, respectively.

RESULTS AND DISCUSSION

Characterization of functionalized polymer and ICs

It is well known that ring-opening polymerization is an efficient method for producing aliphatic polyesters. Chol-(CL)$\overline{10}$ was synthesized by ring-opening polymerization of CL using cholesterol as an initiator and $Sn(Oct)_2$ as a catalyst. The molecular characteristics of the Chol-(CL)$\overline{10}$ functionalized polymer sample were actually determined by using GPC and ^{1}H-NMR. The M_n and the molecular weight (M_w) polydispersity found by GPC are 3040 and 1.64, respectively. The ^{1}H-NMR spectrum of Chol-(CL)$\overline{10}$ was shown in Figure 1, which confirmed the structure of the Chol-(CL)$\overline{10}$ functionalized polymer.

ICs of biodegradable Chol-(CL)$\overline{10}$ functionalized polymer with α-CD was successfully prepared by mixing a solution of α-CD with that of the Chol-(CL)$\overline{10}$, followed by rigorous stirring (Scheme 1). As a representative example, the ^{1}H-NMR spectrum of α-CD-Chol-(CL)$\overline{10}$ ICs was given in Figure 2. It can be clearly seen that both α-CD and Chol-(CL)$\overline{10}$ functionalized polymer components existed in the ICs. In general, by comparing the integral of peak for CD (1H) with that of the oligo(ε-caprolactone)$\overline{10}$ methylene groups, the host-guest stoichiometry of ICs can be calculated by the molar ratio of the monomeric repeating unit of oligo(ε-caprolactone)$\overline{10}$ to CDs, herein, it could be calculated that the stoichiometry is 0.67 (α-CD:CL) for α-CD-Chol-(CL)$\overline{10}$ ICs, which is similar to that for α-CD-PCL ($M_w \geq 2000$) ICs reported in the literatures.[30] But it is a little



Scheme 1 Preparation of supramolecular ICs of Chol-(CL)$\overline{10}$ with α-CD.

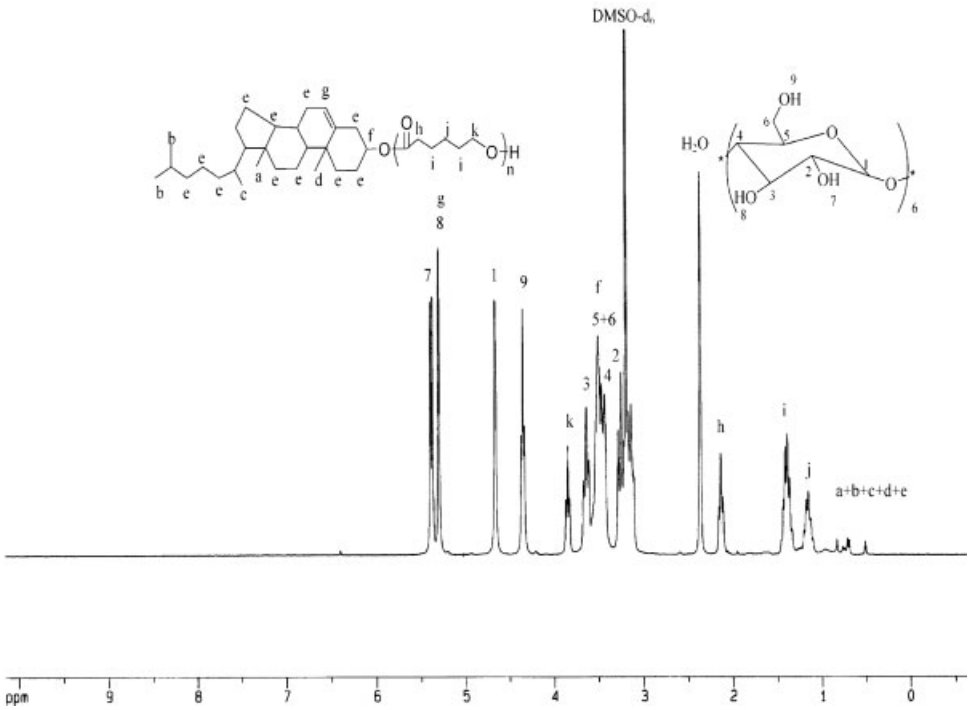


Figure 2 ^{1}H-NMR spectrum (DMSO-d_6) of α-CD-Chol-(CL)$\overline{10}$ ICs formed between Chol-(CL)$\overline{10}$ and α-CD.

