Synthesis, ^{1}H-NMR Characterization, and Biodegradation Behavior of Aliphatic–Aromatic Random Copolyester

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ABSTRACT: Aliphatic-aromatic copolyesters of poly(butylene adipate-*co*-butylene terephthalate) have been synthesized by polycondensation. Molecular weights and thermal properties have been measured. The four samples of copolyesters, with aromatic contents, varying from 40 to 60 mol %, were investigated by ^{1}H-NMR spectroscopy to determine copolymers composition and microstructure. For all samples, the biodegradation experiment was carried out in compost, to study copolyesters degradation behavior. Using ^{1}H-NMR, we noticed that the average sequence length and content of the aliphatic unit decrease and those of the aromatic unit increase. The molecular weights of the samples distinctly drop after composting. In all degraded samples, the trace of growing microorganisms was found on their surfaces by scanning electron microscopy. In combination with the results, the degradation behavior has been studied in the middle stage of copolyester degradation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2643–2649, 2007

Key words: aliphatic-aromatic; biodegradable; composting; copolyester; sequence distribution; polycondensation

INTRODUCTION

In the world today, increasing volumes of plastics are produced and widely used for many everyday applications, mainly because of their low product price and versatility. However, they are resistant to environmental influences such as humidity and microbial attack, especially from short-lived packaging, are considered to cause serious waste problems. Therefore, many scientists made intensive efforts, since the beginning of the 70s of the 19th century to develop new plastics that are biologically degradable and can thus be disposed of by composting.[1] Polyesters play an important role within the group of biodegradable plastics. Until now, the commercially available biodegradable polyesters are mostly aliphatic polyesters, such as the bacterial polyesters poly (hydroxybutyrate) (PHB), and the chemically synthesized poly(caprolactone) (PCL), poly(lactic acid) (PLA), and poly(butylene succinate) (PBS).[2] Even though this polyesters are already available in the market, some weaknesses prevent them from being used in many applications. PHB production lost its competitiveness with other biodegradable plastics since the high material price caused by the relatively expensive technique. The PCL exhibits low melting point of about 60°C, and is easy hydrolyzes during processing that excluded it from many applications. For PLA, the degradation is a combination of chemical hydrolysis and microbial degradation of the intermediates, and the processibility is poor. PBS shows good properties, but the degradation rate is slow and the flexibility is low. Developing new types of biodegradable polymers with different properties of above aliphatic polyesters is desirable because of the great number of specific requirements for polymeric materials.[3]

In this way, modification of biodegradable aliphatic polyesters with nonbiodegradable polyesters, for example, introducing aromatic terephthalate units into the main chains of aliphatic polyesters either by polymer-polymer transesterification or by direct copolymerization of the comonomers,[4] resulting in aliphatic-aromatic copolyester is an interesting way to develop new biodegradable copolymers. The copolymerization by polymer-polymer transesterification is uneconomical because of its multi-step process. And the elevated temperature of the ester exchange reaction of two or more homopolyesters prevents more aliphatic polyesters with low melting point from being used in the synthesis of copolyesters. To overcome these defects, the direct copolymerization techniques are being investigated. The direct copolymerization method is a suitable way to obtain new aliphatic-aromatic copolyesters with better physical properties and biodegradable. Copolyesters synthesized from aliphatic and aromatic comonomers, such as, 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, sebacic acid, adipic acid and terephthalic acid combined in an appropriate range has proven to be biodegradable.[5,6]

On the basis of the previous investigations, biodegradability of aliphatic-aromatic copolyesters is

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$$-\left[O-(CH_2)_4OOC(CH_2)_4COO\right]_x\left[(CH_2)_4OOC\bigcirc COO\right]_y-$$
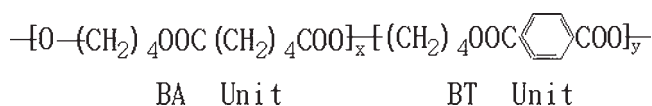
BA Unit   BT Unit

Figure 1 Formula of the copolyester.

dependent on the chemical composition of the co-polyesters, length and sequence distributions of aliphatic, aromatic chains, and crystallinity.[7,8] And bio-degradability of aromatic part of the copolyester is particularly dependent on the number of repeating units.[7,9] Thus, the degree of randomness of the co-polyester chains and the block length distribution within the copolymers are important to investigate and understand the biodegradation behavior of aliphatic-aromatic copolyesters.

