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Synthesis and Characterization of Biodegradable Hexabasic Aliphatic-Aromatic Copolyester[1]

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Abstract—A series of aliphatic-aromatic copolyesters derived from diverse ratios of diols (ethylene glycol, 1,4-butanediol and 1,6-hexanediol) and diacids (succinic acid and dimethyl terephthalate) have been synthesized by melt polymerization. The optimal thermal and mechanical properties as well as biodegradability of prepared copolyesters have been investigated by controlling the content of diols and diacids monomers. Moreover, all synthesized polymers were spun into fibers by melt spinning for further tensile testing. The results indicated that all the synthesized aliphatic-aromatic copolyesters were degradable and the copolyester with the highest content of aliphatic units showed the better degradability. Moreover, degradability and elongation increased with the increment of aliphatic acid units in polymer although the tensile strengths and melting temperature were decreased.

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INTRODUCTION

Semicrystalline aromatic polyesters are widely used in many fields owing to their excellent mechanical and thermal properties. Among them, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are well known candidates and have been supplied in industries extensively [1]. Poly(hexamethylene terephthalate) (PHT) is a less known aromatic polyester and shows high elongation, low melting temperature and good processability due to the flexible long methylene backbones of PHT [2–5]. However, the compact structure and hydrophobicity of aromatic polymers lead to the non-biodegradability of these polymers. Additionally, the high melting point, poor solubility and non-biodegradability restricted the utilization of aromatic polyesters applied in the biomedical materials [6].

On the contrary, most aliphatic polyesters are biodegradable hydrolytically or enzymatically and they are considered to be the most economically competitive biodegradable polymers such as poly(ε-caprolactone) (PCL), poly(*L*-lactic acid) (PLLA), poly(butylene succinate) (PBS) and poly(hydroxybutyrate) (PHB) [7]. Even though these aliphatic polyesters have been commercialized, their high production costs and unsatisfactory inherent physical properties compared with conventional plastics have impeded their applications in different fields [8, 9].

Fortunately, in the past years, a majority of papers reported that aliphatic-aromatic copolyesters with satisfying mechanical properties and biodegradability could be obtained by synthesis of aliphatic and aromatic prepolymers [10]. Polymer blending is one of the most effective method to prepare aromatic-aliphatic copolyesters. Kint, et al. prepared PET/PBS block copolymer by reactive blending. The results showed hydrolytic degradability of PET/PBS increased with the increment of 1,4-butylene succinic units [6]. Another example, Jun and coworkers prepared biodegradable PCL/PET copolyester by transesterification reaction between PCL and PET [11, 12]. As above mentioned, although the biodegradability of PET has been enhanced to a certain degree, these investigations brought some drawbacks in the synthetic routes and cost. In addition, the defect of physical blending is that only the biodegradable polymer segments can degrade while the non-degradable aromatic polymer segment will remain its original state in environment [13]. It is revealed that the aromatic polyesters are degradable when copolymerized with aliphatic polyesters [14]. For instance, Deng LM, et al. has synthesized a biodegradable copolyester named poly(butylene succinate-*co*-ethylene succinate-*co*-ethylene terephthalate) with satisfactory thermal, mechanical properties and biodegradability due to copolymerization between aromatic and aliphatic prepolyesters. However, the multi-step process of copolymerization seems uneconomically. In that case, the direct copolymerization method should be investigated [13]. Consequently, it is necessary to synthesize an aliphatic-aromatic copolyesters with both good mechanical properties and biodegradability through direct copolymerization. And to the best of our knowl-

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edge, there are few papers reporting the synthesis and biodegradability of the hexabasic aliphatic-aromatic random copolyesters.

In this study, a kind of hexabasic aliphatic-aromatic copolyester was synthesized by direct melt copolymerization of dimethyl terephthalate (DMT), succinic acid (SA), ethylene glycol (EG), 1,4-butanediol (BD) and 1,6-hexanediol (HD). A series aromatic-aliphatic polyesters with three diverse diols have been synthesized. In order to obtain the best combination of desired properties, six samples with different weight ratios of SA in copolyesters 0, 10, 20, 30, 40, and 50 wt %, respectively, were prepared. Subsequently, all the polymers were spun into fibers, and the biodegradability, thermal and mechanical properties of polymers and fibers were investigated.

