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Synthesis, characterization and biodegradation of biodegradable-cum-photoactive liquid-crystalline copolyesters derived from ferulic acid

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Abstract

Novel biodegradable-cum-photoactive liquid-crystalline copolyester was prepared by melt polycondensation of ferulic acid (FA), 4-hydroxybenzoic acid (HBA) and D,L-lactic acid (LA) in the presence of acetic anhydride and a transesterification catalyst. The chemical structures and properties of the synthesized copolyesters were characterized by means of viscosity measurements, Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (^{1}H NMR), differential scanning calorimetry (DSC), thermogravimetry (TGA), polarizing light microscopy (PLM) and ultraviolet spectroscopy (UV). It was found that modestly increasing LA content and adjusting feed ratios could enhance the solubility and biodegradability of the copolyesters, still retaining the liquid crystallinity. The obtained copolyester could degrade in phosphate buffer solution (pH 7.2) with enzyme *proteinase K*, and could crosslink by UV-irradiation at ambient temperature.

Keywords: Biopolymers; Liquid-crystalline polymers (LCP); Photochemistry

1. Introduction

In recent years, there has been a great need for biodegradable polymeric materials, since waste polymers cause serious destruction of the environment. A number of biodegradable aliphatic polyesters have been developed and some of them are now commercially available because of their good biodegradability. However, their lower thermal and mechanical properties provide obstacles to their commercialization [1–4]. A wide variety of chemical or physical strategies, including the copolymerization [5–7], polymer blend [8,9] and photocrosslinking networks [10,11] have been explored to match the special requirements.

It is well known that thermotropic main-chain liquid-crystalline polymers (LCP) possess excellent processability and self-reinforced mechanical strength due to the presence of highly oriented aromatic moieties [12]. However, poor solubility, high melting point, and inadequate degradability make LCP of limited application in biodegradable fields, especially as biomedical materials. Thus it would be of considerable interest to develop liquid-crystalline polyesters with enhanced degradability. The basic concept for this would be introducing liquid-crystalline segments into the biodegradable aliphatic polyester backbones, which would combine the biodegradability of aliphatic polyesters and the liquid crystallinity of aromatic polyesters [1]. Furthermore, toxicity of degradation products still deserves particular attention with the monomers selected here. Biodegradable polymers used in the medical field are ideally composed of metabolites found in the living body [13]. Sparse reports were concerned about the developed LCP based on hydroxycinnamic acid (HCA), which has been confirmed nontoxicity and well biocompatible in living body [12,14,15]. However, poor solubilities combined with high melting points make them difficult to process, and their application was thus impracticable.

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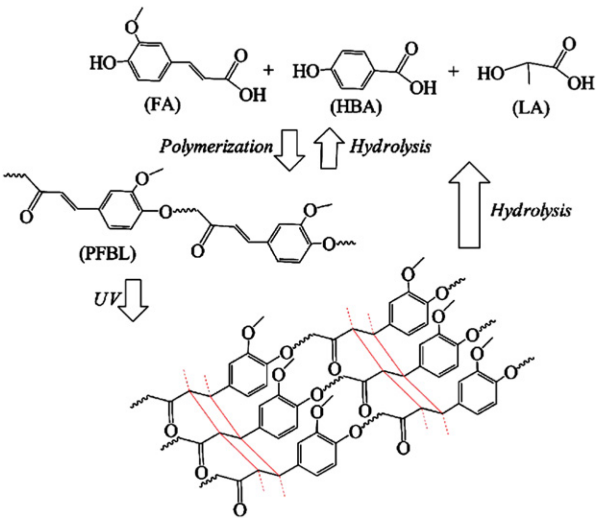

Scheme 1. Synthesis and hydrolysis mechanism of copolyesters.

