

Synthesis, characterization and properties of high molecular weight poly(butylenes succinate) reinforced by mesogenic units

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Abstract

To increase the molecular weights of the synthesized liquid crystalline aromatic/aliphatic copolyesters and to avoid crosslinking, a solution polymerization of the prepolymer and chain extender hexamethylene diisocyanate was adopted. The effects of chain extension on polyester molecular weights, thermal and mechanical properties, and biodegradable behaviors were investigated respectively. The catalysis mechanism and the copolyesters morphological textures were also investigated. The synthesized copolyesters were characterized by means of Fourier transform infrared spectra (FTIR), gel permeation chromatography (GPC), viscosity measurements, differential scanning calorimetry (DSC), X-ray diffraction (XRD), polarizing light microscopy (PLM), scanning electron microscopy (SEM) and mechanical property measurements. It was found that inherent viscosities and the molecular weights of the copolyesters were remarkably increased under the action of catalyst, leading to a increase in the tensile strength. The degree of relative crystallinity, the melting temperature, and the rate of degradation decreased after chain extension.

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1. Introduction

Many investigations on synthesis, properties and degradability of biodegradable polymers have been made during the past decades. A number of biodegradable aliphatic polyesters, such as poly(hydroxy

butyrate) (PHB), poly(L-lactic acid) (PLLA), poly(ϵ -caprolactone) (PCL) and poly(1,4-butanediol succinate) (PBS), are the most extensively investigated because of their good biodegradability and suitable properties. However, their lower thermal and mechanical properties provide obstacles to their commercialization [1–4]. The lack of sufficient mechanical properties can be mainly attributed to their chemical structure and their relatively low molecular weight [5]. In order to obtain biodegradable polyesters with useful mechanical properties, many scientists have worked on the synthesis of

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copolyesters composed of aliphatic and aromatic units [6–10].

It is well known that thermotropic main chain liquid crystalline (LC) polyesters possess more excellent processability and self-reinforced mechanical strength than the simple aromatic copolyesters due to the presence of highly oriented aromatic moieties [11]. However, poor solubility, high melting point, and inadequate degradability make LC polyesters of limited application in biodegradable materials such as packaging. Thus it would be of considerable interest to develop LC polyesters with enhanced degradability. The basic concept for this would be introducing LC segments into the biodegradable aliphatic polyester backbones, which would combine the biodegradability of aliphatic polyesters and the liquid crystallinity of aromatic polyesters [12]. From this point of view, our current research is aimed at exploring the possibility of developing a series of liquid crystalline aromatic–aliphatic copolyesters with better physical properties as well as still having biodegradability.

It is also well known that the increased molecular weight of polyesters usually leads to an increase in the certain mechanical properties [13]. However, owing to the poor copolycondensability of the aliphatic units with the aromatic ones, its degree of polymerization is usually quite limited, and thus copolyesters with high molecular weight cannot be easily achieved. Another possible way to improve the mechanical properties of aliphatic polyesters without a loss of biodegradability could be the incorporation of a chain extender, resulting in increased molecular weight [5]. Thus, employing proper catalysts and coupling reaction could be a solution.

In our previous studies, a series of potentially biodegradable liquid crystalline aromatic/aliphatic random copolyesters poly(butylene succinate-*co*-butylene terephthaloyldioxy dibenzoates) (PBSTs) were prepared by melt polycondensation of a new mesogenic monomer dimethyl 4,4'-(terephthaloyldioxy) dibenzoate (MTB), dimethyl succinate, and 1,4-butanediol. Encouraging results disclosed improved thermal stability and enhanced elongations at break by incorporation of the mesogen moieties into the aliphatic polyester's main chain [14]. Furthermore, high molecular weight extended copolyesters E-PBSTs were synthesized by a melt polymerization of prepolymers and chain extender hexamethylene diisocyanate. Investigation indicated that increased temperature and excess chain exten-

der could not only activate the chain extension reaction, but also accelerate the side reactions such as branching or crosslinking, reducing the solubility of the products. Therefore, ameliorated chain extension need to be conducted to reduce the possibility of crosslinking reaction.

