Supramolecular Polypseudorotaxanes Composed of Star-Shaped Porphyrin-Cored Poly(ϵ-caprolactone) and α-Cyclodextrin

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Star-shaped porphyrin-cored poly(ϵ-caprolactone) (SPPCL) was synthesized using a tetrahydroxyethyl-terminated porphyrin as a core initiator and stannous octoate as a catalyst in bulk at 120 °C. The molecular weight of as-synthesized polymer could be adjusted linearly by controlling the molar ratio of ϵ-caprolactone to porphyrin core initiator, and the molecular weight distribution was reasonably narrow. Supramolecular polypseudorotaxanes were prepared by inclusion complexation of SPPCL with α-cyclodextrin (α-CD) and thoroughly characterized by means of FT-IR, ^{1}H NMR, ^{13}C CP/MAS NMR, DSC, TGA, and WAXD. The results demonstrated that the porphyrin-cored polypseudorotaxanes formed through α-CD molecules threading onto the branch chains of star-shaped SPPCL polymers, and they had a channel-type crystalline structure. Meanwhile, the original crystallization of SPPCL polymers within the polypseudorotaxanes was completely suppressed in the α-CD cavities. Moreover, inclusion complexation between SPPCL and α-CD enhanced the thermal stability of both the guest SPPCL polymers and the host α-CD. Furthermore, both the SPPCL polymers and the polypseudorotaxanes showed similar fluorescent and UV−vis spectra compared with porphyrin core initiator. Consequently, this will not only provide potentially porphyrin-cored poly(ϵ-caprolactone) and its polypseudorotaxanes for photodynamic therapy but also improve the compatibility between poly(ϵ-caprolactone) and peptide drugs for drug delivery.

Introduction

During the last decades much attention has been paid to design and synthesize porphyrin-functionalized polymers and dendrimers, which hold promising potential for various applications such as light-harvesting materials, optoelectronic devices, drug delivery vesicles, and photodynamic therapy for solid tumors.[1−5] Photodynamic therapy is based on delivery of a photosensitizer to the malignant tissue in which highly reactive singlet oxygen generated by laser photoirradiation results in the oxidative destruction of target tissue. Until now, most of the conventional photosensitizers have had low photodynamic efficacy because of self-quenching. Therefore, star-shaped and/or dendritic porphyrin-cored polymers provide a facile method for the efficient delivery of porphyrin even at an extremely high concentration because the polymer shell can prevent self-quenching of the central porphyrin.[6] However, studies on porphyrin-functionalized biodegradable polymers are still limited. As a Food and Drug Administration approved biomedical polymer, poly(ϵ-caprolactone) (PCL) and its related biomaterials have been widely used for drug delivery matrices and tissue engineering scaffolds.[7] However, their in vitro and/or in vivo degradation rate usually cannot be controlled because of the high crystallinity and hydrophobicity of the polymer backbone.[8,9] Moreover, a lack of peptide drugs/PCL compatibility usually leads to stability problems of the peptide drugs during storage or under in vitro and/or in vivo conditions.[10] Therefore, improving the physical and biodegradation properties of PCL-based biomaterials remains an urgent task.

In nature it is known that oligosaccharides/polysaccharides often play an important role in stabilizing the molecular structure of protein and can greatly improve the compatibility between synthetic PCL and peptide drugs.[11,12] Recently, cyclodextrins (CDs), a series of oligosaccharides with a hydrophobic and hollow truncated cavity, have been shown to generate a variety of polypseudorotaxanes through supramolecular inclusion complexation with synthetic polymers.[13,14] These polypseudorotaxanes not only can serve as models for understanding molecular recognition but also have great potentials for drug delivery vesicles and tissue engineering scaffolds. The driving forces for formation of polypseudorotaxanes are mainly the relative geometric size of CDs to that of polymer, hydrophobic interactions between CDs and the polymer, as well as intermolecular hydrogen bonding between neighboring CDs and the functional groups of the polymer.[15−18] As examples, several research groups investigated the polypseudorotaxanes of CDs with biocompatible and hydrophilic poly(ethylene oxide) and poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock copolymers, respectively.[19−23] Moreover, increasing effort was also made for preparation of polypseudorotaxanes from branched polymers and/or biodegradable polymers with CDs.[15,24−28] Therefore, the work reported herein has been motivated by taking advantage of two aspects. One is that the functional porphyrin is used not only as a core initiator for

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Table 1. Synthesis of Star-Shaped Porphyrin-Cored Poly(ϵ-caprolactone) (SPPCL) Using a Tetrahydroxyethyl-Terminated Porphyrin Initiator and $SnOct_2$ Catalyst in Bulk at 120 °C

entry	[M]/[I][a] (mol:mol)	[M]/[$SnOct_2$] (mol:mol)	reaction time (h)	$M_{n,GPC}$[b]	$M_{n,th}$[c]	$M_{n,NMR}$[d]	M_w/M_n[b]	yield (%)
SPPCL1	120/1	1000/1	36	24 340	11 780		1.45	86.1
SPPCL2	160/1	1000/1	36	29 460	17 180	21 270	1.48	89.4
SPPCL3	200/1	1000/1	36	38 890	22 320		1.35	90.5
SPPCL4	240/1	200/1	24	42 130	26 200		1.31	92.5
SPPCL5	320/1	200/1	24	50 710	33 440	35 160	1.36	89.2
SPPCL6	160/1	200/1	24	32 520	18 260		1.13	95.3