Several effective methods of structural modifications to reduce the melting transition and increase solubility have been investigated, including (1) introducing long flexible spaces into mesogen backbones [16]; (2) utilizing aromatic moieties with lateral solubilizing substituents [17–20]. From this point of view, a novel biomonomer ferulic acid (FA) was selected in our study, which is one of the derivatives of cinnamic acid existing as a metabolite in the body and possess a methoxyl group on aryl ring. 4-Hydroxybenzoic acid (HBA) and D,L-lactic acid (LA) have also been proven nontoxic, and can be, respectively, introduced as rigid segments and flexible spacer. We adjusted the feed ratio of the monomers and tried to establish the structure–property relationship in order to make the products have excellent solubility and biodegradability, as well as still retaining liquid crystallinity. In addition, the unsaturated cinnamoyl group has potential photoactivity, which might endue the copolyester with luminous sensitive and photocrosslinkable properties.

This paper is devoted to the synthesis, characterization, and properties of the novel liquid-crystalline copolyesters derived from FA, which was expected to be applied as basic material for tissue engineering. Investigations on the biodegradation and photoactivity of the obtained products were also addressed in detail.

2. Experimental

2.1. Materials

Ferulic acid (FA) was supplied by Qingze Chemical Co. Inc (Nanjing, China); D,L-lactic acid (LA), 4-hydroxybenzoic acid (HBA), acetic anhydride, magnesium acetate tetrahydrate were purchased from Kermel Chemical Reagent Co. (Tianjin, China). All the solvents and monomers were used as received. *Proteinase K* (molecular weight: 28,500; activity: 33.5 units/mg dry weight) was purchased from Merck Calbiochem.

2.2. Polymer synthesis

A series of biodegradable-cum-photoactive liquid-crystalline copolyester were synthesized according to Ref. [12] with minor modifications. Concretely, a mixture monomers of FA (8.73 g, 45 mmol), HBA (4.14 g, 30 mmol) and LA (2.25 g, 25 mmol) was added in a 100 mL three neck flask equipped with a mechanical stirrer, and was dissolved in 20 mL of acetic anhydride (as a condensation reagent) in the presence of magnesium acetate tetrahydrate (0.1 wt%, as a catalyst) at 150 °C. The system temperature was raised to 170 °C after blowing nitrogen to remove moisture and residual air, maintained until almost all of the solvent had evaporated. The mixture was further heated at 200 °C under reduced pressure of 0.5–0.6 Torr for 6 h. Then, the resulting product was removed from the reaction flask, mechanically powdered and washed with acetone several times. Finally, the yellow powder was dried *in vacuum* at 80 °C overnight. The synthesis route is shown in Scheme 1 and the feed ratios are listed in detail in Table 1.

Analysis for PFBL2: FT-IR (KBr, cm^{-1}): $\nu = 2979–3010$ (w, –CH), 1719 (vs, C=O), 1691 (vs, C=O), 1598, 1320 (s, C=C), 1576, 1501 (s, C=C, Ar), 1238 (vs, C–O), 1060 (m, –C–O–C). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.35–1.50$ (d, 3H, CH_3), 3.82 (s, 3H, $-OCH_3$), 5.10–5.25 (d, 1H, CH), 6.6 (d, 1H, –C=C–H), 7.12–7.30 (m, 2H, Ar–H), 7.38–7.42 (m, 2H, Ar–H), 8.18–8.25 (m, 1H, Ar–CH=C).

2.3. Characterization

Inherent viscosities (IV) of the copolyesters were measured in a mixture of trifluoroacetic acid/chloroform (20/80 v/v)

Table 1
Composition and thermal characteristics of the samples

Sample	FA/HBA/LA[a] (molar ratio)	η_{inh}[b] (dL/g)	T_g[c] (°C)	T_m[c] (°C)	ΔH_m[c] ($J\ g^{-1}$)	T_i[c] (°C)	T_d[d] (°C)	T_i[e] (°C)
PF	100/0/0	0.168	64.3	160.1	95.0	212.5	317.2	288.0
PFB	50/50/0	0.212	76.3	120.7	4.4	157.7	315.8	160.0
PFBL1	40/40/20	0.284	75.9	109.9	2.9	144.9	301.8	145.0
PFBL2	45/30/25	0.325	69.9	108.9	6.4	138.9	289.6	142.0

[a] Molar ratio of the feeds.