As described above, chain extension temperature and chain extender content were both factors affecting chain extension reactions. Therefore, our primary purpose of this study was to adopt stable chain extension method by decreasing the reaction temperature and reducing the diisocyanate content, and to obtain high molecular weight copolyesters with linear structures. Then, the effects of chain extension on copolyester molecular weights, thermal behaviors, mechanical properties and biodegradations were investigated respectively.

2. Experimental

2.1. Materials

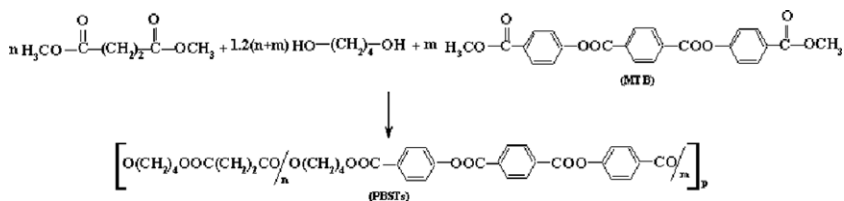
Methyl 4-hydroxybenzoate (MHB) was supplied by Kanto Chemical Co. Inc (Japan), dried at 60 °C *in vacuo* for several hours before use. Terephthaloyl chloride (TC), triethylamine (TEA), dimethyl succinate (DMS), 1,4-butanediol (BD), tetrabutyl titanate (TBT), tetrahydrofuran (THF), dibutyltin dilaurate (DBTDL) were purchased from Kermel Chemical Reagent Co. (Tianjin, China). Hexamethylene diisocyanate (HDI) was provided by Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the solvents were purified by distillation over calcium hydride before use. The other reagents were used as received.

2.2. Synthesis of prepolymer

A series of liquid crystalline aromatic/aliphatic random copolyesters PBSTs were prepared by melt polycondensation of a new mesogenic monomer MTB, dimethyl succinate, and 1,4-butanediol, using TBT as catalyst, as shown in Scheme 1. The synthesis of MTB and PBSTs were reported detailedly in our previous article [14].

2.3. Chain extension reaction

In the process of PBSTs synthesis, a small excess of the diol over the diesters was used, thus hydroxyl terminal groups of the obtained prepolymers



Scheme 1. Synthesis of copolyesters PBSTs.

should be reacted with isocyanate groups of the chain extender.

There were two chain extension methods including solution polymerization [15,16] and melt polymerization [5,17–19] in the similar research works. Regarding the melt polymerization, high temperature would activate the reaction, but simultaneously accelerate crosslinking of the polymer. The solution polymerization was comparatively stable, and therefore employed in this study. Concretely, the method was used as follows: 5 g of dried prepolymer was added in a 100 mL three neck flask with a condensation column, and was dissolved in 50 mL of purified chloroform with stirring at ambient temperature. Then, a solution of chain extender HDI (5 wt% of prepolymer) and catalyst DBTDL (0, or 1 wt% of prepolymer) in 20 mL of purified chloroform were added to the prepolymer mixture and the system was kept at 80 °C under a nitrogen atmosphere. The reaction was allowed to maintain for 8 h, and then the polymer was precipitated by quenching the reaction mixture in cold methanol. Buff precipitate was obtained and then dried *in vacuo* at 80 °C for 10 h.

2.4. Characterization

Inherent viscosities (IV) of the copolyesters were measured in a chloroform solution at 25 °C at a copolymer concentration of 0.5 g/dL with an Ubbelohde viscometer. The Fourier transform infrared (FTIR) spectra (in KBr pellets) were recorded with a Nicolet 20DXB FTIR spectrophotometer. The weight-average molecular weights of the polymers were estimated with gel permeation chromatography (GPC; Waters 201) using polystyrene solution in chloroform as the calibration standard. Phase transitions were measured using a Perkin–Elmer Pyris 6 DSC under a nitrogen flow with a heating rate of 10 °C/min from 20 to 200 °C under a flow of nitrogen (20 mL/min). The maximum points of the endotherm (heating scan) were taken as melting

temperature (T_m). The thermal stabilities were measured by thermo gravimetric analysis (TGA) on a Shimadzu DT-30B at a heating rate of 20 °C/min from ambient temperature to 500 °C in a nitrogen atmosphere. Wide angle X-ray diffraction (WAXD) experiments were performed using a XD-3A diffractometer at room temperature with a Cu K α radiation. The crystalline morphology and mesophases were identified by polarizing light microscopy (PLM), performed on a Leitz LABORLUX 12 POL polarizing microscope with a Linkam THMS 600 heating stage (magnification 200 \times). The tensile strength and elongation at break were measured with a universal test machine (AG-2000A Shimadzu Co.) at a strain rate of 500 mm/min. The effect of the biodegradation upon the polymer surfaces was examined using a JSM-5600LV scanning electron microscopy (SEM).