[a] M = CL monomer, I = initiator. [b] M_w/M_n denotes the molecular weight distribution of polymer where weight-average molecular weight (M_w) and number-average molecular weight (M_n) are determined by GPC. [c] $M_{n,th}$ = [M]/[I] × $M_{monomer}$ × yield + $M_{initiator}$; $M_{n,th}$ denotes the theoretical number-average molecular weight of the SPPCL polymers. [d] $M_{n,NMR}$ was determined from the integral ratio of the signal on the main chain of polymer (−CH_2, 2.20−2.40 ppm) and the signal on the primary hydroxy methylene end group (HOCH_2, 3.68 ppm) from ^{1}H NMR spectra.

adjusting macromolecular architecture of as-synthesized PCL (i.e., star-shaped porphyrin-cored PCL polymers) but also as a luminescent probe or photosensitizer for biological diagnosis and photodynamic therapy.[29,30] The other is that α-CD will play a role in adjusting the hydrophobicity−hydrophilicity balance and the crystallinity of the PCL backbone. To the best of our knowledge, this is the first report that describes the preparation of polypseudorotaxanes composed of star-shaped porphyrin-cored PCL and α-CD. The structures of star-shaped porphyrin-cored PCL and the polypseudorotaxanes have been thoroughly characterized by means of FT-IR, ^{1}H NMR, ^{13}C CP/MAS NMR, UV−vis, and fluorescent spectroscopy as well as DSC, TGA, and WAXD.

Experimental Section

Materials. Stannous octoate ($SnOct_2$, Aldrich) was used as received. ϵ-Caprolactone (CL, Aldrich) and toluene were distilled from CaH_2. α-Cyclodextrin (α-CD, Aldrich) was dried in vacuo for 24 h at 100 °C. Tetrahydroxyethyl-terminated porphyrin was synthesized from tetrakis(4-hydroxylphenyl)-21*H*,23*H*-porphine and bromoethanol according to the literature procedure (50% yield).[31] ^{1}H NMR (DMSO-d_6, ppm): 3.89 (t, 8H, −CH_2–OH), 4.28 (t, 8H, −O−CH_2–CH_2−), 5.03 (s, 4H, −O*H*), 7.38 (d, 8H, *o*-Ar−*H*), 8.12 (d, 8H, *m*-Ar−*H*), and 8.87 (s, 8H, *β*-pyrrole-*H*). All other reagents and solvents were local commercial products and used without further purification.

Methods. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer at frequencies ranging from 400 to 4000 cm^{-1}. Samples were thoroughly mixed with KBr and pressed into pellet form. The molecular weight and molecular weight distribution of polymer were determined on a gel permeation chromatograph (GPC, Perkin-Elmer Series 200) and a refractive index detector at 30 °C, DMF as the eluent (1.0 mL/min), and polystyrene as the calibration standard. ^{1}H NMR spectra were recorded at room temperature on a Varian Mercury-400 spectrometer. $CDCl_3$ and DMSO-d_6 were used as the deuterated solvents for the SPPCL polymers and polypseudorotaxanes, respectively. Differential scanning calorimetry (DSC) analysis was carried out using a Perkin-Elmer Pyris 1 instrument under nitrogen flow (10 mL/min). All samples were first heated from 0 to 90 °C at 10 °C/min and held for 2−3 min to erase the thermal history, then cooled to 0 °C at 10 °C/min, and finally heated to 90 °C at 10 °C/min. Thermogravimetric analysis (TGA) was performed from room temperature to 600 °C at a heating rate of 20 °C/min under nitrogen flow (10 mL/min) using a Perkin-Elmer TGA 7 instrument. Wide-angle X-ray diffraction (WAXD) patterns of powder samples were obtained at room temperature on a Shimrdzu XRD-6000 X-ray diffractometer with a Cu Kα radiation source (wavelength = 1.54 Å). The supplied voltage and current were set to 40 kV and 30 mA, respectively. Samples were exposed at a scan rate of $2\theta = 4°$ min^{-1} between $2\theta = 5°$ and 40°. Solid-state carbon nuclear magnetic resonance spectroscopy using cross-polarization and magic-angle spinning (^{13}C CP/MAS NMR) was performed on a Varian Mercury-400 spectrometer with a sample spinning rate of 6 kHz at room temperature. The spectra were acquired with a contact time of 5 ms, a reception time of 10 ms, and 2000 accumulations. Fluorescent spectra were recorded at room temperature using a Perkin-Elmer LS 50B luminescence spectrometer. UV−vis spectra were recorded at room temperature using a Spectrumlab54 UV−visible spectrophotometer.