[b] Measured with an Ubbelohde viscometer.

[c] The glass transition temperatures (T_g), the melting temperatures (T_m), melting enthalpies (ΔH_m) and the isotropic transition temperatures (T_i) were registered by DSC.

[d] The thermal decomposition temperatures (T_d), at which 5% weight loss occurred, were measured by TGA in N_2.

[e] Determined by the polarizing light microscope.

with an Ubbelohde viscometer. The Fourier transform infrared (FT-IR) spectra (in KBr pellets) were recorded with a Nicolet 20DXB FT-IR spectrophotometer. The ^{1}H NMR spectra were obtained using a Varian INDVA400 spectrometer with TMS as the internal standard. Phase transitions were measured using a Perkin–Elmer Pyris 6 DSC under a nitrogen flow. The thermal stabilities were measured by thermogravimetry (TGA) on a Shimadzu DT-30B in a nitrogen atmosphere. Wide angle X-ray diffraction (WAXD) experiments were performed using a XD-3A diffractometer at room temperature with a Cu Kα radiation. The mesophases were identified by polarizing light microscopy (PLM), performed on a Leitz LABORLUX 12 POL polarizing microscope with a Linkam THMS 600 heating stage. The effect of the biodegradation upon the polymer surfaces was examined using a JSM-5600LV scanning electron microscope (SEM).

2.4. Enzymatic degradation

Film samples were compression molded by a melt-pressing technique (30 × 10 mm in size and 0.2 mm in thickness) by the heating of powdered samples at 180 °C with a spacer under a pressure of about 200 kg/cm^2 and subsequent quenching in ice water and then dried *in vacuum* at 80 °C for 24 h. The film specimens were immersed in a small bottle containing 20 mL of phosphate buffer solution (pH 7.2) with 0.2 mg/mL of *proteinase K* that was kept in a controlled incubator at 37 °C for a period of time. Then the polymer films were washed with water, dried to constant weight *in vacuum* and weighed. The surface morphology was observed by scanning electron microscopy.

2.5. Photoactivity test

The photoactivity of the copolyester was investigated in the form of films and observed the absorption between 285 and 295 nm regions on a 756MC UV spectrophotometer. A typical procedure is as follows [21,22]: a thin film cast from a chloroform solution was placed on a quartz plate and exposed to UV-irradiation from a 500 W high-pressure mercury lamp at various intervals of time. Subsequently, the solutions of irradiated film in chloroform were cast on a quartz plate for UV studies and on a KRS disc for FT-IR studies.

3. Results and discussion

3.1. Synthesis and compositions

A significant effort was made in this study to explore the possibility of developing a series of liquid-crystalline copolyesters with better physical properties as well as still having biodegradability. The expected products should be composed by some aromatic polyester units as mesogenic segments and some aliphatic polyester units as both flexible spacer and biodegradable sites [12]. The basic concept is the combination of lactic acid monomer and aromatic mesogenic biomonomers. From the medical point of view the content of biodegradable moieties ought to be high in order to keep the excellent biodegradability and solubility. From the chemical point of view the reactivity of the comonomers has to be similar in order to obtain good copolymerizability, a uniform molecular structure, and high molecular weights [23]. From the physical point of view the copolyester should have an adequate content of aromatic mesogen moieties in order to show the LC properties. Here in the present study, various ratios of the monomers were employed to search for an appropriate balance between the solubility and liquid crystallinity.