2.5. Microbial degradation in activated sludge

Film samples of the polyesters were compression molded by a melt-pressing technique (30 \times 10 mm in size and 0.5 mm in thickness) by the heating of powdered samples at 240 °C with a spacer under a pressure of about 200 kg/cm² and subsequent quenching in ice water and then dried *in vacuo* at 80 °C for 24 h. Active sludge was collected from Lingshui River (Dalian, China) and placed in poly(vinyl chloride) containers. The film specimens prepared as above were laid down between two layers of soil maintained soft to promote metabolic activity through proper oxygen uptake. The containers were left in an incubator at 25 °C and a humidity of about 70%. The polymer films were washed with water at a definite time, and dried to constant weight *in vacuo* and then weighed. The degree of degradation was estimated from the weight loss per area (W.P.A.) expressed as g/m², which was calculated by dividing the weight loss by the surface area of the film. The weight loss averaged for two specimens was employed.

3. Results and discussion

3.1. Synthesis and compositions

A significant effort was made in this study to increase the molecular weight of prepolymers and simultaneously enhance the mechanical properties of copolymers by chain extension reaction. The detailed analysis prepolymer was described in our previous study [14], and a summary of the results is showed in Table 1.

FTIR spectra of copolymers before and after chain extension were measured to confirm the bridging of polyesters by HDI. The bending (1545 cm^{-1}) and stretching ($3200\text{--}3300\text{ cm}^{-1}$) vibrations of N–H in urethane bond of polyesters appeared after chain extension, accompanying a drastic decrease in O–H vibration peak ($3300\text{--}3400\text{ cm}^{-1}$) of pre-

polymer terminals before chain extension. The representative peaks of the extended copolymers are described as follows: FTIR. (KBr, cm^{-1}): $\nu = 3200\text{--}3300$ s (N–H), 2940 w (C–H), 1760 vs (C=O), 1715 vs (C=O), 1600 w (C=C), 1545 s (N–H), 1530 m (C=C), 1270 vs (C–O), 1160 s (C–O), $1100\text{--}700$ (–(CH₂)_n–).

In the solution polymerization, the effect of catalyst on the chain extension reaction was studied by changing DBTDL content. The synthesis and analysis results are listed in Table 2. It could be observed that the inherent viscosities and the molecular weights of the copolymers were remarkably increased after chain extension under the catalytic action, but the corresponding values of the copolymers in the uncatalyzed system were slightly enhanced. According to the catalysis mechanism showed in Scheme 2, initially occurs the formation

Table 1
Summary of prepolymers analysis results

Prepolymer	MTB/DMS (m/n)	η_{inh} (dL/g)	\overline{M}_w (g/mol)	T_m (°C)	T_d (°C)	X_c (%)	σ_{max} (MPa)	$\varepsilon_{\text{break}}$ (%)
P00	0/100	0.542	53,600	113.6	272.7	69.3	22.7	37.5
P10	90/10	0.463	39,900	101.8	279.5	58.7	21.2	95.8
P20	20/80	0.428	31,700	89.1	283.8	50.6	19.2	118.2
P30	30/70	0.374	32,100	75.5	283.9	46.2	20.5	125.6
P40	40/60	0.363	24,400	62.1	286.8	41.0	18.4	146.4

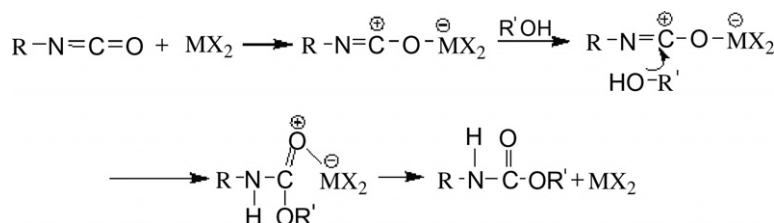
Table 2
Synthesis and molecular weights of the chain extended copolymers