Synthesis of Star-Shaped Porphyrin-Cored Poly(ϵ-caprolactone) (SPPCL). The polymerization tubes were kept at 110 °C for 24 h. CL, porphyrin core initiator, and a dry stirring bar were put into the warm tube quickly. The tube was then connected to a Schlenk line, where an exhausting−refilling process was repeated three times. The tube was put into an oil bath at 120 °C with vigorous stirring for about 5 min. A certain amount of $SnOct_2$ ([CL]/[$SnOct_2$] = 1000 or 200, mol:mol; Table 1) in dry toluene was added to the melt mixture, and the exhausting−refilling process was carried out again for removal of the toluene. The tube was cooled after a desired reaction time. The resulting product was dissolved in CH_2Cl_2 and poured dropwise into an excess of cold methanol under vigorous stirring, and then the precipitate was filtered. The purified SPPCL polymer was dried in vacuo until a constant weight was obtained, and the polymer yield was determined gravimetrically. A typical procedure is as follows: 1.1 mg (2.75 μmol) of the $SnOct_2$ catalyst was added to the melt mixture of the porphyrin core initiator (14.5 mg; 0.017 mmol) and CL monomer (309 mg, 2.71 mmol). Polymerization was carried out in bulk at 120 °C for 36 h. Then, the resulting product was dissolved in 5 mL of CH_2Cl_2 and poured dropwise into 50 mL of cold methanol under vigorous stirring at room temperature. The precipitate was filtered and dried in vacuo at 40 °C to give 276.2 mg of the SPPCL2 sample (89.4% yield).

Preparation of Porphyrin-Cored Polypseudorotaxanes (PCPs). The porphyrin-cored polypseudorotaxanes (PCPs) were prepared by inclusion complexation between SPPCL polymers and α-CD. The representative protocol is as follows: SPPCL2 sample (57.3 mg) was dissolved in 5.0 mL of acetone at 50 °C, and α-CD (234.0 mg) was dissolved in 2.4 mL of distilled water at 60 °C. Then the SPPCL2 solution was added dropwise to the α-CD solution at 60 °C with vigorous stirring. After stirring at 60 °C for 6 h, the mixture was cooled to room temperature and stirred vigorously for another 35 h. The precipitate was collected by filtration, twice washed with acetone (15 mL) to remove possible free polymers, and then twice washed with distilled water (15 mL) to remove uncomplexed α-CD. The white powder was then dried overnight in vacuo at 60 °C to give 152.3 mg of SPPCL2/α-CD polypseudorotaxane (52.2% yield).

Water Uptake. A sample of SPPCL and/or PCPs with a weight of about 25 mg was compressed into a disc with a diameter of about 13 mm and a thickness of about 0.5 mm at room temperature. The disc sample was dried in vacuo to a constant weight (W) and then placed in distilled water at 37 °C for 24 h. The sample was taken out from water, washed rapidly with ethanol, and then put in a stream of nitrogen gas until the surface of sample was visibly dry. The wet weight of the sample was recorded as W_w. The water uptake experiment was carried out in duplicate. Water uptake of sample was calculated according to the following equation: water uptake (%) = $(W_w - W)/W \times 100\%$.

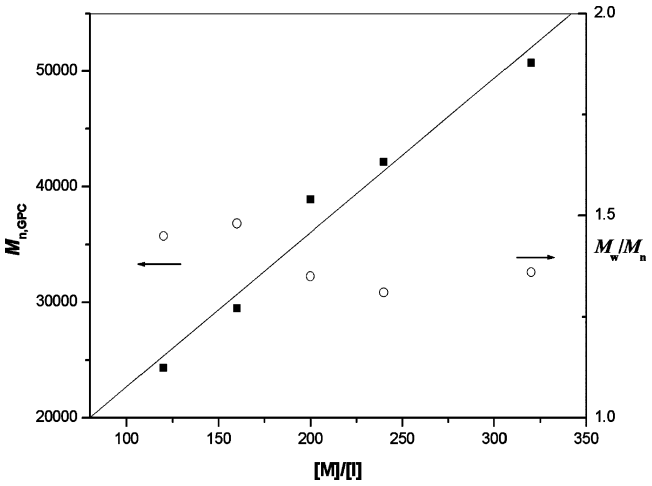

Figure 1. Dependence of $M_{n,GPC}$ on the molar ratio of [M]/[I] with tetrahydroxyethyl-terminated porphyrin initiator and $SnOct_2$ catalyst in bulk at 120 °C.

Results and Discussion

Synthesis of Star-Shaped Porphyrin-Cored Poly(ϵ-caprolactone) (SPPCL). Owing to the promising applications for biological diagnosis and photodynamic therapy, the design and synthesis of biodegradable polymers containing luminescent moiety have been investigated. In this work, we first utilized a tetrahydroxyethyl-terminated porphyrin as the core initiator and $SnOct_2$ as the catalyst to synthesize a family of star-shaped porphyrin-cored PCL (SPPCL) polymers. The ring-opening polymerization of CL monomer was performed in bulk at 120 °C, and the results are summarized in Table 1. As demonstrated in Figure 1, the number-average molecular weight of the as-synthesized SPPCL polymers determined by GPC ($M_{n,GPC}$) increases linearly with the molar ratio of monomer to initiator ([M]/[I]), and the molecular weight distribution (M_w/M_n) is reasonably narrow. The typical GPC curves of the as-synthesized SPPCL polymers showed symmetrical elution peaks at different elution times, denoting a progression of the polymer molecular weight (see Supporting Information S1). Furthermore, the polymer molecular weight determined by ^{1}H NMR ($M_{n,NMR}$) is reasonably consistent with the theoretical molecular weight of polymer ($M_{n,th}$), where $M_{n,th} = [M]/[I] \times M_{monomer} \times \text{yield} + M_{initiator}$. This indicates that the molecular weights of the SPPCL polymers can be accurately predicted by the molar ratio of monomer to initiator. Meanwhile, when the amount of initiator used is constant (such as [M]/[I] = 160, mol:mol), it can be seen that lower amount of $SnOct_2$ catalyst used to some extent broadened the molecular weight distribution of polymer (such as SPPCL2 and SPPCL6 samples in Table 1). This is attributed to the fact that some intra- and/or intermolecular transesterification reactions possibly occurred in the polymerization process because of the long polymerization time ([M]/[$SnOct_2$] = 1000, polymerization time = 36 h).[32,33] As a note, $M_{n,GPC}$ is apparently higher than $M_{n,th}$, which can be attributed to the different hydrodynamic volume of SPPCL polymers when polystyrene was used as a calibration standard for GPC measurement.

