

Synthesis and Properties of Degradable Copolymers Composed of Poly(ϵ -caprolactone) and 3,4-Dihydroxycinnamic Acid

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Photoreactive and degradable hyperbranched (HB) copolymers with various 3,4-dihydroxycinnamic acid (DHCA) compositions, poly(ϵ -caprolactone)-*co*-poly(3,4-dihydroxycinnamic acid) (PCL-*co*-PDHCA), were obtained by thermal melt-polycondensation of PCL and DHCA. The HB structures and the branching degree (BD) of the PCL-*co*-PDHCA copolymers were confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (^1H NMR). The melting points (T_m) of the PCL-*co*-PDHCA copolymers changed depending on the PCL and DHCA composition by differential scanning calorimetry (DSC) measurements. Wide angle X-ray diffraction (WAXRD) analysis showed semi-crystalline of the PCL and PCL-*co*-PDHCA polymers. The PCL-*co*-PDHCA copolymers showed good photoreactivities and fluorescent properties. Crosslinking of the cinnamoyl groups in the copolymers caused by UV irradiation affected the thermal stability and wettability slightly. Moreover, the hydrolysis experiments revealed that copolymers are facile degradable.

Keywords degradability, hyperbranched structure, photoreactivity

Introduction

The widespread application of polymeric materials has made a major contribution to our life. However, these polymers are not suitable for some special occasions. Thus, degradable polymeric materials have been paid much attention recently. Degradable polymers are good materials showing ecological advantages over other nondegradable polymers, although the development of the degradable polymers is not as perfect as nondegradable polymers. Degradable polymers are widely used in a variety of areas such as tissue engineering, drug delivery systems, absorbable sutures and implantable devices.^[1,2]

Typical degradable polymers include poly(ϵ -caprolactone) (PCL), polylactide (PLA), poly(hydroxyalkanoate)s (PHA), poly(butylene succinate) (PBS), *etc.*, and their copolymers, which are widely used in the application of environmental, industrial and biomedical fields.^[3-6] Among them, PCL is one of the most attractive and promising aliphatic polyesters for drug delivery system because of its excellent biocompatibility, biodegradability, drug permeability and nontoxicity.^[7-9] However, PCL shows poor hydrophilicity, low melting temperature (T_m), unsatisfied mechanical properties, and slow degradation rate, which limit its applications. Therefore, various PCL copolymers with soft segments

have gained substantial attention,^[8,10-14] and their properties have been improved. Moreover, functional materials with environmental stimuli responses such as photoresponse could be introduced into PCL to widen the application in tissue engineering, controlled drug delivery systems and other fields.

3,4-Dihydroxycinnamic acid (DHCA), one of a coumaric acid derivative, is a typical biomonomer, which exists in coffee beans. DHCA has well known photoreactive cinnamoyl group.^[15,16] PDHCA homopolymer with hyperbranched structure shows well photoreactivity, thermal properties, degradability and cell compatibility, but low solubility and brittleness. Akashi and coworkers selected 4-hydroxycinnamic acid (4HCA), lactic acid (LA) to copolymerize with DHCA, and the copolymers showed good thermal and mechanical properties and high solubility besides excellent photoreactivity, biocompatibility, and biodegradability.^[17,18] However, fluorescence properties and the influences of UV irradiation on the thermal properties of these polymers have not been investigated.

In order to increase the thermal and stimuli response properties of the PCL polymer, a novel photoreactive and degradable copolymer, poly(ϵ -caprolactone)-*co*-poly(3,4-dihydroxycinnamic acid) (PCL-*co*-PDHCA) was prepared in this research. The copolymers are ex-

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pected to have the characteristics of both PCL and PDHCA, such as control in thermal stability, photoreactivity, fluorescence and degradable properties. The effect of the monomer composition and UV irradiation on the degradable, photoreactive and thermal properties of the copolymers was investigated in detail.

Experimental

Materials

DHCA used as monomer was purchased from Wako pure chemical industries, Japan and used directly. ϵ -CL was purchased from Acros Organics USA and used without further purification. Anhydride acetic acid (Ac_2O), sodium acetate (NaOAc), N,N -dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM) and methanol purchased from Shanghai chemi-

cal reagent station were used directly.