Chain extended polymer	Prepolymer	DBTDL (wt%)	η_{inh}^a (dL/g)	\overline{M}_w^b (g/mol)	Color	Slope (min^{-1})	K^c ($\text{min}^{-1} \text{M}^{-1}$)
E-P00-1	P00	0	0.558	55,900	White	–	–
E-P00-2	–	1	0.785	76,500	–	–	–
E-P10-1	P10	0	0.470	42,300	Buff	–	–
E-P10-2	–	1	0.658	59,400	–	–	–
E-P20-1	P20	0	0.435	34,000	Yellow	0.070	5.645
E-P20-2	–	1	0.534	44,500	–	0.152	12.258
E-P30-1	P30	0	0.380	34,500	Yellow	–	–
E-P30-2	–	1	0.550	45,200	–	–	–
E-P40-1	P40	0	0.372	24,900	Brown	0.045	3.629
E-P40-2	–	1	0.508	37,500	–	0.167	13.468

^a Inherent viscosities were measured in a chloroform solution at 25 °C at a concentration of 0.5 g/dL with an Ubbelohde viscometer.

^b Measured by GPC analysis of chloroform solution with polystyrene standards.

^c $k = \text{Slope}/[\text{HDI}]_0$ ($[\text{HDI}]_0 = 1.24 \times 10^{-2} \text{ M}$).



Scheme 2. The mechanism of organo catalysis.

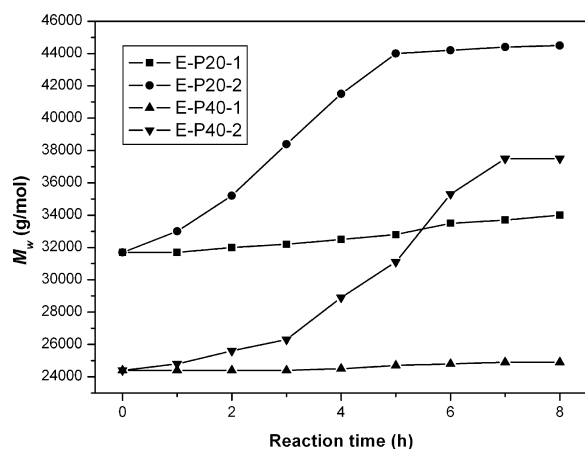


Fig. 1. The development of weight-average molecular weights in HDI chain extension.

of a complex between the organotin catalyst and the isocyanate group, activating the NCO group and making easier the reaction with the OH group. Afterwards the complex is decomposed, forming carbamate and regenerating the organotin. The series of E-P20 and E-P40 were chosen as typical samples for further understanding into the process of the chain extension reaction. A certain amount of samples taken from the system every hour during the chain extension period were used for the molecular weights measurement. The development of weight-average molecular weights is shown in Fig. 1. As seen, the molecular weights of copolyesters were gradually increased with increasing reaction time, which indicated that no crosslinking segments formed during the reaction period, and the solution polymerization was much stabler than the melt polymerization adopted in our previous work. It was also observed that under the action of catalyst, the increasing rates of copolymer molecular weight were much more remarkable than that in the uncatalyzed systems. The results indicated that DBTDL could activate the reaction, thus efficiently accelerate the chain extension.

Further kinetic studies of E-P20 and E-P40 series were conducted to research more about the chain extension by using the simple second-order kinetic model to simulate the reaction [20]. Adequate amount of the samples were taken from the system every 15 min in the first 2 h of the reaction period. The NCO concentration was determined by a standard titration method using *n*-dibutylamine [21]. The plot of the initial NCO concentration over the concentration at time t , $[(\text{NCO})_0]/(\text{NCO})_t$ vs. time]