Compared with that of porphyrin core initiator (see Supporting Information S2), the ^{1}H NMR spectrum of a representative SPPCL polymer is shown in Figure 2. It clearly shows that besides the typical proton signals of its main chain at 1.35−1.45 (δH^c), 1.55−1.79 (δH^b), 2.20−2.40 (δH^a), and 4.05−4.19 ppm (δH^d), there are additional proton signals of its end groups, i.e., signals assigned to the proton on the primary hydroxy methylene end group (HOCH_2, δH^e = 3.68 ppm) and the protons on the methyleneoxy groups assigned to the porphyrin core initiator residue (PhOCH_2CH_2O, δH^f = 4.48−4.53 ppm; δH^g = 4.64−4.69 ppm). Under the assumption that each branch of SPPCL was selectively capped by a primary hydroxyl group at one end and a methyleneoxy group at the other end, $M_{n,NMR}$ calculated from the ^{1}H NMR spectra was nearly in agreement with $M_{n,th}$ (Table 1). Moreover, the integral ratio of the proton signals on primary hydroxy methylene end group (H^e) to the methyleneoxy group (H^f) is 1.16, which is close to the theoretical value (H^e/H^f = 1.0). This observation confirms that star-shaped porphyrin-cored PCL having four branch chains was successfully synthesized and that CL monomers have been inserted into the "CH_2O-H" bonds of the porphyrin core initiator through selective acyl-oxygen cleavage of the monomer, as shown in Scheme 1. This also suggests that the functional porphyrin core initiating ring-opening polymerization of CL conforms to the known "coordination−insertion" mechanism.[32,33] In all, the above results indicate that well-defined SPPCL polymers were successfully synthesized from the ring-opening polymerization of CL using a tetrahydroxyethyl-terminated porphyrin initiator and $SnOct_2$ catalyst in bulk at 120 °C.

Preparation of Porphyrin-Cored Polypseudorotaxanes (PCPs). Well-defined SPPCL polymers were used for inclusion complexation with α-CD to generate a new class of porphyrin-cored polypseudorotaxanes (PCPs). The PCPs were prepared by adding dropwise the SPPCL of acetone solution into aqueous α-CD solution under rigorous stirring (Scheme 1). It was observed that the mixed solution turned turbid, and then a white crystal powder precipitated from the solution. This implies that the PCPs probably formed between SPPCL and α-CD in this process. The PCP was purified by washing with acetone and distilled water to remove possibly uncomplexed SPPCL and α-CD, respectively, and the yield of PCPs was about 50% (Table 2). In order to calculate the molar ratio of the repeating monomeric unit of SPPCL polymers to α-CD within polypseudorotaxanes, ^{1}H NMR spectra of the PCPs and α-CD are given in Figure 3 and Supporting Information S3, respectively. It can be clearly seen that the proton peaks at ^{7}H and ^{8}H split from one signal (α-CD) into two separate signals (PCPs), and the relative peak height between ^{1}H and ^{9}H within PCPs greatly decreased in comparison with that of α-CD. This indicates that inclusion complexation between SPPCL and α-CD occurred, which is clarified as follows. Comparing the integration of the peak for α-CD (^{1}H) with that of the methylene groups of SPPCL, the host−guest stoichiometry (i.e., CL:α-CD, mol:mol) of PCPs was calculated by the molar ratio of the monomeric repeating unit of SPPCL to α-CD (Table 2). It can be seen that the stoichiometry is 1.56 for SPPCL2/α-CD PCPs, which is higher than that for polypseudorotaxane of linear PCL and α-CD (CL:α-CD = 1:1, mol:mol) reported in the literature.[34,35] This could be attributed to the steric hindrance induced by the star-shaped architecture of SPPCL compared with linear PCL, which resulted in a few CL units near the linking porphyrin core not being included by α-CD molecules.[16,20] Meanwhile, the stoichiometry of SPPCL5/α-CD (or the repeated sample SPPCL5/α-CD′ in Table 2) PCPs was apparently less than that of SPPCL2/α-CD PCPs. This was due to the decreased branch chain density (i.e., branch chain number per molecular weight of SPPCL), which was induced by the increasing polymer molecular weight. These results indicate that both the macromolecular architecture and the polymer molecular weight controlled the stoichiometry of these PCPs.