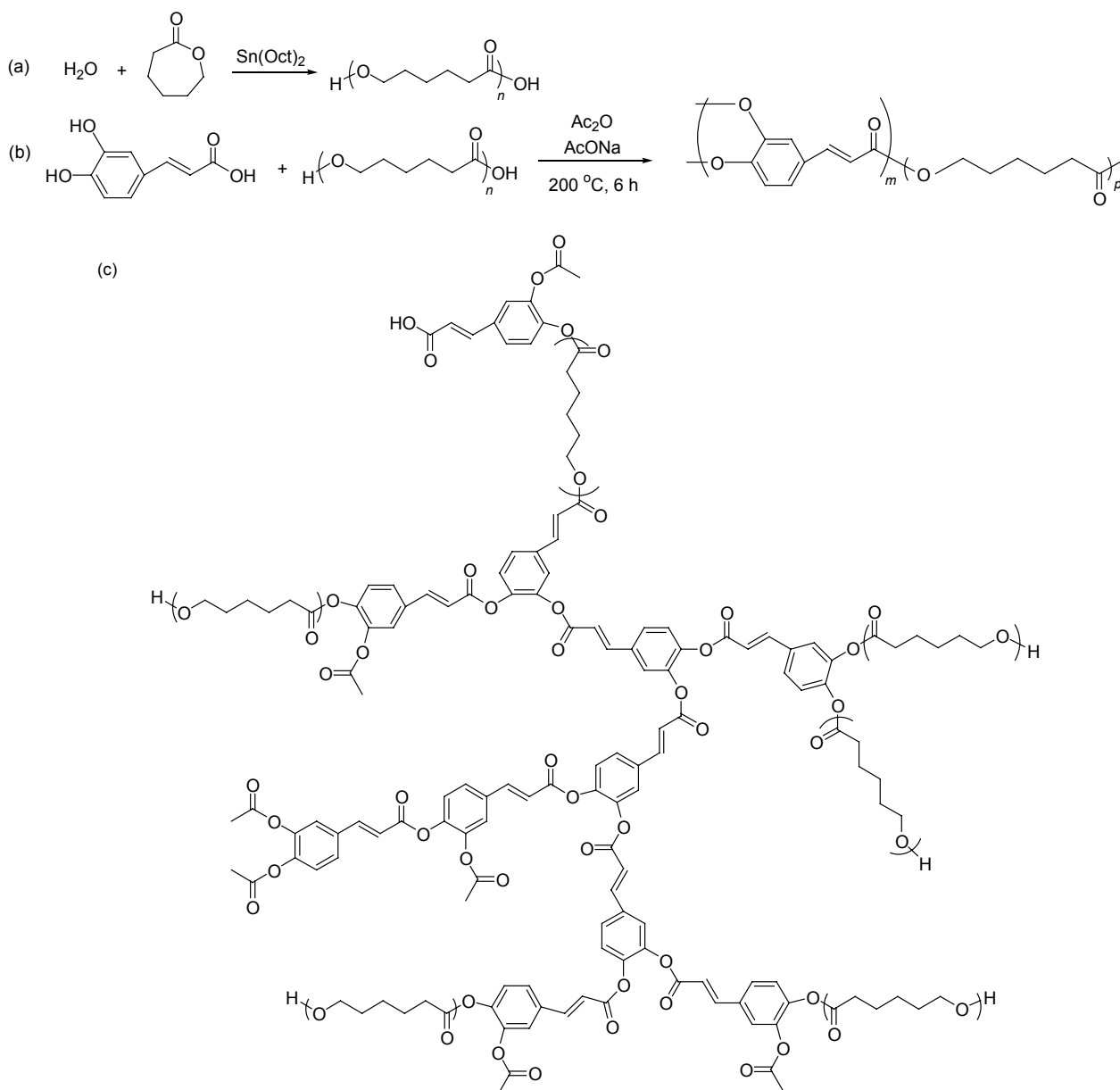
Synthesis of PCL

PCL was synthesized by ring-opening polymerization as Scheme 1(a). ϵ -CL was filled into a dry round bottom flask under a nitrogen atmosphere. Then, a solution of $\text{Sn}(\text{oct})_2$ (0.3 mol% of ϵ -CL) in DCM as catalyst was added into the flask. The reaction was heated at 110 °C in a vacuum and kept for 8 h. After that, the reaction mixture was cooled to room temperature, dissolved in a minimal amount of THF, and precipitated by dropwise addition to methanol with stirring. The obtained precipitation production was dissolved in THF again, and reprecipitated over cold water. The final production was dried by freeze drying for 24 h.

Synthesis of PCL-co-PDHCA

PCL-co-PDHCA copolymers were synthesized via thermal polycondensation method as Scheme 1(b).

Scheme 1 Synthesis of PCL (a) and PCL-co-PDHCA (b) and hyperbranched structure of PCL-co-PDHCA copolymer (c)



DHCA monomer and PCL (a certain amount) were put into a round bottom flask containing Ac_2O (30 mL) with NaOAc (1 mol% of the monomers). After purged with dry nitrogen to remove moisture and oxygen in the flask, the mixture was placed in a silicon oil bath at 150 °C and stirred for about 1 h until the solution became homogeneous. The reaction system was further heated to 200 °C for additional 6 h. The viscosity of the solution increased gradually along with reaction time. The product was cooled to room temperature and washed with ethanol twice. All the polycondensation reactions were carried out under shading and nitrogen atmosphere conditions.

Preparation of the polymer sheet

The polymer sheets (30 mm × 10 mm, 0.2 mm in thickness) were prepared by melt-pressing method at 180 °C under the pressure of 15 MPa for 10 min, and cooled at room temperature.