The chemical structures of the polymers were analyzed by elemental analysis, FT-IR and ^{1}H NMR spectroscopy. A typical FT-IR spectrum of a PFBL thin film exhibited the characteristic carbonyl stretching band of the ester groups at 1691 and 1719 cm^{-1}, which corresponded to the aliphatic–aromatic ester bond and the aliphatic–aliphatic ester bonds, respectively. The sharp absorptions arising from the ethylene group appeared at 1598 and 1320 cm^{-1}, indicating that a *trans* cinnamoyl group was successfully introduced into polymer backbone. The double bond was also confirmed by the ^{1}H NMR spectrum, which exhibited two doublet signals at 6.6 and 8.2 ppm, characteristic for a *trans* cinnamoyl moiety. The methoxy protons of the ferulic acid moieties appeared as a singlet at 3.82 ppm. The homopolymer of PF and the copolyesters of PFB and PFBL1 were partly soluble in chloroform, but well soluble in pentafluorophenol and trifluoroacetic acid. The copolyester of PFBL2 was well soluble in chloroform and methylene chloride, but insoluble in tetrahydrofuran, diethyl ether and methanol. The intrinsic viscosity listed in Table 1 revealed that the product had moderate molecular weight.

3.2. Thermal and LC properties

DSC measurements were performed for polymer samples in order to investigate their thermal properties. The second heating curves for melt-quenched samples were chosen in order to remove previous thermal history and to make the T_g more clear and obvious. The determined data are listed in detail in Table 1 and the representative DSC curves are shown in Fig. 1. Consequent to the DSC studies, we compared the T_g and T_m of the copolymer with different comonomer feed ratios. It was observed that for PFB, the value of T_g was 76.3 °C and this was higher than the value of T_g of PFBL1 and PFBL2, whose values were 75.9 and 69.9 °C, respectively. This was due to the introduction of the flexible aliphatic ester. As the LA contents increased, the polymer chain became more flexible, T_g of the copolymers thus decreased. It was also noticed that T_m of the copolyesters was much lower than that of homopolyester PF, and decreased gradually with increasing LA content. These changes in the melting behaviors were due to the lowered regularity of the copolyester backbones caused by the introduction of the HBA and LA units. As the main-chain structure of the copolyesters became more random and harder to crystallize, T_m of the copolyesters decreased. The trend of decreasing T_i was also found in Fig. 1. With increasing LA content, T_i of copolyester decreased and the enthalpies reduced, until disappeared when LA exceeded

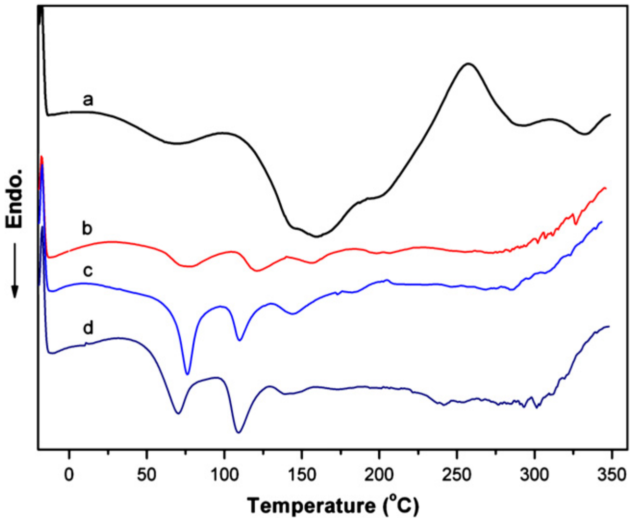

Fig. 1. DSC curves of homopolyester and copolyesters: (a) PF; (b) PFB; (c) PFBL1; (d) PFBL2.

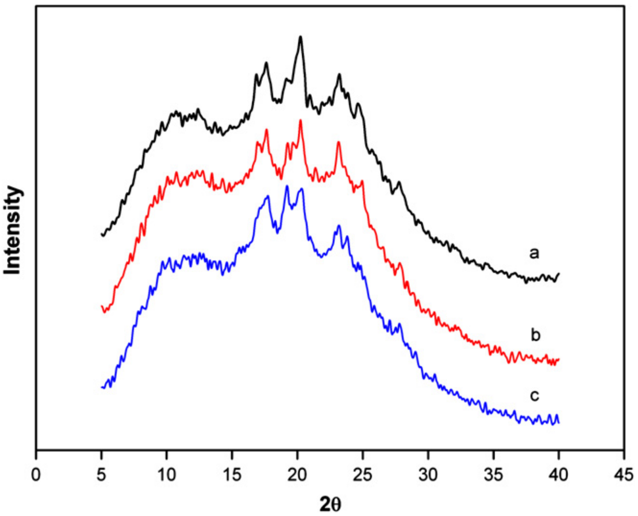

Fig. 3. Wide angle X-ray diffraction patterns of the copolyester: (a) PFB; (b) PFBL1; (c) PFBL2.