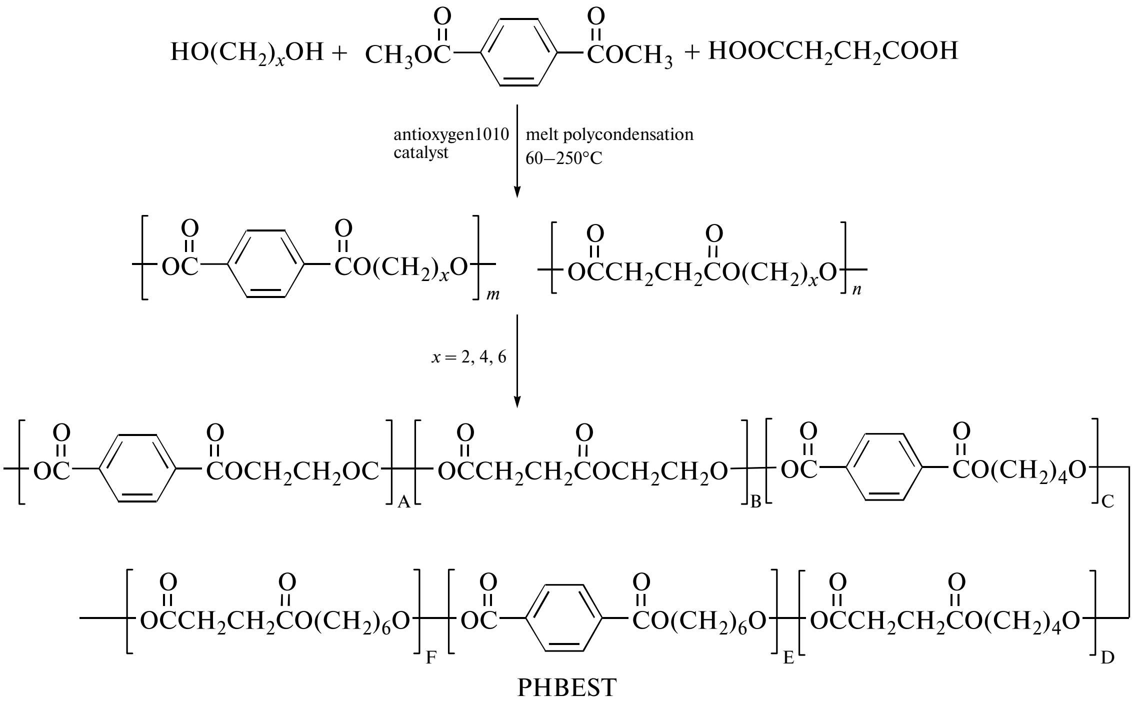
EXPERIMENTAL

Materials

DMT (CP grade) was purchased from Sinopharm Chemical Reagent Co.Ltd., BD (AR grade), SA (AR grade), EG (AR grade) and HD (AR grade) were received from Kelong Chemical Reagent Factory (Chengdu, China). Zinc acetate and tetrabutyl titanate were used as catalyst and tetrakis[methylene 3-(3',5'-di-*tert*-butyl-4'-hydroxyl phenyl)propionate] methane (Irganox 1010) was employed as antioxidant. All the reagents were used as received.

Synthesis of Copolyesters

Copolyesters were prepared by traditional melt polycondensation. Firstly, a certain amount of DMT, BD, EG, HD and SA were added to a 100 mL three-necked round flask equipped with a mechanical stirring, a thermometer and a nitrogen inlet, and the mixture were stirred under nitrogen atmosphere at 60°C for 0.5 h. After that, it was slowly heated to 140°C, and then the catalysts for esterification (zinc acetate: 0.3 wt % and tetrabutyl titanate: 0.3 wt %) and antioxidant (Irganox 1010: 0.3 wt %) were added. Followed, the reaction mixture was heated to 200°C and kept for 1.5 h of transterification. Subsequently, it was heated to 250°C, and then maintained under reduced pressure for 1.5 h. In this study, six kinds of polymers have been synthesized. According to the proportion of SA segments in copolyesters 0, 10, 20, 30, 40, and 50 wt %, the copolyesters were named as PEHT, PHBEST-1, PHBEST-2, PHBEST-3, PHBEST-4, and PHBEST-5, respectively. The synthetic process and chemical structure of PHBEST are shown in Scheme 1. Meanwhile, the feed ratios and physical properties of copolyesters are given in Table 1.



Scheme 1.