UV irradiation procedure

The polymer solutions filled in the quartz cuvette were irradiated by UV light at $\lambda = 302$ nm (1 mW/cm², UV-100, Tanon Science and Technology Co. Ltd.) for various times to carry out the GPC and UV-visible spectrum measurement. The polymer sheets were irradiated by UV light at $\lambda = 302$ nm directly for 90 min to carry out the TG, contact angles and hydrolysis experiments.

Characterization

Fourier transform infrared (FTIR, FTLA2000, ABB Bomen) and nuclear magnetic resonance (¹H NMR, Bruker AVANCEIII, 400 MHz) were used to identify the polymer structures and the compositions of the PCL-co-PDHCA copolymers. The average molecular weight of the copolymers was determined by Gel Permeation Chromatography (GPC, Aligent 1100) using DMF as eluent and polystyrene as standard with a flow rate of 1 mL/min at 35 °C. A UV-visible spectrum (UV-1100, Beijing Rayleigh Analytical Instruments Co.) was used to determine the absorption of the PCL-co-PDHCA copolymers in DMF solution. Fluorescence spectra (Shimadzu RF-5301PC) were measured at room temperature. The samples were dissolved in THF (0.5 mg/mL) and the excitation and emission slit widths were set at both 3 nm. The thermal properties were analyzed by differential scanning calorimetry (DSC 822e, Mettler Toledo) and thermogravimetric analysis (TGA/DSC1/1100SF, Mettler Toledo). The samples were scanned at a heating rate of 10 °C/min from 20 to 130 °C for the DSC measurements. The thermal degradation behavior of the samples was observed from the TG curves by heating from 50 to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere with a flow rate of about 50 mL/min. X-ray diffraction (XRD, Bruker D8 Advance) was used to investigate the crystallinity of the polymers. The contact angle of the sheets was measured using an

OCA 40 (Dataphysics Co., Ltd.) with ultra-pure water droplets. Several drops were placed on the sheet surface, and the average value was obtained. Each sheet with or without UV irradiation was placed in a test tube with stopper of phosphate buffered saline (pH = 7.4) at 37 °C for predetermined periods of time. The hydrolytically degraded sheets were washed thoroughly with distilled water at room temperature and dried at 40 °C for 24 h. The degree of degradation was estimated from the weight percentage (W_t) of the remaining products, which was calculated using the following equation: W_t (wt%) = $100 \times W_t/W_0$, where W_0 and W_t are the weights of the dry sample before and after the degradation. The weight percentage was the average of three experiment values.

Results and Discussion

Chemical structure of the PCL-co-PDHCA copolymers

Figure 1 shows the FTIR spectra of PDHCA, PCL-co-PDHCA and PCL. The C=O stretching peak of carboxylic acid at 1652 cm⁻¹ in the spectrum of DHCA monomer was changed to the carbonyl (C=O) stretching bands of the ester group at 1733 and 1739 cm⁻¹ appearing in the spectra of PDHCA and PCL-co-PDHCA polymers, suggesting that the carboxylic acids were successfully converted to esters. The peaks at about 1622 and 1635 cm⁻¹ in the spectra of DHCA, PDHCA and PCL-co-PDHCA were assigned to the double carbon (C=C) of the cinnamoyl groups, which were not changed during the high-temperature polycondensation. The peaks at 1772 cm⁻¹ in PDHCA and PCL-co-PDHCA spectra were assigned to the characteristic carbonyl (C=O) stretching bands of the acetyl groups.

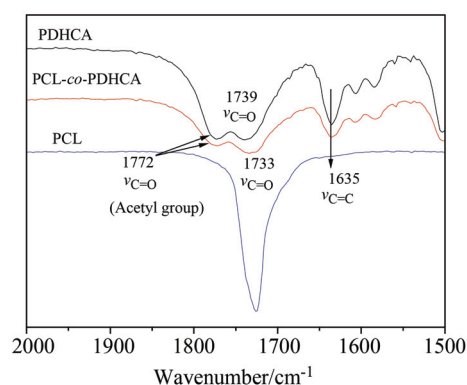


Figure 1 FTIR spectra of PDHCA, PCL-co-PDHCA, and PCL homopolymers.

The chemical structures of the PDHCA and PCL-co-PDHCA polymers were further identified by ¹H NMR spectra as shown in Figure 2. Multiple peaks at δ_a : 8.12–6.88 in Figures 2a and 2b were assigned to protons of the benzene and double carbon groups, respec-

tively. The chemical shifts in PCL-*co*-PDHCA57 spectrum at δ_c : 4.30, 1.82, 1.54, and 2.56 were attributed to the protons of PCL. Moreover, the compositions of DHCA in the copolymers were calculated by comparing the peak areas of double carbon groups in PDHCA (d) and methylene groups in PCL (f). The obtained results were showed in Table 1, and were almost corresponding to the feed amounts.