25 mol%. The thermal stability of the copolyesters was evaluated by TGA in a nitrogen atmosphere and the thermal decomposition temperature (T_d) is also listed in Table 1, indicating that the copolyester had a better thermal stability than aliphatic polyesters, which was thought to be ascribed to the introduction of the more thermally stable aromatic units.

The morphological texture was examined by polarizing light microscopy. All of the samples had typical coloured streak textures that were consistent with the anisotropic mesophases in the polarizing light microscope. Intuitively, PFB and PFBL2 could exhibit a schlieren texture characteristic of nematics at 150 and 120 °C, respectively, as shown in Fig. 2. The isotropic transition temperature determined by PLM is listed in Table 1, which is almost coincident with that obtained by DSC. In order to investigate the structure, wide angle X-ray diffraction (WAXD) studies of the copolyester samples were performed. The WAXD patterns were almost identical and showed four distinct diffractions at $2\theta = 10.7$, 17.7, 20.2, 23.2°, corresponding to spacings of 0.83, 0.50, 0.44, and 0.38 nm, respectively, as shown in Fig. 3. The X-ray diffraction pattern was typical of the nematic state.

3.3. Enzymatic degradation

The aromatic copolyesters with lactide moieties in the main chain were found to degrade in the presence of *proteinase K* [18]. Weight loss could be caused by the hydrolysis of ester linkages, followed by the subsequent reduction of molecular weight, to result in water-soluble oligomeric and/or monomeric products [21]. The weight losses of the film samples against degradation time in phosphate buffer solution (pH 7.2) at 37 °C without and with 0.2 mg/mL of *proteinase K* are shown in Fig. 4. It could be found that the degradation rate of copolyesters was remarkably enhanced in the presence of *proteinase K*. It was also found that the degradation rate of copolyesters increased with increasing LA content. The results indicated that introducing aliphatic components into the polyester backbones increased the flexibility of the polymer main chain, enhanced the probability of chemical bonds cleavage, and thus accelerated the enzymatic degradation. Surface morphology changes were investigated by scanning electron microscopy. Fig. 5 presents micrographs of PFBL2 film after

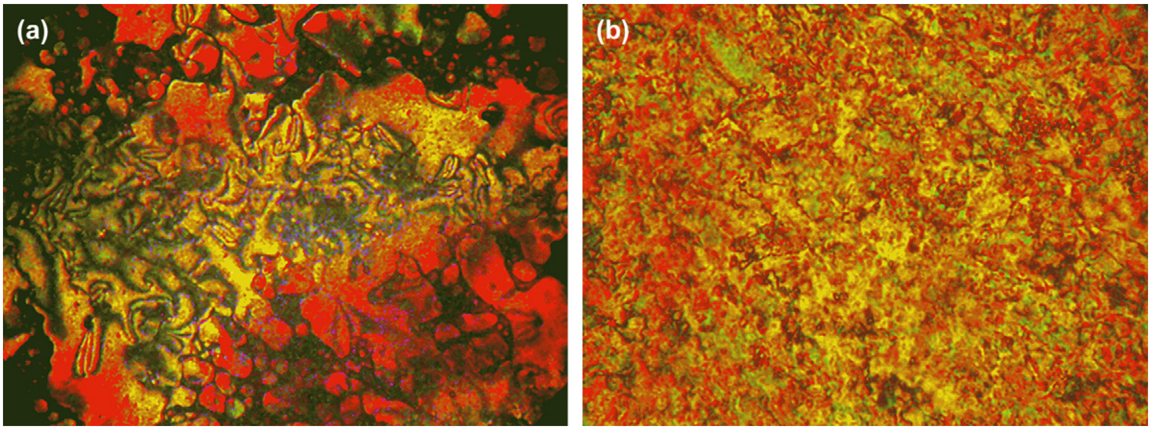

Fig. 2. Optical micrographs of textures: (a) PFB at 150 °C (magnification 200×); (b) PFBL2 at 120 °C (magnification 200×).