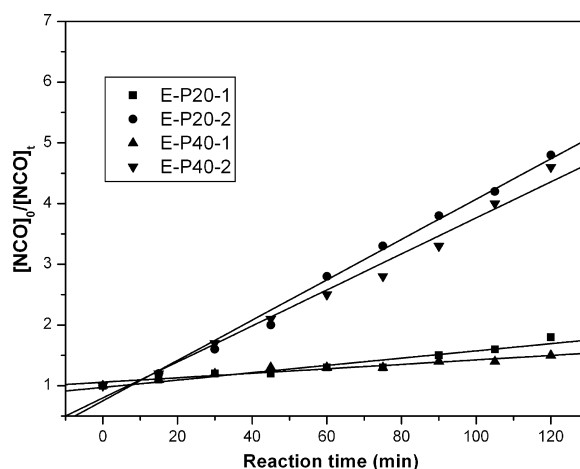


Fig. 2. Variations of $[\text{NCO}]_0/[\text{NCO}]_t$ with reaction time.

was exhibited in Fig. 2. The second-order rate constants, k , were obtained from the slopes of the plots [15]. Values of the slopes and the rate constants are summarized in Table 2. It was found that the rate constants were remarkably increased by the action of DBTDL, proving that the catalyst could veritabably accelerate the chain extension reaction.

3.2. Physical properties and optical microscopy

DSC measurements were performed for melt-quenched samples in order to remove previous thermal history, and the determined data are listed detailedly in Table 3. It could be observed that the melting temperatures of the copolyesters were slightly decreased after chain extension, which was probably due to the fact that the segments of chain extender in the copolymer macromolecular chain act as an impurity, disturbing crystal growth and lowering the regularity of copolymer main chains. It has been practiced in our previous work that the degree of crystallinity of thermoplastic is determined by dividing an observed heat of fusion from the first heating trace by the theoretical value for a 100% crystalline polymer. The theoretical ΔH_μ value for PBS was 13.4 Jg^{-1} [22]. The degree of relative crystallinity X_c thus determined are listed in Table 3. It was found that the X_c values of copolyesters were decreased after chain extension. Relative study was further conducted by comparing the X-ray diffraction patterns of the prepolyester P20 and chain extended copolyester E-P20-2, as given in Fig. 3. The sharp diffraction peaks were indicative of the presence of crystallites in the copolyesters. As

Table 3

Thermal and tensile properties of the chain extended copolyesters

Chain extended polymer	T_m^a (°C)	ΔH_m^a (Jg ⁻¹)	X_c^b (%)	T_d^c (°C)	σ_{max}^d (MPa)	ϵ_{break}^d (%)
E-P00-2	113.2	68.6	60.5	272.0	28.5	48.5
E-P10-2	100.8	57.4	50.6	280.0	26.5	92.8
E-P20-2	88.5	48.2	42.5	285.0	24.8	98.6
E-P30-2	73.5	43.5	38.6	284.0	25.2	103.2
E-P40-2	65.5	34.2	30.2	286.0	25.4	115.5

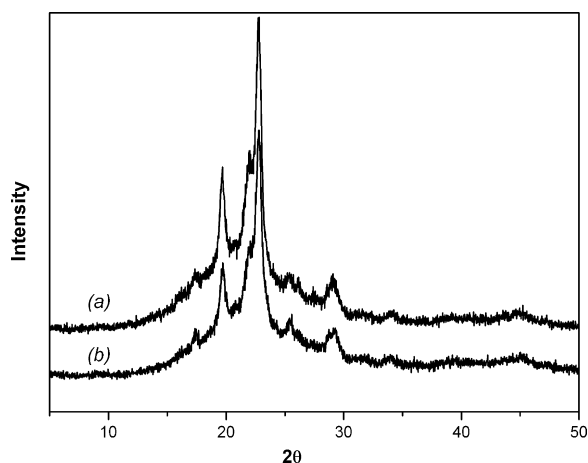
^a The melting temperatures (T_m) and melting enthalpies (ΔH_m) were registered by DSC at a heating rate of 10 °C/min.^b The degree of relative crystallinity (X_c) was calculated by dividing the observed ΔH_m from the first heating trace by the theoretical value (113.4 Jg⁻¹) for a 100% crystalline PBS.^c The thermal decomposition temperatures (T_d), at which 5% weight loss occurred, were measured by TG in N₂.^d The tensile strength (σ_{max}) and elongation at break (ϵ_{break}) were measured with a universal test machine at a strain rate of 500 mm/min.