lower than rates of molecular modeling studies (α-CD: CL $\approx$ 1) probably due to the low dispersibility of Chol-(CL)$\overline{10}$ ($M_w > 2000$) in aqueous solution, on the other hand, incorporation of cholesterol to the polymer chains increases steric hindrance effect which possibly induces a few CL units near the linking points in the Chol-(CL)$\overline{10}$ functionalized polymer not to be included by α-CD molecules. Furthermore, from the result of ^{1}H-NMR, we can guess that the cholesterol block of the polymer is not included by α-CD.

Figure 3 showed the FTIR spectra in the region from 400 to 4000 cm^{-1} obtained for α-CD, Chol-(CL)$\overline{10}$, physical blend of α-CD and Chol-(CL)$\overline{10}$, α-CD-Chol-(CL)$\overline{10}$ ICs, PCL and α-CD-PCL ICs. From spectra it can be seen that α-CD-Chol-(CL)$\overline{10}$ ICs spectrum was very similar to that of α-CD-PCL ICs, but different from that of physical blend. The center of the symmetric and antisymmetric O—H stretching modes band shifted to higher frequency for the α-CD-Chol-(CL)$\overline{10}$ ICs (3405 cm^{-1}) compared with α-CD which was at 3385 cm^{-1}. This shift may be also be accounted for in terms of O—H stretching modes associated with the α-CD bridged systems.[31] A new band appeared at 1735 cm^{-1} in the α-CD-Chol-(CL)$\overline{10}$ ICs spectrum, which was absent from the α-CD spectrum, and this is the C = O stretching band for amorphous bulk phases of oligo (ε-caprolactone)$\overline{10}$ block, it is consistent with the latter DSC results which showed no free crystalline oligo(ε-caprolactone)$\overline{10}$ block in the α-CD-Chol-(CL)$\overline{10}$ ICs sample. The appearance of this band confirmed that the oligo(ε-caprolactone)$\overline{10}$ block was included the channels provided by α-CD.

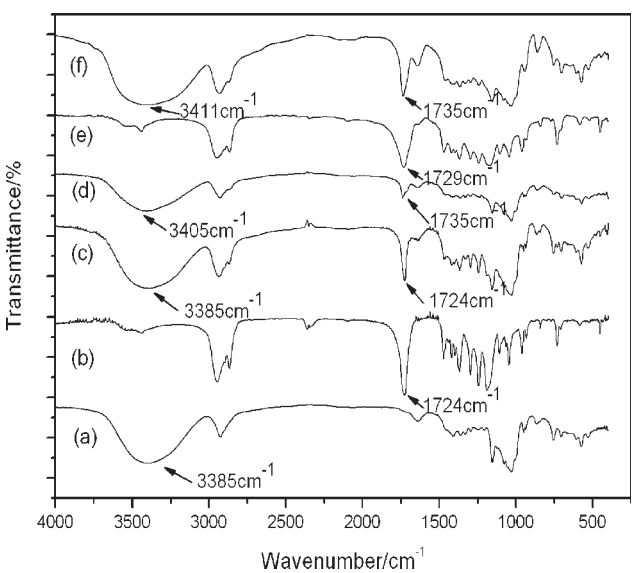


Figure 3 FTIR Spectra of (a) α-CD, (b) Chol-(CL)$\overline{10}$, (c) α-CD and Chol-(CL)$\overline{10}$ physical blend, (d) Chol-(CL)$\overline{10}$ -CD-IC, (e) PCL, and (f) PCL-CD -IC.