The results from FTIR and ^1H NMR spectra suggested successful preparation of the PCL-*co*-PDHCA copolymers.

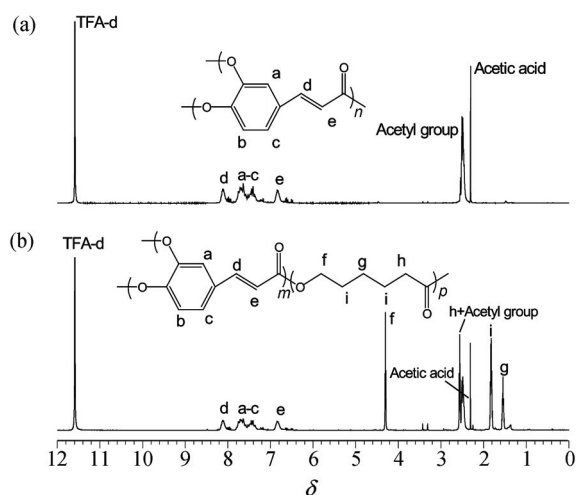


Figure 2 ^1H NMR spectra of PDHCA (a) and PCL-*co*-PDHCA57 (b) polymers.

DHCA is an AB₂-type biomonomer with polymerizable dihydroxyl-acid groups, and the polymers composed of DHCA are hyperbranched (HB) structures. The HB structures of PDHCA and PCL-*co*-PDHCA were characterized by ^1H NMR. In order to investigate the branching degree (BD) of these polymers, we focused on a variety of acetyl groups in DHCA. There are three formations of the DHCA dots in the polymers, as shown in Figure 3. The number of the terminal acetyl group is regarded as equaling the DHCA unit number at high polymerization degree. The two hydroxyl groups in DHCA might both (E_{DHCA}) and only one of them (S_{DHCA}) join the reaction.^[17,19] Therefore, the integral ratios of the end acetyls to the total acetyls, $E/(S+E)$, were cal-

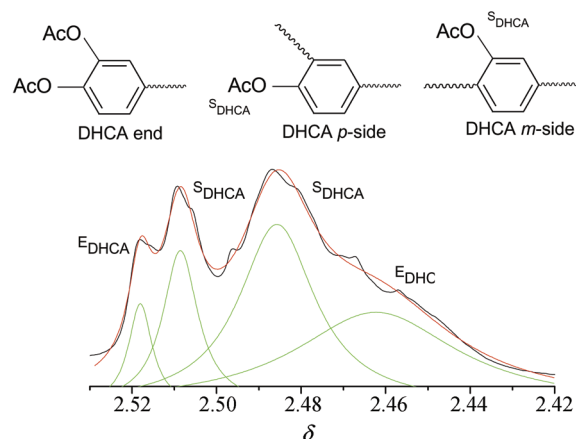


Figure 3 ^1H NMR spectrum of PCL-*co*-PDHCA57 focusing on the acetyl groups over a chemical shift range from 2.42 and 2.53. The acetyl peaks were composed of two small peaks marked by DHCA end chains, E_{DHCA} , two peaks marked by DHCA side chains, S_{DHCA} , as the corresponding structures shown.

culated, where S refers to the integral signal intensity of the side acetyls and E refers to the integral signal intensity of the end acetyls. Actually, the $E/(S+E)$ value was governed only by the DHCA units, because PCL had a linear structure and BD was defined here as the branching unit molar ratio which was only contributed to DHCA component of all monomer units, and was simply calculated using equation as follows:

$$\text{BD} = E/(S+E) \times f_{\text{DHCA}}$$

where f_{DHCA} was molar percentage of DHCA in the copolymers.^[19] The BD value of PCL-*co*-PDHCA increased with the increasing of f_{DHCA} , as showed in Table 1, which indicated the formation of the hyperbranched structure.

The molecular weight (M_n) and its distribution of PCL were 5.1×10^4 and 1.32, respectively. The PCL-*co*-PDHCA copolymers with various compositions were synthesized from PCL and DHCA, which introduced photoreactive groups into the main chains, by the thermal polycondensation method as Scheme 1(b). When DHCA content was low, M_n of the copolymers (PCL-*co*-PDHCA11 and PCL-*co*-PDHCA26) were higher. However, M_n decreased with further increasing DHCA

Table 1 Synthesis conditions of PCL-*co*-PDHCA polymers

Sample	DHCA : CL ^a (mol%)	DHCA : CL ^b (mol%)	$M_n \times 10^{-4}$ ^c / (g·mol ⁻¹)	M_w/M_n ^c	$M_n \times 10^{-4}$ ^d / (g·mol ⁻¹) (UV)	M_w/M_n ^d (UV)	BD/%
PDHCA	100 : 0	100 : 0	2.1	1.68	2.3	1.76	44.0
PCL- <i>co</i> -PDHCA 63	80 : 20	63 : 37	3.0	1.93	4.0	2.00	29.8
PCL- <i>co</i> -PDHCA 57	60 : 40	57 : 43	4.6	1.96	5.1	1.97	27.1
PCL- <i>co</i> -PDHCA 26	40 : 60	26 : 74	5.8	1.87	6.4	1.77	13.2
PCL- <i>co</i> -PDHCA 11	20 : 80	11 : 89	5.5	1.78	5.6	1.73	3.1
PCL	0 : 100	0 : 100	5.1	1.32	—	—	—