Table 1. Composition, inherent viscosity and molecular weight of PHBEST copolyesters

Polymer	n(EG)/n(BD)/n(HD)^a	n(DMT)/n(SA)^b	n(EG)/n(BD)/n(HD)^c	n(DMT)/n(SA)^d	η^{e}_{inh}, dL/g	M_w/M^{f}_n	M^{g}_n, g/mol
PEHT	80/0/20	100/0	69.2/0/30.8	100/0	0.725	2.392	15.216
PHBEST-1	72/10/18	90/10	61.5/20.8/17.7	90.9/9.1	0.748	1.937	15.891
PHBEST-2	64/20/16	80/20	57.0/23.2/19.8	82.3/17.7	0.627	3.275	12.456
PHBEST-3	56/30/14	70/30	48.5/30.5/21.0	72.3/27.7	0.660	2.848	12.848
PHBEST-4	48/40/12	60/40	41.3/36.5/22.2	61.7/38.8	0.710	2.770	14.220
PHBEST-5	40/50/10	50/50	35.6/41.9/22.5	50.7/49.3	0.702	1.761	13.769

[a, b] Feed molar ratio before copolymerization.
[c, d] Molar ratio of monomer in resulting copolyesters obtained from ^{1}H NMR.
[e] Measured at a concentration of 0.5 g/dL in *m*-Cresol at 30°C.
[f, g] Obtained from GPC.

Preparation of PHBEST Fibers

Fibers were obtained by using a self-made laboratory scale single-hole melt spinning machine with diameter of spinneret equal to 0.7 mm. All copolyesters showed excellent fiberizability and spinnability. Subsequently, the as-spun fibers were stretched double and then the heat setting process was carried out before tensile strength measurement. The characteristic temperatures of PHBEST in fiber-forming process are summarized in Table 2.

Preparation of PHBEST Films

The films were prepared by solution casting. Firstly, 1 g of each copolyester was dissolved in 10 mL of chloroform. Then, the solution was dropped on to a glass pane stewing for 24 h at ambient environment in order to evaporate the solvent slowly. After that, the formed films were removed from the glass pane and put in a vacuum oven at 45°C for 48 h under vacuum to remove the residual solvent.

CHARACTERIZATION

The chemical structure and composition of PHBEST were studied by ^{1}H NMR spectroscopy using Brucker DMX-600 in $CDCl_3$ at ambient temperature. Wide-angle X-ray diffraction (WAXRD) of PHBEST copolyesters was recorded on X-ray diffractometer (Philips) with CuK_α radiation. The experiment was taken at a scan rate of 2 grad/min from 10° to 45° at room temperature. GPC was performed on an Agilent 110 HPLC with chloroform as eluent at a rate of 0.6 ml/min under 40°C, molecular masses were calculated using calibration with PS standards. Melt temperature of copolyesters was characterized by SHIMADZU DSC-60, samples were heated from 50 to 200°C under nitrogen atmosphere at a heating rate of 10 grad/min. Thermal stability was studied by TGA SHIMADZU DTG-60(H) from 50 to 600°C at a heating rate of 10 grad/min under nitrogen atmosphere. The mechanical properties of copolyester fibers were determined by YG004C and the drawing speed was 10 mm/min under 25°C at a relative humidity of 65%. Each sample was tested 10 times and the average value was reported.

Enzymatic Degradation

Film samples of copolyesters (40 × 10 × 0.1 mm in size) were immersed in conical flasks containing fresh phosphate buffer solution (pH 7.0) and in the presence of pancreatic lipase (Ourchem: 100 μg/mL). The conical flasks were kept in an electro-thermostatic water bath at constant 37°C. The media was refreshed every 24 h. Each sample was taken out from the conical flasks at a predetermined time interval, after that the films were washed and dried at 40°C in vacuum for 24 h, then weighed. The weight loss of the samples was

Table 2. The characteristic temperatures of prepared PHBEST copolyester fibers

Polymer	Spinning temperature, °C	Drawing temperature, °C	Heat setting temperature, °C
PEHT	215	60	60
PHBEST-1	215	60	60
PHBEST-2	210	60	60
PHBEST-3	206	60	60
PHBEST-4	197	60	60
PHBEST-5	190	60	60