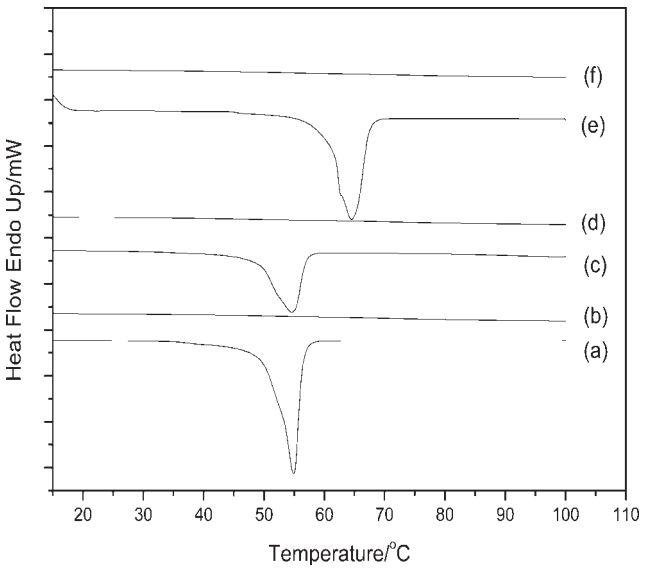


Figure 4 The heating DSC curves of (a) Chol-(CL)$\overline{10}$, (b) α-CD, (c) α-CD and Chol-(CL)$\overline{10}$ physical blend, (d) Chol-(CL)$\overline{10}$ -CD-IC, (e) PCL, and (f) PCL-CD-IC.

Crystal structures of ICs

The DSC technique was employed to determine the formation of ICs and to determine whether the ICs contain free polymers. The melting and crystallization behavior of pure polymer and the ICs were shown in Figures 4 and 5. As showed in Figure 4, for Chol-(CL)$\overline{10}$, α-CD, physical blend of α-CD and Chol-(CL)$\overline{10}$, α-CD-Chol-(CL)$\overline{10}$ ICs, PCL and α-CD-PCL ICs during the heating run from 25°C to 100°C, it was found that the pure bulk Chol-(CL)$\overline{10}$ melted at 55°C. However, no melting peak was observed in α-CD-Chol-(CL)$\overline{10}$ ICs, which indicate that there is no free crystalline polymer in the ICs. That is to say, the crystallization of Chol-(CL)$\overline{10}$ functionalized polymer was completely suppressed in the α-CD cavities, and the ICs contained negligible free guest polymer. In addition, from Figure 4, it could be seen that all these are very similar to that of α-CD-PCL ICs, but different from that of physical blend. The physical blend thermogram was nearly identical to that of pure functionalized polymer, and showed an endothermic peak at ~ 55°C. Similarly, the cold crystallization peak was not observed for the α-CD-Chol-(CL)$\overline{10}$ ICs in the cooling run as showed in Figure 5.

Figure 6 was the comparison of WAXD patterns observed for α-CD, Chol-(CL)$\overline{10}$, physical blend of α-CD and Chol-(CL)$\overline{10}$, α-CD-Chol-(CL)$\overline{10}$ ICs, PCL and α-CD-PCL ICs at room temperature from $2\theta = 5^\circ$ to 40°. A series of peaks were detected for α-CD powder. The prominent peaks were located at 9.9, 12.2, 14.5, 19.5, and 21.9, almost identical to the results as found in the previous reported.[31] Chol-(CL)$\overline{10}$ showed two strong reflections at $2\theta = 21.1$ and 23.5, just like PCL. The diffractogram of α-CD-Chol-(CL)$\overline{10}$ ICs showed quite a different diffraction pattern from Chol-(CL)$\overline{10}$ and α-CD, which constitutes primary evidence that a different crystal type was formed. The strong peak for α-CD-Chol-(CL)$\overline{10}$ ICs at ~ 19.8 and 22.5, which was very similar to that formed between the PCL and α-CD, also indicated that the inclusion compound formed with Chol-(CL)$\overline{10}$ included inside the α-CD channels. It is