^a Molar ratios were calculated by amounts of the feed monomers. ^b Molar ratios were estimated by ^1H NMR spectra. ^c M_n and M_w/M_n were determined by GPC measurement. ^d M_n and M_w/M_n were determined after UV irradiation for 90 min by GPC measurement.

content. This phenomenon might be due to the high BD inducing the complex multiblock HB structure [Scheme 1(c)]. On the other hand, transesterification might also occur during the polymerization according to the result of GPC and FTIR. M_n of PCL-*co*-PDHCA63 and PCL-*co*-PDHCA57 were far lower than PCL, this phenomenon indicated the long molecular chains of PCL were broken up into shorter ones and combined with DHCA unit. This hypothesis could also be confirmed by FTIR spectra. As shown in supporting information, the C=O stretching peaks of PCL and PDHCA are 1739 and 1726 cm^{-1} respectively, and the one of PCL-*co*-PDHCA shifts to 1734 cm^{-1} slightly. This phenomenon indicates a new structure is generated which is due to the transesterification during the reaction. In other words, a complex multi block copolymer structure is occurring.

Photoreactivity

Since cinnamic acid and its derivatives show the well known *cis-trans* isomerization and inter- and intramolecular [2+2] cycloaddition with UV irradiation,^[20–24] the photoreactivities of the PCL-*co*-PDHCA copolymers were examined by UV-visible spectra in DMF solutions. Figure 4 shows the changes in the absorption spectra of PCL-*co*-PDHCA26 with various irradiation times during UV irradiation at $\lambda = 302$ nm. The peak at 313 nm was assigned to the characteristic absorption of the cinnamoyl group. The absorption decreased with increasing irradiation time, indicating the formation of the cyclobutane bond (crosslink). The PCL-*co*-PDHCA copolymers with different DHCA compositions showed the same photoreactive behaviors with UV irradiation, as showed in Figure 5. PCL-*co*-PDHCA with higher DHCA composition showed higher photoreactive speed. Moreover, the crosslinking degree (C. D.) of PCL-*co*-PDHCA decreased with the decreasing of the DHCA composition. Moreover, M_n of the UV irradiated copolymer increased as compared to that of

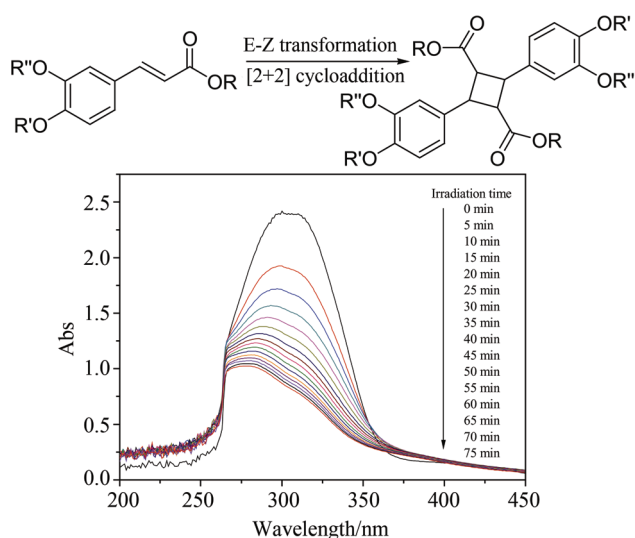


Figure 4 UV-vis spectra of PCL-*co*-PDHCA26 in DMF during UV irradiation at $\lambda = 302$ nm.

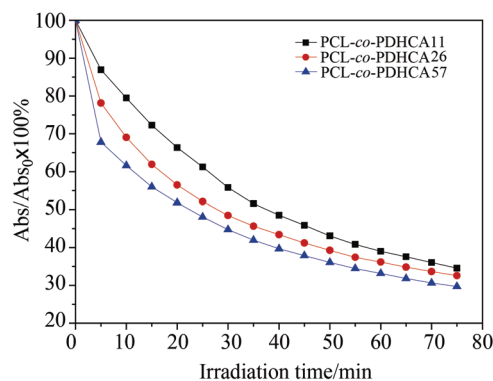


Figure 5 Absorption ($\lambda_{\text{max}} = 313$ nm) changes of the PCL-*co*-PDHCA copolymers with UV irradiation at $\lambda = 302$ nm.

the unirradiated copolymer (Table 1).