Fig. 3. Wide angle X-ray diffraction patterns of the copolyester samples (a) P20; (b) E-P20-2.

seen, P20 and E-P20-2 showed the similar XRD pattern, proving that the patterns of copolyesters depend strongly on the composition of the predominant crystal unit, and the chain extension cannot affect the crystalline domains. It could also be observed that the crystalline peaks of E-P20-2 were relatively weaker than that of P20, as a result of crystalline region limitation as already mentioned above. The thermal stabilities of the chain extended copolyesters were evaluated by thermo gravimetric analysis (TGA) in a nitrogen atmosphere. The thermal decomposition temperatures (T_d) are summarized in Table 3. The effect of chain extension on the thermal stabilities was not obvious in this study.

The morphological textures of chain extended copolyesters were examined by polarizing microscopy, as shown in Fig. 4. When the concentration of the mesogenic components increased in the copolyester series, the arrangement of the individual lamellar crystallites into a large scale of organiza-

tion (anisotropic ordering of spherulites) gradually decreased. The copolyester E-P30-2 and E-P40-2, containing 30 and 40 mol% mesogenic monomer MTB respectively, did not clearly display the morphology of well developed spherulites, but exhibited the morphology of semi-crystalline polymer. This implied that a large portion of noncrystallizable comonomeric units (MTB-BD) might be trapped in the crystal lattice in the form of crystalline imperfection; when the content of the noncrystallizable units was increased, the perfection of spherulites declined and the crystallizable link of the chains became shorter and shorter. The morphological textures of the prepolyesters were similar to that of the corresponding chain extended polyesters, which indicated that the effect of chain extender on the crystal morphology was negligible.

The tensile strengths and the elongations at break of the extended copolyesters are given in Table 3. As seen, the tensile strengths of copolyesters were increased as expectation after chain extension, being probably associated with the remarkable increase in molecular weight, while the elongations at break were not changed remarkably.

3.3. Microbial degradation

The biodegradation of prepolyester and chain extended polyesters (P20, E-P20-2, P40 and P-40-2) were traced by soil burial test. The weight losses of the copolymer films against biodegradation time in activated sludge are showed in Fig. 5. It could be found that the degradation rate of chain extended copolyesters was slightly decreased compared with that of the prepolyester. The probable conclusion was that the increased molecular weight and the formation of urethane band in chain extended polyesters would retard the degradation rate. It was also