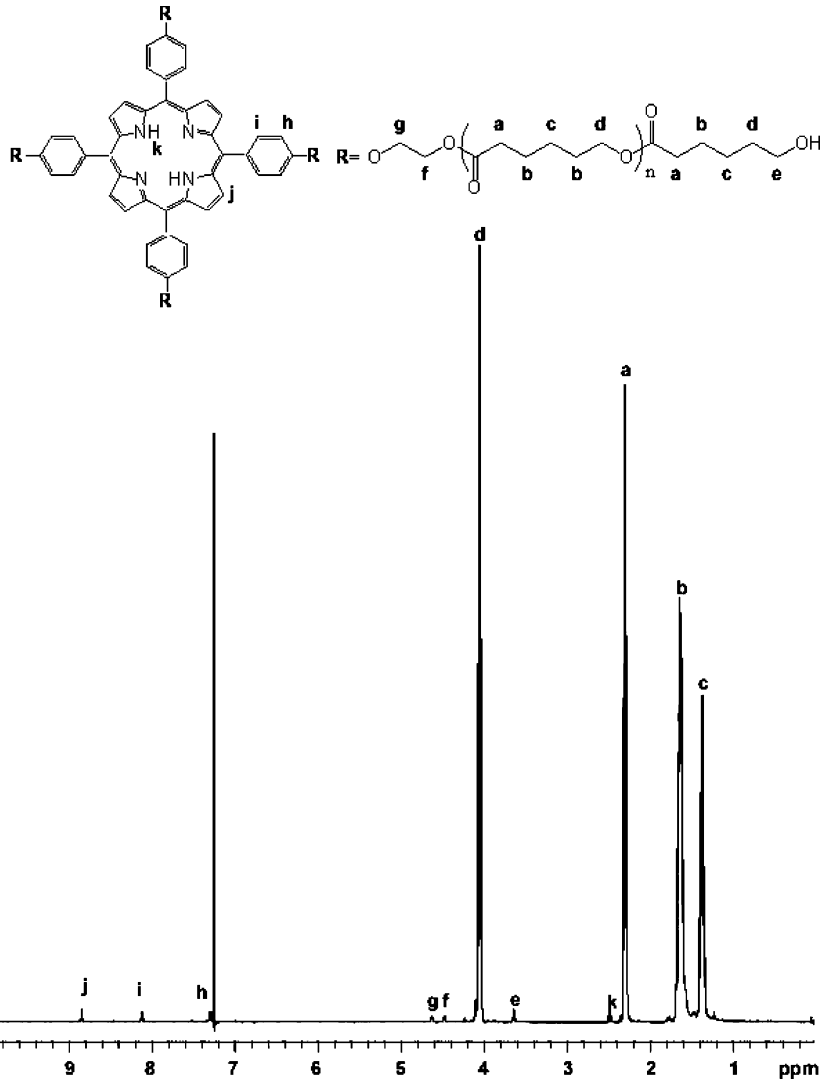

Figure 2. ^{1}H NMR spectrum ($CDCl_3$) of a SPPCL2 polymer sample.

Binding Mode of the PCPs. FI-IR is a very simple tool to confirm the presence of both host and guest components in the PCPs and can give some information about the binding mode of PCPs (Figure 4). The spectrum of α-CD shows a broad band at 3387 cm^{-1} due to the symmetric and antisymmetric O−H stretching mode and three other intense bands at 1151 cm^{-1} (C−O−C glycosidic bridge) coupled with 1072 (C−C) and 1031 cm^{-1}(C−O). The free SPPCL polymers are characterized by a distinct carbonyl stretching band at 1723 cm^{-1} for both SPPCL2 and SPPCL5. Notably, the spectra of PCPs confirmed the presence of both host and guest components in their crystals, although the positions and relative intensities of a few bands were to some extent different from those of SPPCL and α-CD. Moreover, it can be observed that the C═O band of SPPCL2 at 1723 cm^{-1} was shifted to higher frequency at 1732 cm^{-1} in its PCPs, meanwhile the broad O−H band of α-CD at 3387 cm^{-1} was also shifted up at 3404 cm^{-1}. This indicates that the PCPs were probably formed through α-CD threading onto the branch chains of star-shaped SPPCL polymers, as shown in Scheme 1. This is further supported by the ^{13}C CP/MAS NMR and WAXD analyses below. In addition, the characteristic band shifts within PCPs could be attributed to formation of hydrogen bonds, which occurred between the hydroxyl groups of α-CD molecules and the carbonyl groups of the guest SPPCL polymers as well as between the hydroxyl groups of α-CD threading on adjacent branch chains of the SPPCL polymers.[13,15]