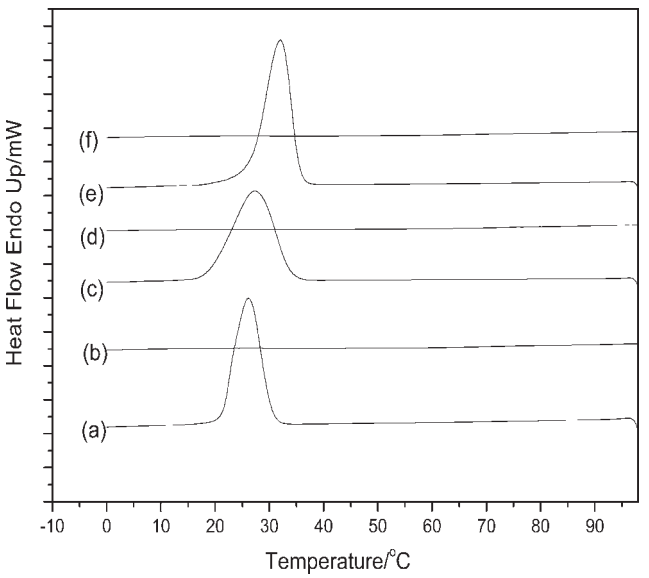


Figure 5 The cooling DSC curves of (a) Chol-(CL)$\overline{10}$, (b) α-CD, (c) α-CD and Chol-(CL)$\overline{10}$ physical blend, (d) Chol-(CL)$\overline{10}$ -CD-IC, (e) PCL, and (f) PCL-CD-IC.

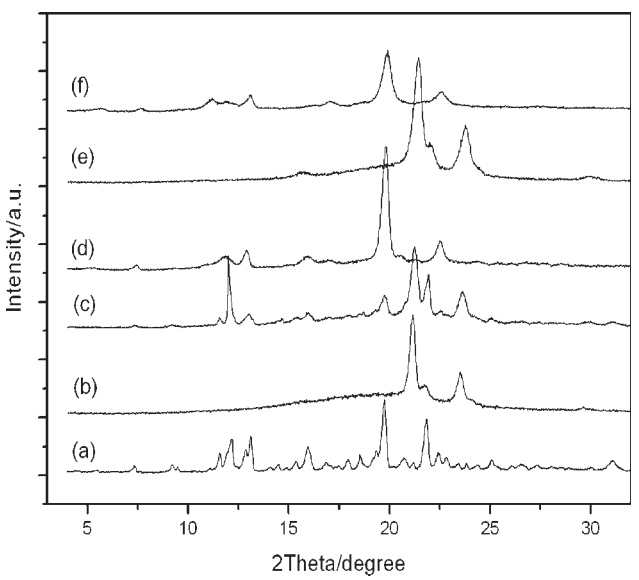


Figure 6 WAXD thermograms of (a) α-CD, (b) Chol-(CL)$\overline{10}$, (c) α-CD and Chol-(CL)$\overline{10}$ physical blend, (d) Chol-(CL)$\overline{10}$ -CD-IC, (e) PCL, and (f) PCL-CD-IC.

well-known fact that polymer ICs have a channel-type crystalline structure because of the long chain nature of guest molecules. The diffraction pattern of α-CD-Chol-(CL)$\overline{10}$ ICs is coincident with that observed for α-CD-PCL ICs, which have been previously proven to have channel-type structures.[24,30] As a result, α-CD-Chol-(CL)$\overline{10}$ ICs can be considered to have the channel-type crystalline structure. In the channel structure, the CD rings are stacked on the top of each other to produce cylindrical central cavities, while pure α-CDs form the cage structure where the α-CD cavity is closed on both sides by adjacent molecules.

Considering the earlier analyses, such as ^{1}H-NMR and WAXD results, it should be noted that the α-CD with a smaller cavity could not form IC with cholesterol block because the cholesterol is too large to fill into the α-CD cavity, so only oligo(ε-caprolactone)$\overline{10}$ chains of the Chol-(CL)$\overline{10}$ were included into the hydrophobic α-CD cavities (Scheme 1).