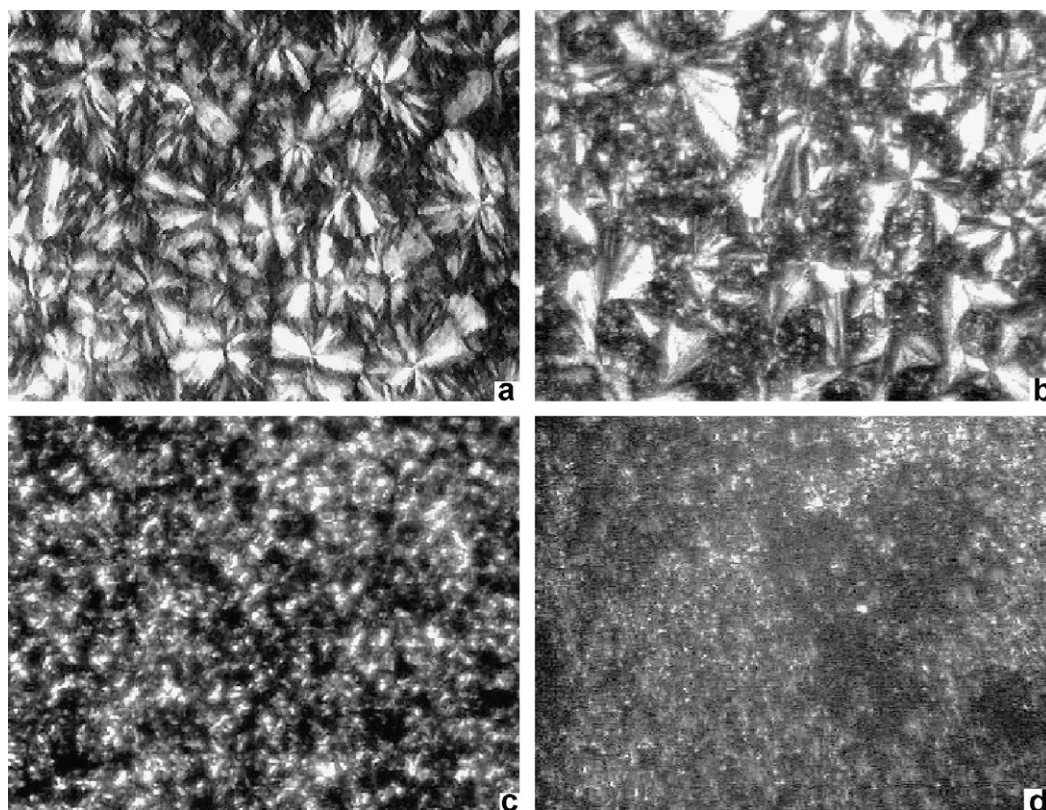


Fig. 4. Polarized optical micrographs of the chain extended copolyesters (200 \times) (a) E-P10-2, 65 $^{\circ}$ C; (b) E-P20-2, 60 $^{\circ}$ C; (c) E-P30-2, 55 $^{\circ}$ C; (d) E-P40-2, 50 $^{\circ}$ C.

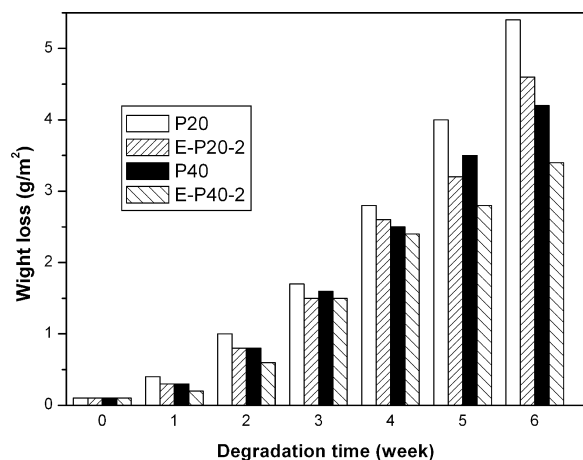


Fig. 5. Weight loss of the copolyesters films against degradation time in soil burial.

found that the degradation rate of copolyesters decreased with increased mesogenic unit content. The results indicated that introducing mesogenic components and urethane bonds into the aliphatic polyester backbones increased the rigidity of poly-

mer main chain, enhanced the difficulty in chemical bonds cleavage, and thus retarded the microbial degradation. It was ever reported that the reduced crystallinity could enhance the degradation rate of copolyesters [5]. However, the effect of the degree of crystallinity on the degradation rate could not be observed in this study. After 4 weeks the copolyester films became brittle and fragmented very easily. The mass loss accompanied by a considerable mechanical loss indicated that the copolyesters were fairly sensitive to microbial degradation in activated sludge [23]. The SEM micrographs of copolyesters E-P20-2 after soil burial is given in Fig. 6. The presence of large cavities was observed after 6 weeks, indicating that the biodegradation occur uniformly from the film surface.

In order to investigate whether or not only the aliphatic chains in the copolyesters were biodegraded and to which extent the chemical bonds were cleaved, further investigations on finding out the biodegradation process were conducted by FTIR measurement according to some reports [11,24]. In the FTIR spectrum of typical sample E-P20-2, the