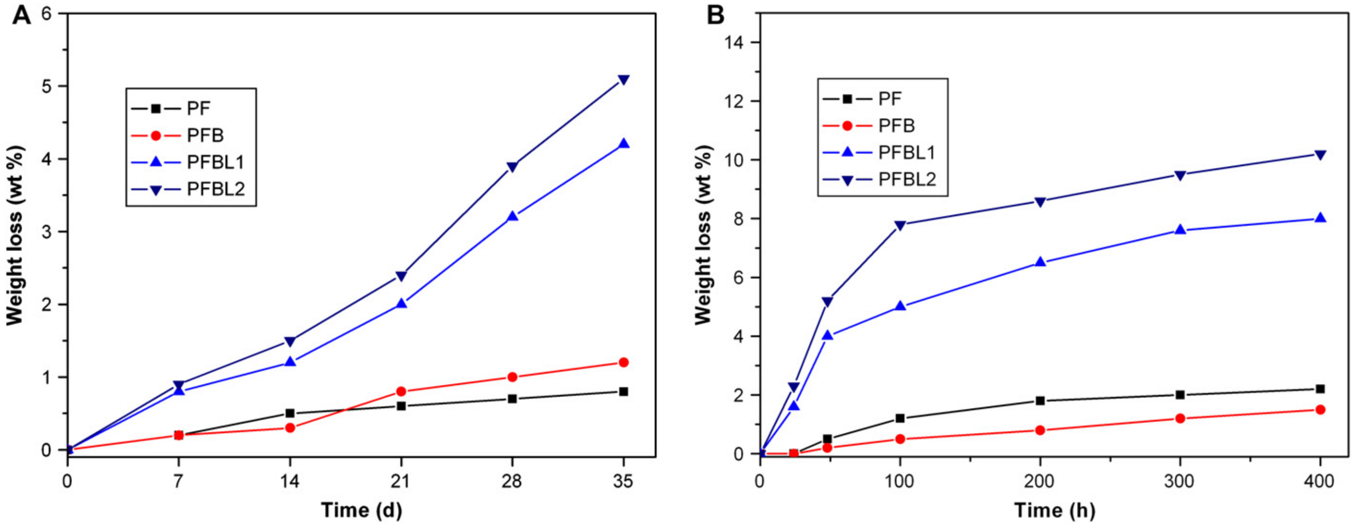

Fig. 4. The weight losses of the film samples against degradation time in phosphate buffer solution (pH 7.2) at 37 °C (A) without *proteinase K*; (B) with 0.2 mg/mL of *proteinase K*.

enzymatic degradation in the presence of *proteinase K*. The surface of the films after 24 h degradation was smooth but slightly cracked. After degradation for 100 h, the smooth surface of the copolyester films became porous. These results indicated that the enzymatic degradation of the copolyester films occurred predominantly on the film surfaces. It has been practiced in our previous work that FT-IR measurement could be conducted to investigate whether or not only the aliphatic chains in the copolyesters were biodegraded and to which extent the chemical bonds were cleaved [24]. In the FT-IR spectrum of typical sample PFBL2, the characteristic carbonyl stretching frequencies of the ester groups (C=O) appeared at 1719 and 1691 cm^{-1}, which corresponded to the lactide ester group and the benzoic ester group, respectively.