Fluorescence property

Fluorescence properties of the copolymers were also measured. The fluorescence emission spectra are shown in Figure 6 (the excitation was set at 375 nm). PDHCA and PCL-*co*-PDHCA polymers have a broad and strong fluorescence emission peak around 375–600 nm corresponding to the benzene rings and double carbon bonds conjugated system of the polymers. The maximum emission peak intensity at 450 nm increased with increasing of the DHCA composition. However, the emission peak intensity of the PDHCA homopolymer was slightly lower than PCL-*co*-PDHCA63, possibly due to the much higher BD compared with the other PCL-*co*-PDHCA copolymers. A higher branching degree will make the larger steric effects, thus might cause the fluorescent quenched. It was also confirmed that the reaction between DHCA and PCL has been accomplished successfully.

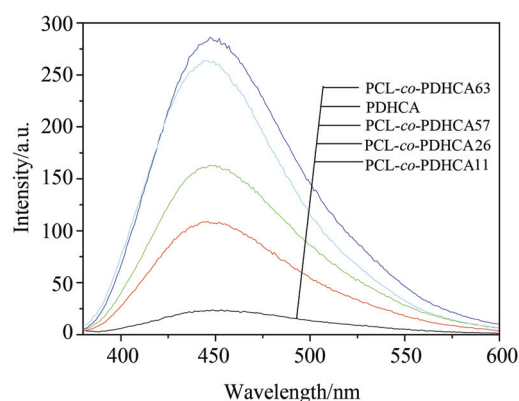


Figure 6 Fluorescence emission spectra of PDHCA and PCL-*co*-PDHCA polymers.

Thermal property

The thermal properties of the polymers were analyzed from DSC curves (Figure 7). The melting endotherm peaks appeared obviously in the DSC heating curves of the PCL and PCL-*co*-PDHCA copolymers.

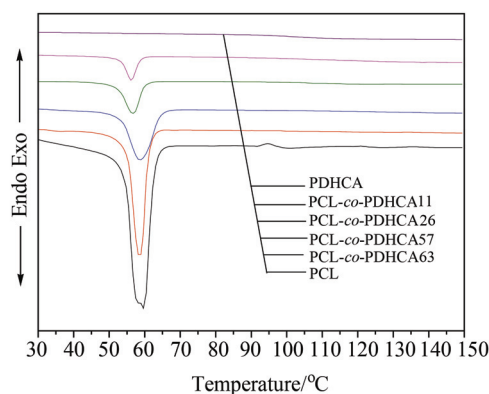


Figure 7 DSC curves of PDHCA, PCL-co-PDHCA and PCL.

However, glass transition temperatures of the polymers were unobvious in DSC curves. The phase transition temperatures of the polymers of these polymers were summarized in Table 2. The heat of fusion (ΔH_m) and the relative crystallinity of polymers (X_c) were also summarized in Table 2. X_c of the polymers could be estimated with respect to PCL content in the polymer by the following formula:

$$X_c/\% = 100 \times \Delta H_m / \omega \times \Delta H_m^0$$

where ΔH_m^0 is the heat of fusion of 100 % crystalline of the PCL homopolymer (135 J/g),^[25] ΔH_m is the fusion heat of the sample, and ω is the weight fraction of PCL in the polymers. The melting temperature (T_m) of PCL was 55.6 °C. With increasing the PCL chain in the PCL-co-PDHCA copolymers, the melting endotherm peak at 56–60 °C increased. T_m and X_c of the PCL-co-PDHCA polymers were almost lower than those of pure PCL, and the results illustrated that the DHCA chain disturbed the crystal growth of the PCL compositions.

The thermal stabilities of PDHCA, PCL and PCL-co-PDHCA polymers were also measured by thermogravimetric analysis (TG), and the results are showed in Table 2. The half-decomposition temperature ($T_{1/2}$) of PDHCA and PCL were 566 and 406 °C, respectively. $T_{1/2}$ and the weight remaining at 500 °C (ω_{500}) of PCL-co-PDHCA decreased with decreasing the DHCA composition in the copolymers. These results suggested that the excellent thermal stabilities of the

PDHCA and PCL-co-PDHCA polymers, which were attributed to the high branched structure, abundant rigid benzene ring, and the conjugated structure formed by benzene rings and double carbon bonds in PDHCA chains. Moreover, the thermal stabilities of the PDHCA and PCL-co-PDHCA polymers after UV irradiation were similarly investigated. From Table 2, ω_{500} of all sample increased. However, $T_{1/2}$ of the copolymers was regulated by the DHCA composition. For the copolymers with high DHCA composition, $T_{1/2}$ of the crosslinked copolymers increased as compared to the uncrosslinked one. However, $T_{1/2}$ decreased for the crosslinked copolymers with low DHCA composition. The phenomena might be the formation of [2 + 2] cycloaddition (crosslinking) of the cinnamoyl group under UV irradiation. The branching degree and crosslinking degree of the polymers with higher DHCA composition would be much greater, resulting in the increase of the thermal stabilities. The branching degree of the copolymers with less DHCA composition would be lower and the structures were more inclined to straight-chain. These results indicated the photoreaction and branched structure would significantly affect the thermal stabilities of the copolymers, and UV irradiation destroyed the regularity and the conjugated structure of the copolymers.