The ^{13}C CP/MAS NMR spectra of the PCPs and α-CD are shown in Supporting Information S4. The host α-CD within PCPs had fewer splitting resonance peaks compared with the multiple resonance peaks of free α-CD. It is demonstrated that α-CD within PCPs adopted a more symmetrical cyclic conformation, while α-CD in its pure crystal had a less symmetrical conformation. This suggests that the PCPs formed through α-CD threading onto the branch chains of SPPCL polymers, which has already been observed in other α-CD/polymer polypseudorotaxanes.[13,19−28,34,35] WAXD is a useful method to elucidate the structure of these PCPs in the solid state. Figure 5 shows the diffraction patterns of α-CD, the SPPCL polymers, and the PCPs. As a representative example, the SPPCL2 sample showed prominent peaks at 21.3° and 23.5°, which was consistent with that for linear PCL crystals located at 21.4° and 23.8°. This indicates that star-shaped porphyrin-cored PCL retained crystalline structure similar to that of linear PCL in the solid state. However, the PCPs showed new strong diffraction peaks at 19.5° and 22.4° for SPPCL2/α-CD and at 19.8° and 22.6° for SPPCL5/α-CD, while the major crystalline peaks for SPPCL polymers disappeared. This convincingly shows that the PCPs adopted a channel-type crystalline structure.[13,15,34,35] In all, the

Scheme 1. Preparation of Star-Shaped Porphyrin-Cored Poly(ϵ-caprolactone) (SPPCL) and Its Related Polypseudorotaxanes

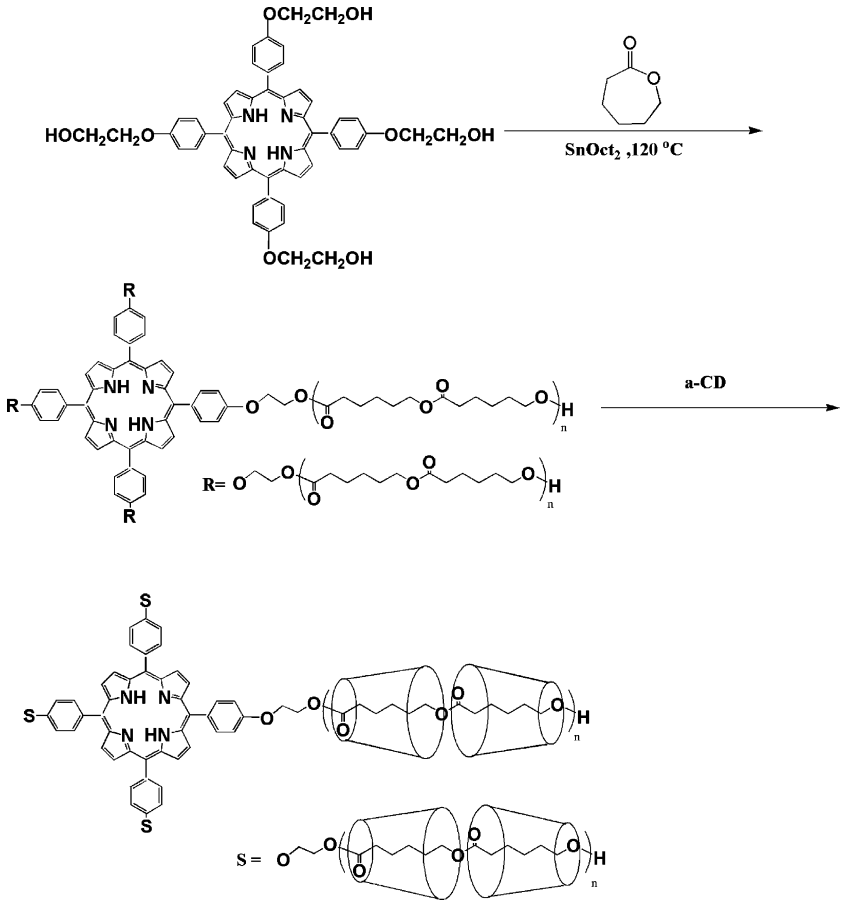

Table 2. Synthesis of SPPCL/α-CD Polypseudorotaxanes and Thermal Properties of α-CD, Free SPPCL Polymers, and Polypseudorotaxanes

entry	yield (wt. %)	CL:CD[a] (mol:mol)	$T_{d,free}$ (°C)[b] α-CD	$T_{d,free}$ (°C)[b] SPPCL	$T_{d,PCPs}$ (°C)[c] α-CD	$T_{d,PCPs}$ (°C)[c] SPPCL
SPPCL2/α-CD	52.2	1.58	306.7	393.1	338.88	393.7
SPPCL4/α -CD	49.1		306.7	334.9	343.47	397.8
SPPCL5/α -CD	54.5	1.02	306.7	310.4	336.7	389.0
SPPCL5/α -CD[d]	50.1	1.03				

[a] The stoichiometry (CL:CD, mol:mol) of each SPPCL/α-CD polypseudorotaxane was determined by ^{1}H NMR. [b] $T_{d,free}$ denotes the initial decomposition temperature of free α-CD and free SPPCL polymers, respectively. [c] $T_{d,PCPs}$ denotes the initial decomposition temperature of the host α-CD and the guest SPPCL polymers included in the PCPs, respectively. [d] SPPCL5/α-CD′ denotes the sample obtained from repeated experiments of SPPCL5/α-CD sample.