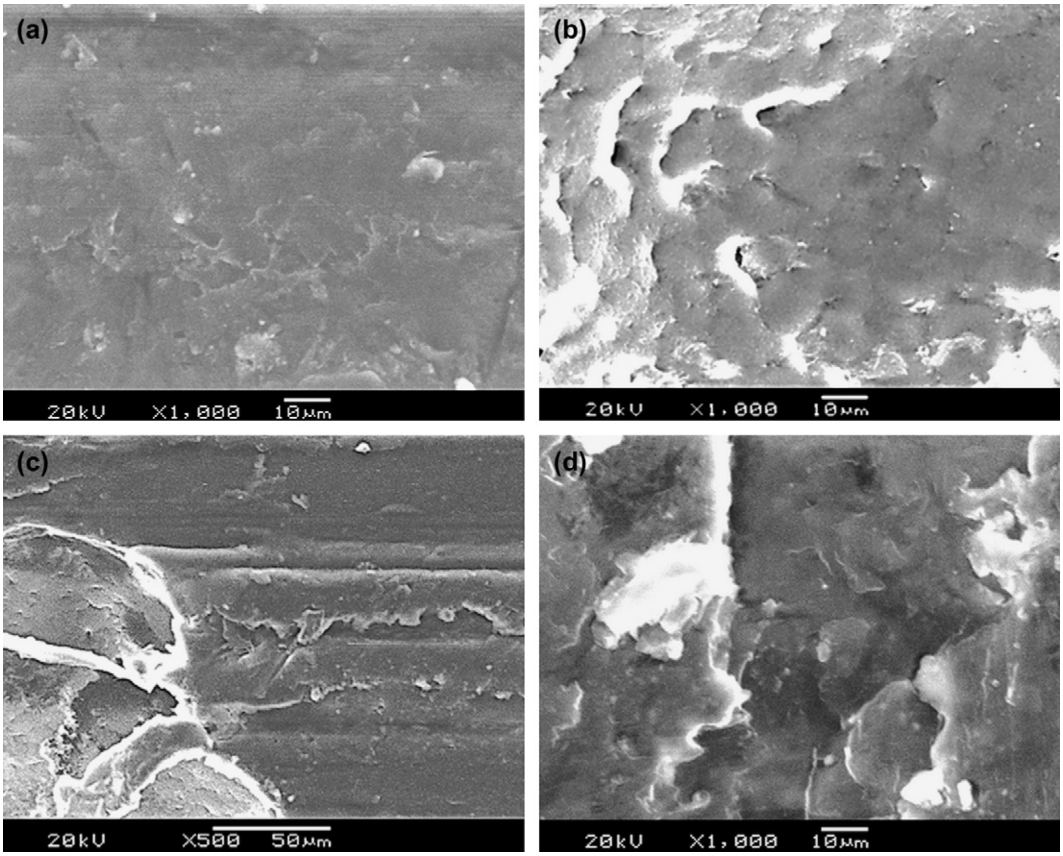

Fig. 5. SEM micrographs of PFBL2 film after enzymatic degradation: (a) original; (b) after 24 h; (c) after 100 h; (d) after 200 h.

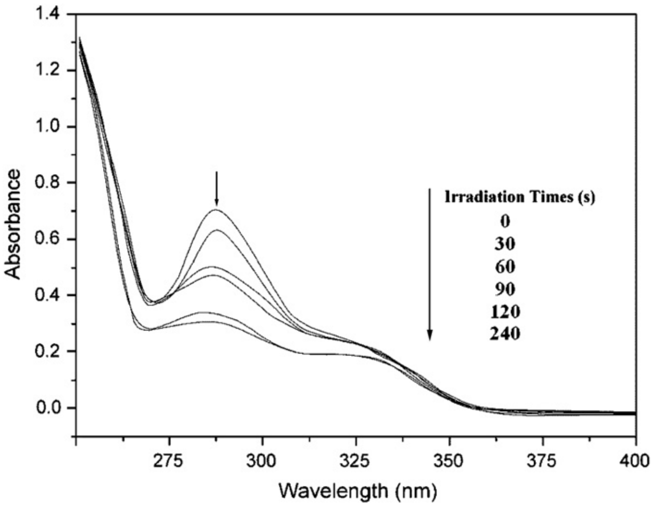

Fig. 6. Change in the UV spectrum of PFBL2 thin film upon UV-irradiation at ambient temperature.