Crystallinity

The crystallinity of PDHCA and PCL-co-PDHCA polymers were characterized by WXR measurements, as showed in Figure 8. PDHCA shows broad peak, which indicates the amorphous property of the PDHCA homopolymer, due to its highly branched structure. PCL showed two strong crystal diffraction peaks at $2\theta = 21.2^\circ$ for the diffraction of the (110) plane and 23.2° for the (200) plane^[26,27] (θ = diffraction angel), and the phenomenon indicated that the PCL homopolymer was crystalline. Besides, very slight changes in the diffraction angles of PCL and PCL-co-PDHCA copolymers with low DHCA composition were observed. When the composition of DHCA in PCL-co-PDHCA copolymers increased, diffraction peaks assigned to PCL phase became weakened and broad suggesting the PCL-co-PDHCA copolymers trend to be amorphous, which was induced by the hyperbranched structure. The results indicated that PCL-co-PDHCA copolymers are crystal-

Table 2 Thermal properties of PCL, PDHCA and PCL-co-PDHCA polymers

Sample	$T_m/^\circ\text{C}$	$\Delta H_m/(\text{J} \cdot \text{g}^{-1})$	$X_c/\%$	Before UV		After UV	
				$T_{1/2}/^\circ\text{C}$	$\omega_{500}/\%$	$T_{1/2}/^\circ\text{C}$	$\omega_{500}/\%$
PDHCA	—	—	—	566	54.8	598	57.5
PCL-co-PDHCA63	56.5	5.6	12.0	559	53.6	577	54.8
PCL-co-PDHCA57	57.0	11.1	20.4	476	48.3	497	49.8
PCL-co-PDHCA26	59.0	21.8	22.5	427	41.3	418	43.1
PCL-co-PDHCA11	59.4	34.6	29.2	397	30.6	349	30.6
PCL	59.7	55.6	41.2	406	6.3	—	—

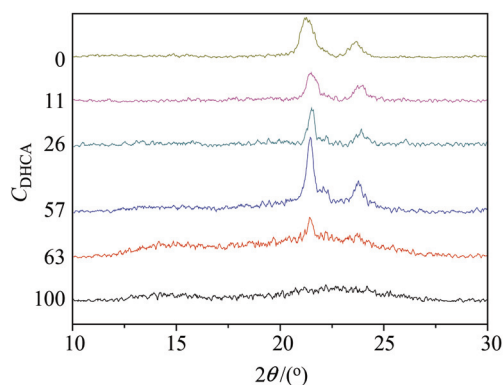


Figure 8 WAXRD patterns of PDHCA, PCL-co-PDHCA and PCL polymers. From up to down: CL, PCL-co-PDHCA11, PCL-co-PDHCA26, PCL-co-PDHCA57, PCL-co-PDHCA63 and PDHCA.

line fractionally, and the HB structure led the copolymer to become amorphous after introduction of the DHCA units.

Wettability

Since the interaction between water and the materials for the biological fields is very important, the contact angles of the PCL-co-PDHCA sheets were evaluated. Figure 9 shows the contact angles of the copolymer with different DHCA compositions. The water contact angles of the PCL-co-PDHCA11, PCL-co-PDHCA26 and PCL-co-PDHCA57 sheets were $(87 \pm 3)^\circ$, $(76 \pm 3)^\circ$ and $(63 \pm 2)^\circ$, respectively, which decreased with the increasing of the DHCA composition, possibly due to the slightly lower hydrophobicity of the DHCA chains than that of PCL. Moreover, after the UV irradiation, the contact angles of crosslinked PCL-co-PDHCA sheets slightly increased to $(91 \pm 2)^\circ$, $(77 \pm 2)^\circ$ and $(68 \pm 5)^\circ$. These results suggested that the crosslinking caused by UV irradiation increased the surface hydrophobicity. Therefore, the surface wettability of the PCL-co-PDHCA sheets was controllable by adjusting the chemical composition and the UV irradiation.

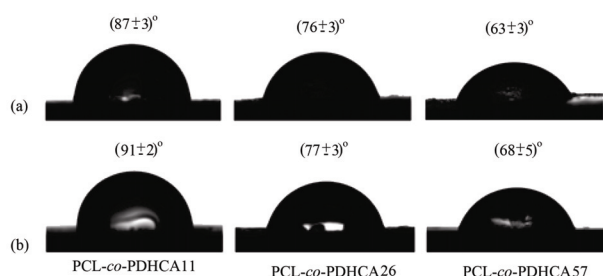


Figure 9 Contact angle images of the PCL-co-PDHCA sheets without (a) and with (b) UV irradiation for 30 min.