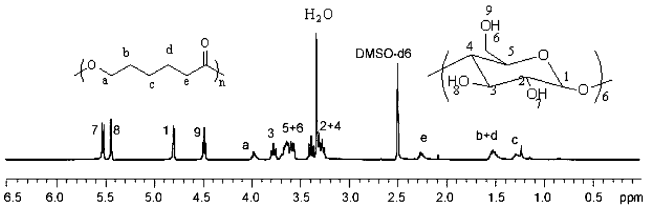

Figure 3. ^{1}H NMR spectrum (DMSO-d_6) of a SPPCL2/α-CD polypseudorotaxane sample.

above analyses showed that the PCPs formed through α-CD molecules threading onto the branch chains of star-shaped SPPCL polymers (i.e., the branch chains of star-shaped SPPCL polymers were included into the hydrophobic cavities of α-CD) and assumed a channel-type crystalline structure.

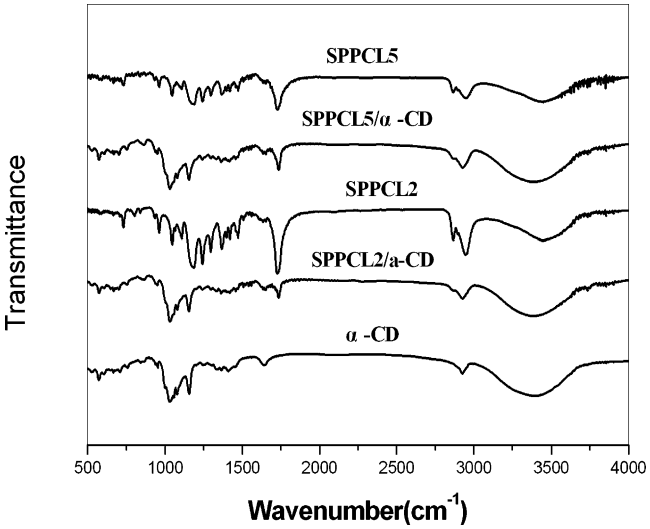

Figure 4. FT-IR spectra of α-CD, SPPCL polymers, and SPPCL/α-CD PCPs.

Thermal Properties of PCPs. The melting and crystallization behavior of α-CD, free SPPCL polymers, and the PCPs were investigated by DSC, as presented in Figure 6. The maximal melting peaks of the free polymers were observed at 57.4 and 58.0 °C for SPPCL2 and SPPCL5 in the first heating run, respectively, and no melting peak was observed for α-CD. However, no melting peak was observed for these PCPs in the first heating run. Similarly, both the crystallization and second melting peaks were not observed for the PCPs in the cooling run and in the second heating run, respectively, although the free guest SPPCL polymers showed their related crystallization and the second melting peaks, respectively. These observations

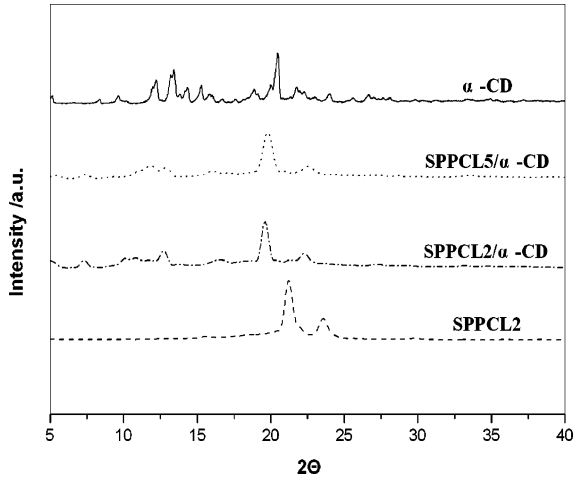

Figure 5. WAXD patterns of α-CD, SPPCL polymers, and SPPCL/α-CD PCPs.

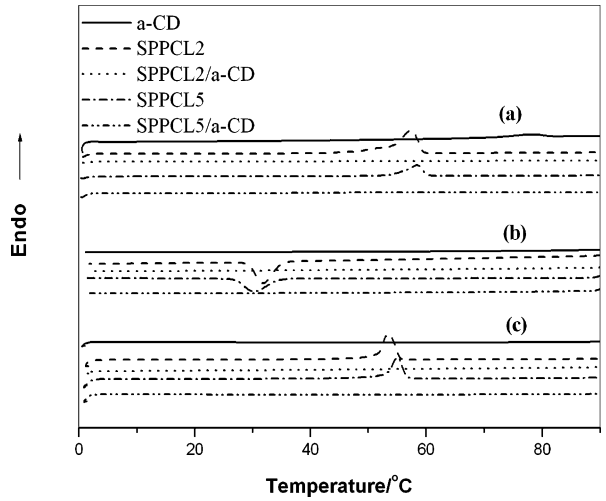

Figure 6. DSC curves of α-CD, SPPCL polymers, and SPPCL/α-CD PCPs in the first heating run (a), cooling run (b), and second heating run (c).

indicate that the original crystallization of SPPCL polymers within the PCPs was completely suppressed in the α-CD cavities and that the PCPs contained negligible free guest polymers. Thus, this will potentially provide a convenient method to adjust the crystallization and biodegradation properties of PCL-based biomaterials, which are important parameters for drug delivery matrix and tissue engineering scaffold.