The sharp absorption peaks at 1576 cm^{-1} were assigned to the C═C stretching vibrations on the *para*-disubstituted aromatic ring, which could not be affected by degradation. The change in the FT-IR absorbance ratio, A_{1719}/A_{1576}, gave a direct evidence for the scission of the lactide ester group during degradation (0.5–0.1 after 200 h). Regarding the FT-IR absorbance ratio of A_{1691}/A_{1576} (0.4–0.2 after 200 h degradation), the puny change could testify that a part of aromatic ester group was cleaved during hydrolysis.

3.4. Photoactivity test

The cinnamoyl group is well known to undergo a [2 + 2] photocycloaddition resulting in the formation of a cyclobutane ring. The photocrosslinking reaction was performed at ambient temperature in a thin film cast from a chloroform solution on a quartz plate, by irradiation with a 500 W high-pressure mercury lamp at $\lambda > 280$ nm and monitored by UV spectrophotometer. Fig. 6 shows the changes in the UV spectroscopic absorption of a PFBL2 thin film with irradiation time. The cinnamoyl absorption at 285–295 nm decreased very rapidly with increasing irradiation time. More than 80% of cinnamate moieties react within 4 min of irradiation in the absence of a photosensitizer. The same photocrosslinking reaction was conducted followed by FT-IR spectroscopy. Fig. 7 shows the FT-IR spectra of PFBL2 thin film prior to and after UV-irradiation. After irradiation, the absorptions of the *trans* C═C bond at 1598 and 1320 cm^{-1} decreased, indicating that the cleavage of the unsaturated bond led to the formation of a cyclobutane ring. After completion of the photocrosslinking, the film was insoluble in chloroform solvent and did not show liquid-crystalline property attributed to restricted molecular mobility and flexibility in the polymer backbone.

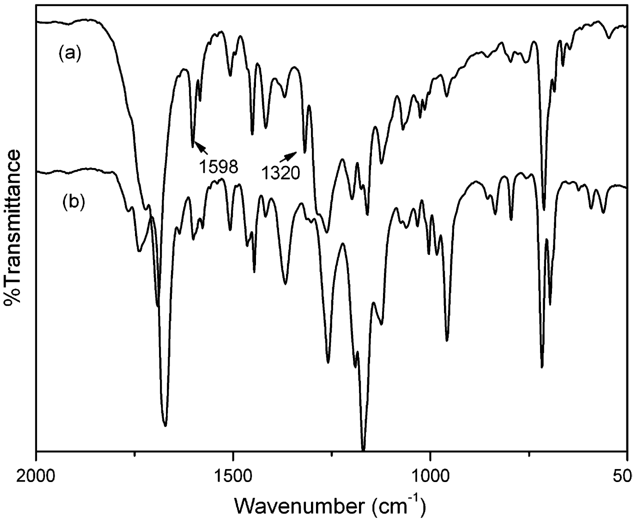

Fig. 7. Change in the FT-IR spectrum of PFBL2 thin film (a) prior to UV-irradiation; (b) after 4 min UV-irradiation at ambient temperature in the absence of a photosensitizer.

4. Conclusion

A kind of biodegradable-cum-photoactive liquid-crystalline copolyester PFBL was synthesized by the melt polycondensation of ferulic acid (FA), 4-hydroxybenzoic acid (HBA) and D,L-lactic acid (LA). The compositions of the copolyester were confirmed by FT-IR and ^{1}H NMR spectrum. When the monomer molar ratio was 45/30/25 (FA/HBA/LA), the obtained copolyester had a good solubility in chloroform and simultaneously exhibited a schlieren texture characteristic of nematics at 120 °C. The copolyester possessed biodegradability in buffer solution in the presence of enzyme *proteinase K* at 37 °C. The sample films were easily crosslinkable by UV-irradiation at ambient temperature with a photosensitizer. After completion of the photocrosslinking, the film lost the liquid-crystalline property. Further investigations on the biodegradability and biocompatibility of the photocrosslinked copolyesters are in progress and will be reported in a forthcoming paper.

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