Degradation behavior

PCL and PDHCA are both degradable materials, and the copolymers should also have the property of degradable properties. Thus, the hydrolytic degradation

behaviors of the PCL-co-PDHCA sheet with and without UV irradiation were investigated in buffer solutions of pH=7.4 at 37 °C. Figure 10 shows weight losses of the PCL-co-PDHCA copolymers with degradation time. A rapid weight loss was observed in the initial period of incubation at pH=7.4, and the hydrolysis rate became slower and steady during the latter period of degradation. The first weight loss might be caused mainly by the degradation of the low molecular weight polymer chains. Moreover, the hydrolysis rate of PCL-co-PDHCA increased with increasing the DHCA composition. The different biodegradation rates of the copolymers were attributed to the different degrees of crystallinity. The PCL-co-PDHCA copolymers showed lower melting point and lower degree of crystallinity, and had a higher biodegradation rate. This result confirmed that biodegradation occurs initially in the amorphous parts of the polyesters, which is in accordance with the reported study.^[28] It is well known that PCL has a slow biodegradation profile due to its high hydrophobicity and degree of crystallinity, and the copolymers combined with PDHCA component may contribute to the increasing of the degradation speed. With UV irradiation of the PCL-co-PDHCA copolymers, the degradation behavior has no significant change.

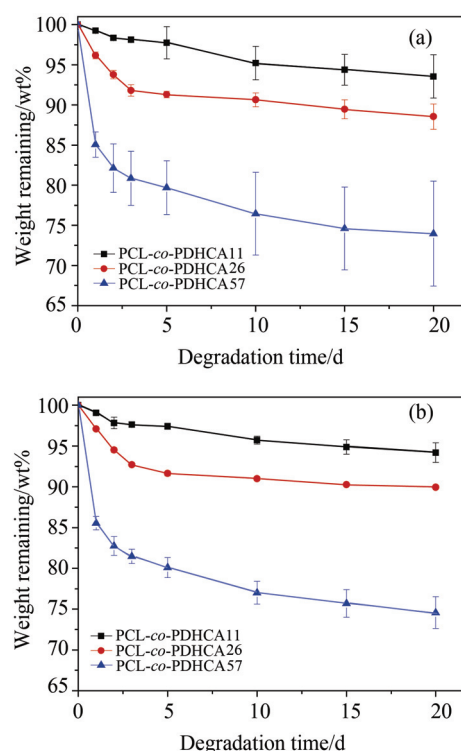


Figure 10 Degradation behaviors of the PCL-co-PDHCA polymer sheets with hydrolysis time. The weight remaining percentages of PCL-co-PDHCA polymer sheets in buffer solutions at 37 °C (pH = 7.4). (a) Without or (b) with UV irradiation for 30 min.

SEM images provided further information on the

morphology of the PCL-*co*-PDHCA11 sheets before and after hydrolytic degradation (Figure 11). The surface morphology of the sheet before hydrolysis was smooth. However, the surface after hydrolyzed for 20 d eroded markedly and existed a great deal of crack, due to polymer chain broken, suggesting the degradation occurred.

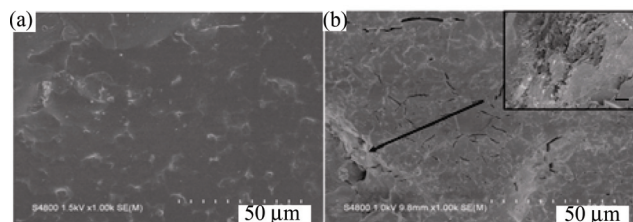


Figure 11 SEM images of PCL-*co*-PDHCA polymer sheets (a) before and (b) after degradation in phosphate-buffered saline (pH = 7.4) at 37 °C for 20 d (inset: scale bar 1 μm).

Conclusions

A series of the hyperbranched PCL-*co*-PDHCA copolymers were synthesized successfully by thermal polycondensation of DHCA with PCL, and the branching degree increased with increasing of the DHCA composition, suggesting the formation of hyperbranched structure. The melting endotherm peaks decreased with the increasing of the DHCA composition in the copolymers chains, and the WXR patterns also indicated that the copolymers were semi-crystalline related to the DHCA component. The TG results indicated the thermal stability of the copolymers increased with the introduction of the rigid conjugated DHCA composition, which was also affected by the photoreaction and hyperbranched structure of the copolymers. The PCL-*co*-PDHCA copolymers showed the fluorescence and photoreactive property, and the fluorescence intensity increased with the increasing of the DHCA composition. The water contact angles of the PCL-*co*-PDHCA sheets decreased with the increasing of the DHCA composition and were affected slightly by UV irradiation. The results of the invasion and accelerated degradation tests showed that the copolymer could be hydrolytically degraded in buffer solution, and the degradation rate increased with the increasing of DHCA composition of copolymers. Therefore, the properties of the copolymers could be controlled by changing the composition of the copolymer and the UV irradiation.

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