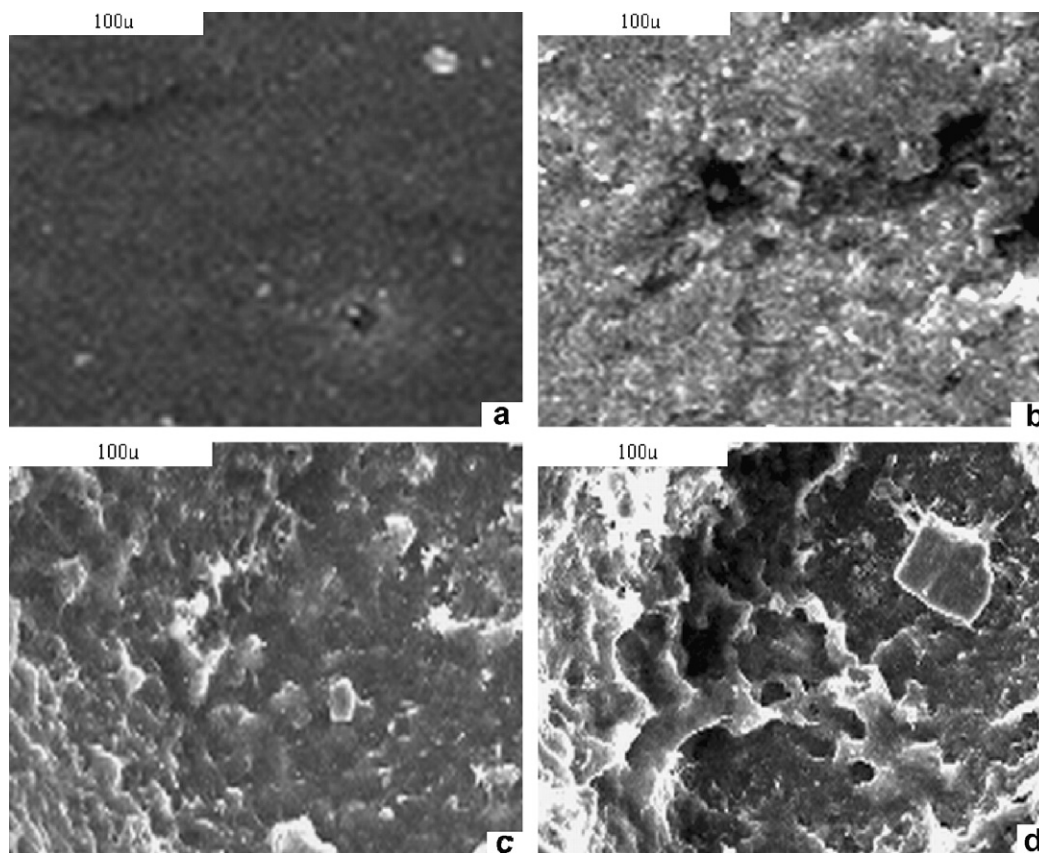


Fig. 6. SEM micrographs of copolyester E-P20-2 in soil burial (a) original; (b) after 3 weeks; (c) after 5 weeks; (d) after 6 weeks.

characteristic carbonyl stretching frequencies of the ester groups ($\text{C}=\text{O}$) appeared at 1760 and 1715 cm^{-1} , which corresponded to the aliphatic butanediol ester group and the aromatic ester group, respectively. The sharp absorption peaks at 1600 cm^{-1} were assigned to the $\text{C}=\text{C}$ stretching vibrations on the *para*-disubstituted aromatic ring, which could not be affected by degradation. The change in the FTIR absorbance ratio, A_{1760}/A_{1600} , gave a direct evidence for the scission of the butanediol ester group during degradation (1.2 to 0.5 after 6 weeks). Regarding the FTIR absorbance ratio of A_{1715}/A_{1600} (0.8–0.6 after 6 weeks degradation), the puny change could also testified that a part of aromatic ester group was cleaved by some esterase during burial in the activated sludge.

4. Conclusion

A series of high molecular weight chain extended poly(butylene succinate-*co*-butylene terephthaloyldioxy dibenzoates) polyesters (E-PBSTs) were

synthesized by a solution polymerization of pre-polyesters and chain extender hexamethylene diisocyanate. The effects of chain extension reaction on development of molecular weight, thermal and mechanical properties, and biodegradability of E-PBSTs were investigated respectively. The inherent viscosities and the molecular weights of the copolyesters were remarkably increased after chain extension using DBTDL as catalyst. The chain extension reaction between the isocyanate groups of chain extender and the hydroxyl terminal groups of prepolymers was confirmed by FTIR spectra. The disturbance of crystal growth process by chain extender segments led to decrease the melting temperature and the degree of relative crystallinity. After chain extension, the tensile strength of polyesters increased owing to the increased molecular weight, and the biodegradability slightly decreased due to the increased molecular weight and the formation of urethane band. The presence of mesogenic groups in the polymer chain retarded its biodegradation. Further investigations on enzy-

matic degradation of biodegradable liquid crystalline copolyesters are in progress and will be reported in a forthcoming paper.

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