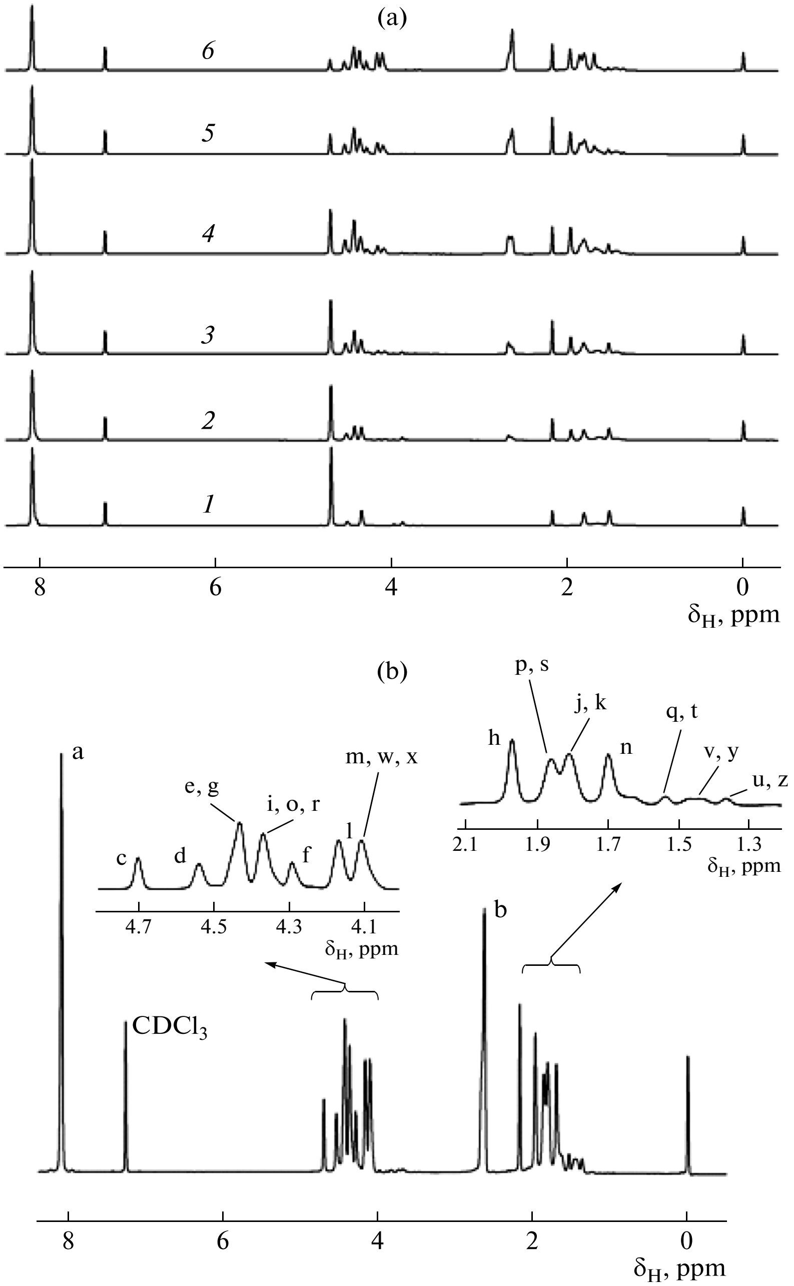


Fig. 1. ^{1}H NMR spectra of (a) PHBEST: (*1*) PEHT, (*2*) PHBEST-1, (*3*) PHBEST-2, (*4*) PHBEST-3, (*5*) PHBEST-4, (*6*) PHBEST-5, and (b) spectrum of PHBEST-5.

used to characterize the degradation. The following formula shows the calculation method:

$$\text{weight loss} = [(W_o - W_t)/W_t] \times 100\%, \qquad (1)$$

where W_o represents the original weight of the sample and W_t stands for the weight of samples after degradation and dried. Every sample was tested for five times and the averages were calculated. The surface patterns of the samples before and after enzymatic degradation were observed with scanning electron microscopy (SEM, JEOL JSM-7500F).

RESULTS AND DISCUSSION

The chemical structure of PHBEST was characterized by ^{1}H NMR. Figure 1a shows the ^{1}H NMR spectra of copolyesters. As the reactivity of SA and DMT in copolyester formation is the same [13], so obtained molar ratios of monomers from ^{1}H NMR spectra agreed with theoretical ones. As an example, Fig. 1b and Scheme 2 illustrates the assignment of PHBEST protons to the resonance signals. It is seen, that with increasing of SA units in the main chain, the signals at $\delta_H = 2.66$ ppm, which ascribed to methylene groups of