The thermal properties of the PCPs were investigated by the TGA technique, as shown in Supporting Information S5. Compared with α-CD and the free SPPCL polymers, the PCPs presented a two-step thermal degradation. The first step can be mainly attributed to decomposition of α-CD, while the second step is mainly that of the guest SPPCL polymers included by α-CD. The initial decomposition temperatures of α-CD, the SPPCL polymers, and the PCPs are compiled in Table 2. For example, the initial decomposition temperature for both α-CD and the guest SPPCL5 within PCPs was 336.7 and 389.0 °C, while both the free α-CD and the free SPPCL5 decomposed at the initial temperature of 306.7 and 310.0 °C, respectively. This clearly indicates that inclusion complexation between SPPCL polymers and α-CD not only enhanced the thermal stability of the guest SPPCL polymers but also improved that of α-CD and that the PCPs were more thermally stable.

UV−vis and Fluorescence Analyses. The obtained SPPCL polymers and PCPs were further characterized by UV−vis and fluorescence spectroscopy. The UV−vis spectra of both SPPCL and PCPs showed the Soret (435 nm) and Q bands (500−700 nm), which are known to be the characteristic of porphyrin. This indicates that the luminescent property of the porphyrin moiety was retained within SPPCL and PCPs (see Supporting Information S6). The fluorescence spectra of porphyrin core initiator, SPPCL, and SPPCL/α-CD PCPs are shown in Figure 7. Being excited at a wavelength of 425 nm, both SPPCL and PCPs exhibited a strong emission peak at 661 nm, which is consistent with that of porphyrin core initiator. This suggests that the luminescence functionality of the porphyrin core within SPPCL polymers and PCPs was site-isolated from the outer encapsulated polymer main chain.[30,31] It is noted that the relative fluorescence intensity of PCPs was higher than that of the porphyrin core initiator or SPPCL, which implies that inclusion complexation between SPPCL and α-CD will be to some extent beneficial for detection of the luminescent moiety. Thus, this will potentially enable both SPPCL and PCPs for biological probe and photodynamic therapy applications.[29,30] In addition, water uptake of both the SPPCL and the polypseudorotaxanes was used preliminarily to evaluate their hydrophilicity. There was an apparent increase of water uptake for the polypseudorotaxanes compared with the SPPCL (water uptake increased from 3.1% to 9.1%, see Supporting Information S7). Thus, the host α-CD of polypseudorotaxanes should to some extent improve the compatibility between polypeptide drugs and SPPCL backbone for drug delivery.

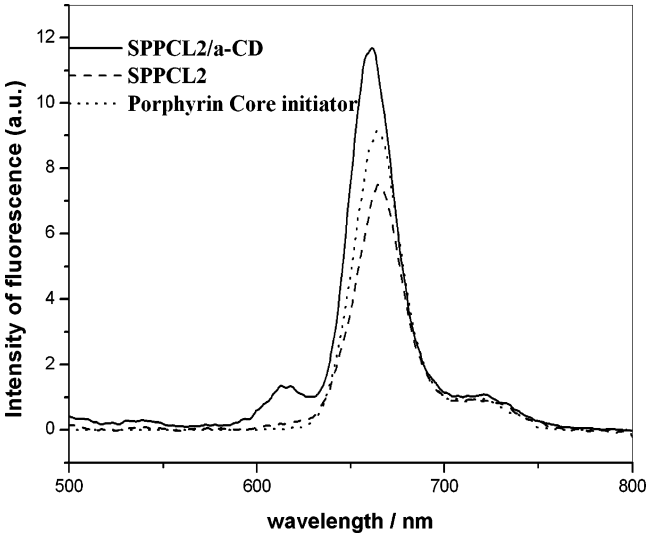

Figure 7. Fluorescence spectra of porphyrin core initiator, SPPCL2, and SPPCL2/α-CD PCPs in DMSO solution ($C = 3.33 \times 10^{-5}$ mol L^{-1}).

Conclusions

Star-shaped porphyrin-cored PCL (SPPCL) has been successfully synthesized using tetrahydroxyethyl-terminated porphyrin as core initiator and $SnOct_2$ as catalyst in bulk at 120 °C. The molecular weight of SPPCL polymers could be adjusted linearly by varying the molar ratio of CL to porphyrin core initiator, and the molecular weight distribution was reasonably narrow. Porphyrin-cored polypseudorotaxanes (PCPs) were conveniently prepared by inclusion complexation of SPPCL and α-CD, in which the PCPs formed through α-CD molecules threading onto the branch chains of SPPCL polymers. Moreover, the original crystallization of SPPCL polymers within PCPs was completely suppressed in the α-CD cavities, while PCPs were

more thermally stable than SPPCL. Furthermore, the luminescent functionality of the porphyrin core within SPPCL polymers and PCPs was site-isolated from the outer encapsulated polymer main chain. Significantly, this will not only provide potentially porphyrin-cored PCL and its polypseudorotaxanes for biological diagnosis and photodynamic therapy but also improve the compatibility between PCL-based biomaterials and peptide drugs for drug delivery.

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Supporting Information Available. GPC for SPPCL polymers, ^{1}H NMR for porphyrin core initiator, and α-CD, ^{13}C CP/MAS NMR spectra, TGA, UV−vis spectra, water uptake of SPPCL2 and SPPCL2/α-CD PCPs. This material is available free of charge via the Internet at http://pubs.acs.org or from the authors.

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