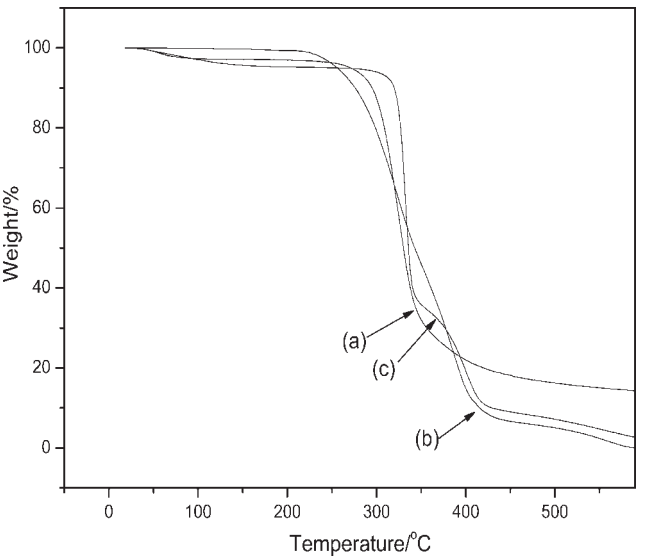


Figure 8 TGA thermograms of (a) α-CD, (b) PCL, and (c) PCL-CD-IC.

Thermal properties of ICs

The thermal properties of the ICs were investigated by the TGA technique shown in Figures 7 and 8. As showed in Figure 7, the physical blend of α-CD and Chol-(CL)$\overline{10}$ had two decomposition temperatures, which belong to those of pure Chol-(CL)$\overline{10}$ and pure α-CD, respectively. Compared with α-CD and the free Chol-(CL)$\overline{10}$ polymer, α-CD-Chol-(CL)$\overline{10}$ ICs presented a two-step thermal degradation. The first step can be mainly attributed to the decomposition of α-CD, while the second step is mainly that of the guest Chol-(CL)$\overline{10}$ polymer, the same phenomenon has also been observed in α-CD-PCL ICs in Figure 8. The decomposition temperature for both α-CD and the guest Chol-(CL)$\overline{10}$ in α-CD-Chol-(CL)$\overline{10}$ ICs is 322°C and 381°C, while both the free α-CD and the free Chol-(CL)$\overline{10}$ decomposed at the temperature of 301°C and 250°C, respectively. This indicates that the ICs are more thermally stable. That is to say, both the α-CD and the guest Chol-(CL)$\overline{10}$ in ICs have a higher decomposition temperature than that of the free α-CD or the free Chol-(CL)$\overline{10}$ polymer. It is demonstrated that the inclusion complexation between the Chol-(CL)$\overline{10}$ polymer and α-CD not only enhances the thermal stability of the guest Chol-(CL)$\overline{10}$ functionalized polymer but also improves that of α-CD.

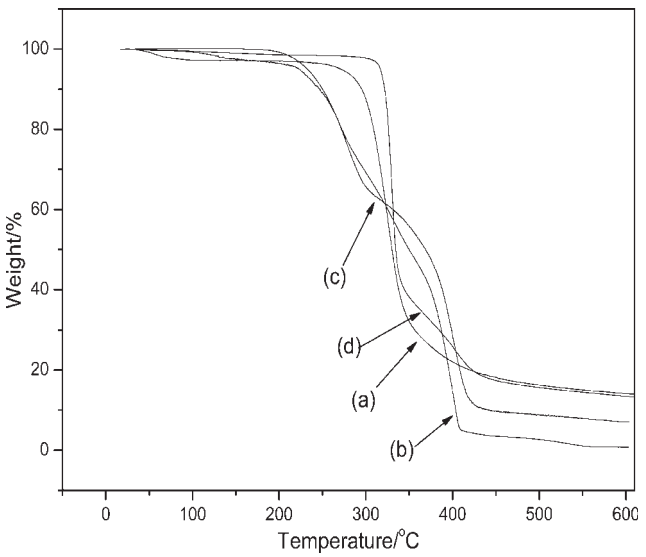


Figure 7 TGA thermograms of (a) α-CD, (b) Chol-(CL)$\overline{10}$, (c) Chol-(CL)$\overline{10}$ and α-CD physical blend, and (d) Chol-(CL)$\overline{10}$-CD-IC.