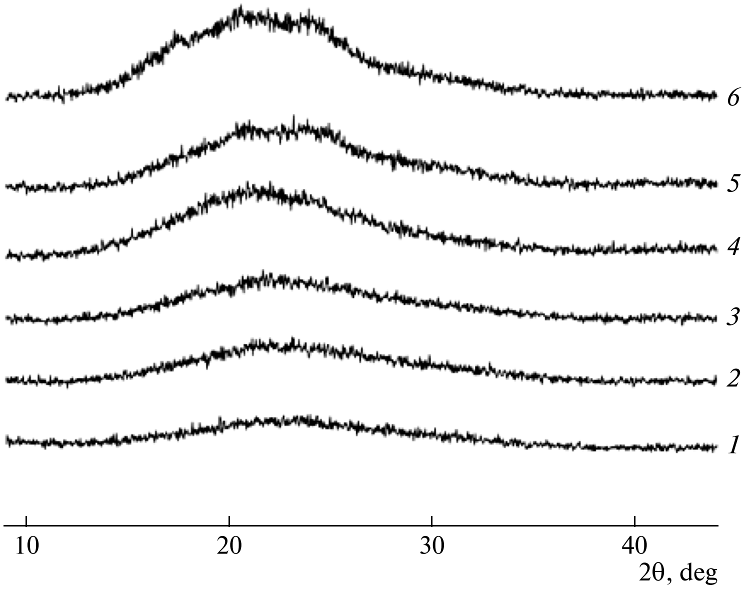
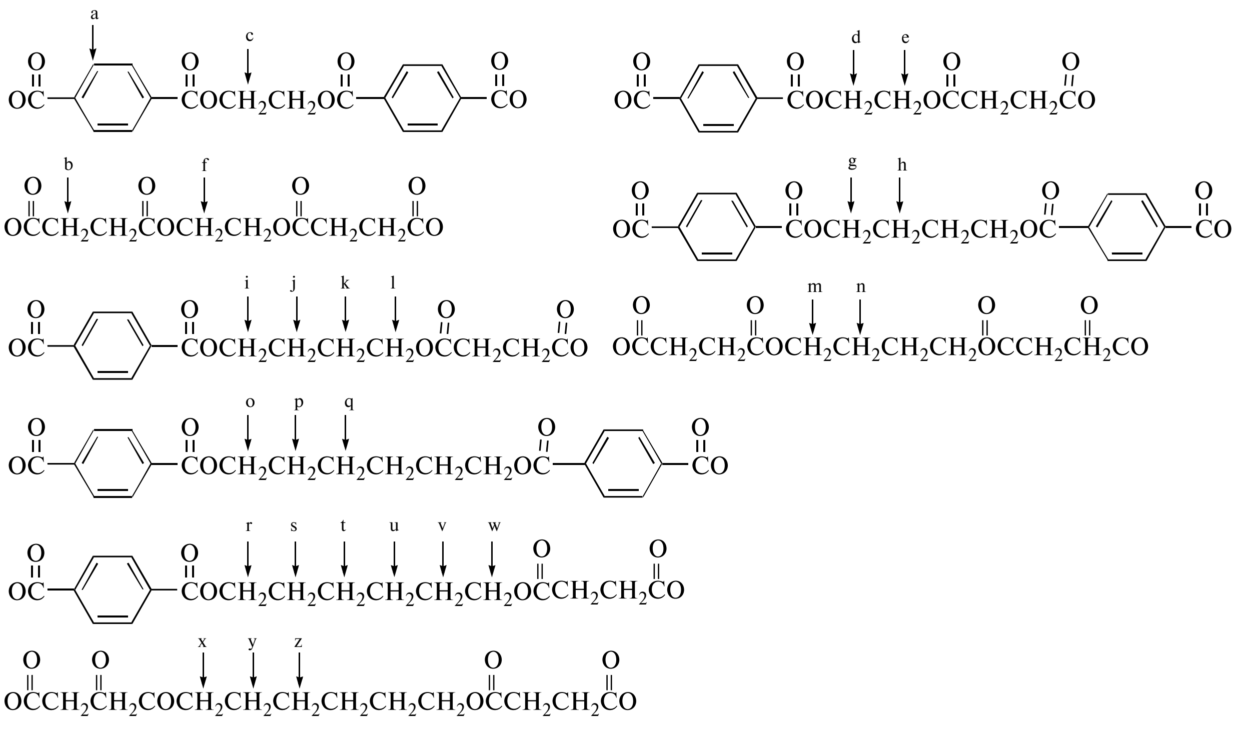


Fig. 2. The X-ray diffraction patterns of PHBEST copolyesters: (*1*) PEHT, (*2*) PHBEST-1, (*3*) PHBEST-2, (*4*) PHBEST-3, (*5*) PHBEST-4, and (*6*) PHBEST-5.

SA became stronger as expected. Otherwise, there are 9 possible dyads in PHBEST, namely, SHS, THT, THS, SBS, TBT, TBS, SES, TET, and TES. Scheme 2 also illustrates all the homo- and hetero- linkages dyads and proton assignments of PHBEST. Summarizing, the analysis of NMR data it may be concluded that the PHBEST copolyesters have been successfully synthesized.



Scheme 2.

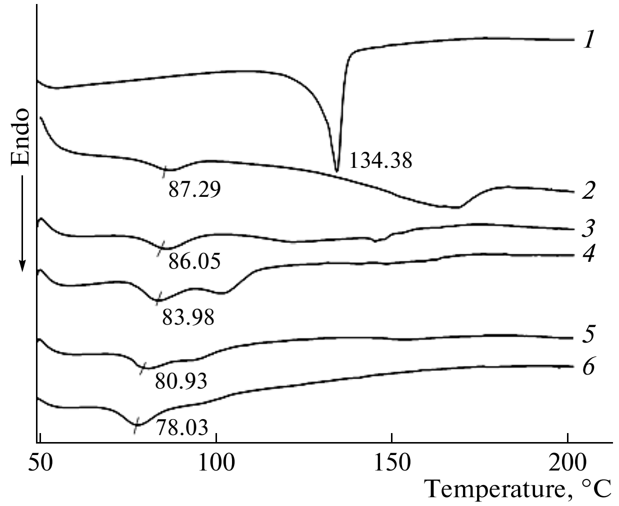


Fig. 3. The DSC curves of PHBEST copolyesters: (*1*) PEHT, (*2*) PHBEST-1, (*3*) PHBEST-2, (*4*) PHBEST-3, (*5*) PHBEST-4, and (*6*) PHBEST-5.

Figure 2 illustrates the X-ray diffraction patterns of PHBEST copolyesters. The prominent diffraction peaks indicated the presence of crystallites in copolyesters. It can be seen from the XRD patterns that the diffraction peaks of all the samples are very weak indicating that the crystallization of PHBEST copolyesters is poor. This would be explained by violation of the chain regularity in the multi-component polymers [15]. Otherwise, the diffraction peaks of PHBEST-5 are approximately similar to PBS at 18.8°, 21.6° and 22.5° [16]. This indicated that the PHBEST-5 has the similar crystalline structure to PBS. Although the other units such as PET and PHT can participate in crystallization, they are in amorphous state due to lower content. While as the content of PBS decreased, the reduction in intensities of diffraction peaks occurred at around $2\theta = 20°$. It is supposed that according to the profile shapes in each sample, only one crystalline phase is present [17]. Meanwhile, when the content of PBS continue to decline, the XRD patterns appear to be a bell shape and totally absence of reflections such as the curve of PHBEST-3, -2, -1 and PEHT. The incorporated comonomers served as impurities that disturbed the crystallinity of the copolyesters, thus the polymers transformed to amorphous state [18].

Thermal properties of PHBEST copolymers were determined by TGA and DSC. The melting temperatures and DSC curves are shown in Fig. 3. It can be seen that the melt temperature of PEHT was 134°C, and with the incorporation of aliphatic units into the polymer the melting temperature of PHBEST decline significantly to approximately 80°C. This can be explained by that the aromatic substituents in DMT units showed higher thermal stability. Additionally, the incorporation of aliphatic unit disrupted the crystalline structure of copolyesters, therefore the melt temperature decreased with the increasing SA content. Although the melting point changed dramatically with the incorporation of aliphatic units into the backbone of the copolyester, the thermal stability changed slightly. The TGA curves are given in Fig. 4 and the characteristic temperatures are listed in Table 3. It is found that all the samples exhibited single step decom-