The solid-state ^{13}C-NMR spectroscopy was also used to investigate the formation of the ICs, and the spectra of α-CD-Chol-(CL)$\overline{10}$ ICs was shown in Figure 9, Chol-(CL)$\overline{10}$ functionalized polymer can be clearly observed in the spectra of the α-CD-Chol-(CL)$\overline{10}$ ICs, at 20–45 ppm for methylene carbons, and at 173 ppm for carbonyl carbons which come to oligo(ε-caprolactone) block of the polymer. In addition, all C1-C6 of α-CD showed a single resonance in Figure 9, indicating that α-CD adopts a more symmetric conformation and each glucose unit of α-CD is in a similar environment in the IC. While α-CD in its pure crystal presents a less symmetrical conformation, which is similar to that in α-CD-PCL ICs.[24,30,32,33] This result is consistent with the earlier analyses, such as WAXD results, and it implies that the ICs of Chol-(CL)$\overline{10}$ functionalized polymer with α-CD formed through α-CD threading onto the oligo(ε-caprolactone)$\overline{10}$ block of the functionalized polymer.

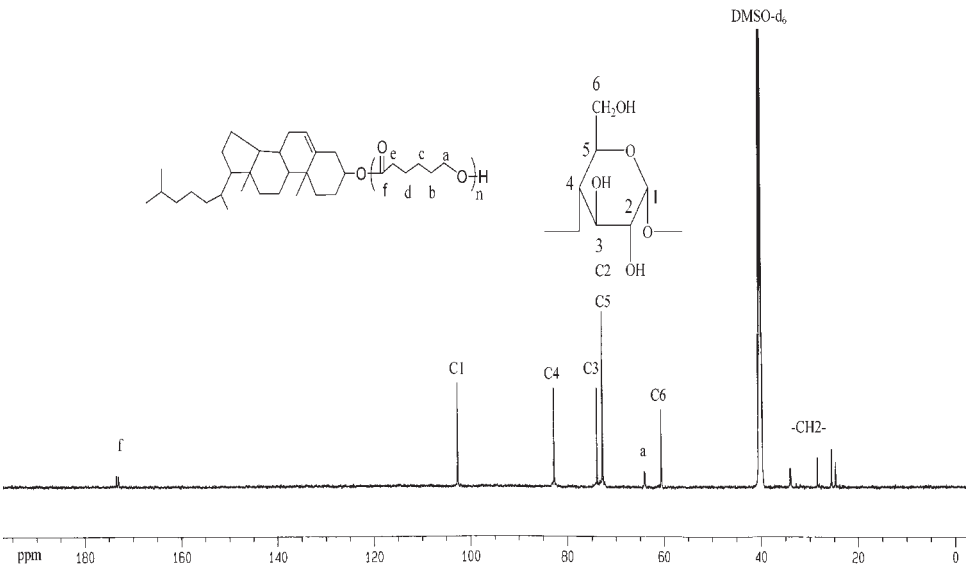


Figure 9 ^{13}C-NMR spectrum of the α-CD-Chol-CL_{10} ICs in DMSO-d_6. The chemical structure indicates carbon assignments.

CONCLUSIONS

Supramolecular ICs of biodegradable Chol-(CL)$\overline{10}$ functionalized polymer with α-CD was successfully prepared by mixing a solution of α-CD with that of the polymer. The ICs of Chol-(CL)$\overline{10}$ functionalized polymer with α-CD formed through α-CD threading onto oligo(ε-caprolactone)$\overline{10}$ block of functionalized polymer, whose original crystalline properties were completely suppressed in the hydrophobic α-CD cavities. Moreover, the ICs of Chol-(CL)$\overline{10}$ functionalized polymer with α-CD had a channel-type crystalline structure similar to that formed between the poly(ε-caprolactone) (PCL) and α-CD. Further more, the TGA results showed that the inclusion complexation between the Chol-(CL)$\overline{10}$ functionalized polymer and α-CD enhanced the thermal stability of the guest Chol-(CL)$\overline{10}$ as well as that of α-CD.

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