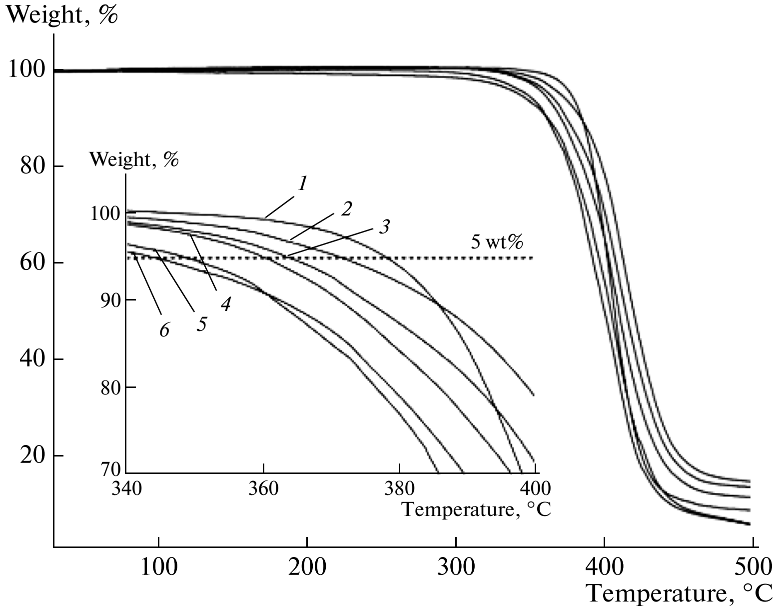


Fig. 4. The TGA curves of PHBEST copolyesters: (*1*) PEHT, (*2*) PHBEST-1, (*3*) PHBEST-2, (*4*) PHBEST-3, (*5*) PHBEST-4, and (*6*) PHBEST-5.

Table 3. The degradation characteristic temperatures of PHBEST copolyesters

Polymer	T_5^a, °C	T_{20}, °C	T_{50}, °C	Char yield, wt % at 500°C
PEHT	378	392	407	9.0
PHBEST-1	371	398	419	14.9
PHBEST-2	363	390	414	13.8
PHBEST-3	360	385	409	11.6
PHBEST-4	349	376	400	5.9
PHBEST-5	344	378	404	6.0

[a] 5 wt % decomposition temperature.

position. In the TGA curve, the 5 wt % weight-loss temperature (T_5) was used to estimate the thermal stability of polymer. It can be seen from Table 3, all the PHBEST copolyesters showed relatively good thermal stability with the T_5 all above 344°C. Moreover, with the increasing of DMT content the T_5 of copolyesters increased because of the richer content of aromatic segment in the main chains.

The mechanical properties are important for polymers to be used as fiber. Therefore, the tensile strength and elongation at break of PHBEST fibers were tested. The results are listed in Fig. 5. It is obviously that the tensile strength increased with the increment content of aromatic unites in copolyesters and the tendency is similar to that of melting temperature. However, the tensile strength of PEHT was inferior to PHBEST-1 and this phenomenon could be explained by the lower polymer molecular weight of PEHT (Table 1) [19]. Otherwise, the elongations of PHBESTs are higher than PEHT, and increased with the increasing of aliphatic unit content [20].

The biodegradability of PHBEST copolyesters were evaluated by weight loss ratios and polymer morphology. It is reported that the biodegradability of copolyesters is influenced by chemical structure, hydrophilic/hydrophobic balance, crystallinity, orientation and morphology domains [21]. Figure 6 shows the SEM graphs of PHBEST-5 and PHBEST-3 copolyesters before and after 7-day enzymatic degradation. It can be seen that the initial surface of PHBEST copolyesters were smooth and without holes. While after degradation, it became rougher as expected. The results indicated that the random PHBEST copolyesters are biodegradable. In addition, micro cracks appeared on the surface of PHBEST-5, which means that PHBEST-5 copolyester has better degradability. The weight loss of the PHBEST copolyesters during degradation is shown in Fig. 7. After degradation, the weight loss of PHBEST-5 reached 6.7%, however, the weight loss ratio of PHBEST-1 is only 4.1%. Additionally, there is almost no significant weight loss in PEHT polyesters. The weight loss of copolyesters increased with the increasing content of aliphatic units in PHBEST; hence the degradation ability of copolyesters with lower aromatic units is higher. Beside, among all the copolyesters tested, PHBEST-5 always has a slightly higher crystallinity. However, it showed a better degradability. This is because the influence on chemical structure is of greater significance on biological and mechanical properties than the degree of crystallinity [22].

CONCLUSIONS

A novel hexabasic aliphatic-aromatic copolyester named PHBEST contained six polymer units have been successfully synthesized by direct melt polymerization of three kinds of diols and two kinds of diacids. The obtained copolyesters all showed satisfactory biodegradability, fiber forming abilities, thermal and

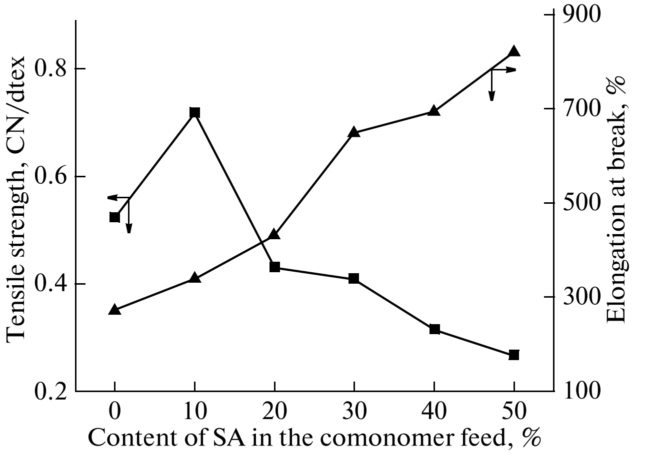


Fig. 5. The tensile strength and elongation at break of PHBEST copolyesters.

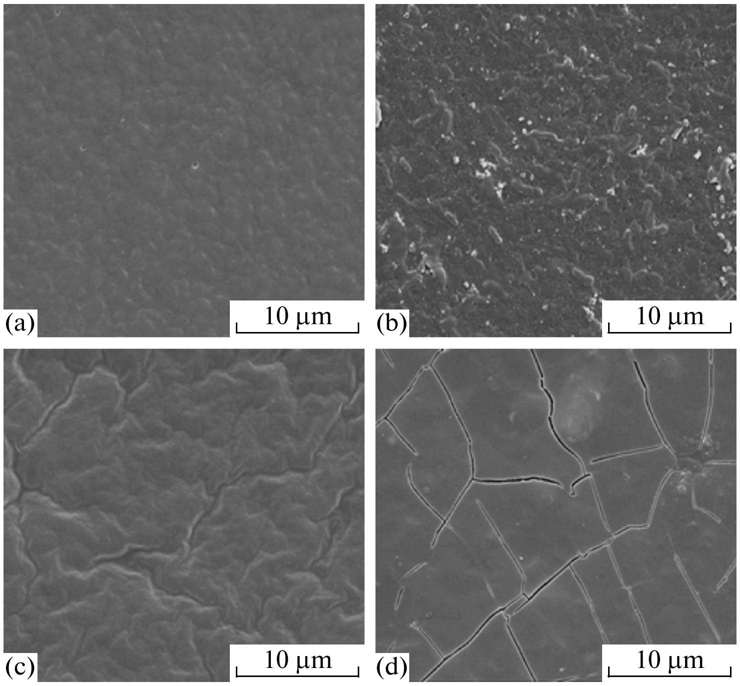


Fig. 6. SEM microphotographs of (a) PHBEST-3 and (b) PHBEST-5 copolyesters before enzymatic degradation, (b) PHBEST-3 and (d) PHBEST-5 after 7-day enzymatic degradation.

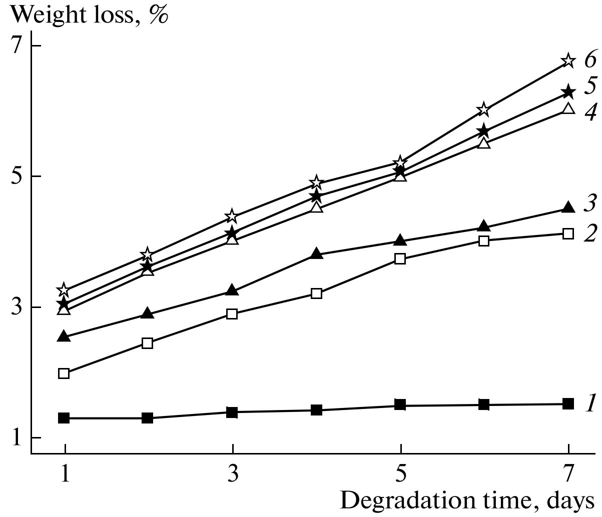


Fig. 7. The weight loss of PHBEST copolyesters during enzymatic degradation: (*1*) PEHT, (*2*) PHBEST-1, (*3*) PHBEST-2, (*4*) PHBEST-3, (*5*) PHBEST-4, and (*6*) PHBES-5.

mechanical properties. Meanwhile, the mechanical properties and thermal behaviors were increased with the increment content of aromatic units. From the enzymatic degradation test, it is concluded that the biodegradability of PHBEST copolyester is much higher than the PEHT, owing to the introduction of aliphatic diacid in the polymer chain of PHBEST. Additionally, more aliphatic diacid in copolyesters result in a better degradation.

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