The investigations of the composition, the chain length and the sequence distribution of copolyesters containing poly(butylenes terephthalate) (PBT) units with high-field ^{13}C nuclear magnetic resonance (NMR) spectroscopy and the final biodegradability of PBT-based copolyesters have already been described in the literature.[9,10] But PBT-based copolyesters show small differences in chemical shifts of the tetramethylene carbon signals of only 0.02 ppm. Thus, the use of ^{1}H-NMR spectroscopy enables an easy investigation of the sequence distribution of this copolyester.

In this work, we have synthesized aliphatic-aromatic poly(butylene adipate-*co*-butylene terephthalate) copolyesters with BT contents, varying from 40 to 60 mol %. We have checked the composition, the average sequence length and average molecular weight of the copolyesters after composting by ^{1}H-NMR and gel permeation chromatography (GPC). Thus, it is important to study biodegradation behavior of the copolyesters.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), 1,4-butanediol (1,4-BD), adipic acid, and tetrabutylorthotitanate (TBOT) were all reagent grade and used as received.

Synthesis of P(BA-*co*-BT) random copolyesters

All aliphatic-aromatic copolyesters were prepared by transesterification polycondensation. Polymerization reactor was a 500-mL four neck flask, which equipped with a leakproof stirrer, a nitrogen inlet, and condensation column. DMT and 1,4-BD were placed into flask with calculated molar diacid and diol rations, then monomer DMT of 0.4 wt % of TBOT as catalyst was added to the flask. The mixture was heated to 160°C, under N_2 gas atmosphere, and methanol was distilled out. After 2.5 h, adipic acid was added into the reaction mixture and the temperature was raised to 180°C and maintained for 2 h. Then, polycondensation was carried out at 270°C, with the pressure reduced, ranging from 3 to 1 mbar for 4 h.

Measurements

Gel permeation chromatography analysis was performed on a Waters 208. With tetrahydrofuran (THF) as eluant at a rate of 1 mL/min at 30°C. The system was calibrated by polystyrene standards. The glass transition temperature and the melting temperature were measured on a Pyris 1 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling system. Heating and cooling rate were 10°C/min under the nitrogen atmosphere. Surfaces of degraded samples after the composting were also observed with a FEI XL-30 scanning electron microscopy (SEM).

^{1}H-NMR characterization

The 300-MHz ^{1}H-NMR spectra were carried out on a Bruker av-300 spectrometer operating at room temperature with 5411Hz spectra width. The polymers were dissolved in $CDCL_3$ and tetramethylsilane (Me_4Si) was used as an internal chemical shift standard.

RESULTS AND DISCUSSION

Synthesis of copolyesters

All copolyesters used in this study were prepared by melt polycondensation of 1,4-butanediol, dimethyl terephthalate, and adipic acid under vacuum in the pres-

TABLE I
Characterization and Properties of P(BA-*co*-BT) Copolyesters

No.	Initial feeding composition (mol %)	$\overline{M_n}$[a]	$\overline{M_w}$[b]	$\overline{M_z}$[c]	PD[d]	T_g(°C)	T_m(°C)
1	BA60BT40	30,000	54,000	91,000	1.82	−38	94
2	BA55BT45	55,000	95,000	140,000	1.71	−26	115
3	BA50BT50	14,000	38,000	75,000	2.79	−20	125
4	BA40BT60	26,000	40,000	65,000	1.52	−10	150

[a] Number–average molecular weight of the synthesized copolyesters.
[b] Weight–average molecular weight of the synthesized copolyesters.
[c] z-average molecular weight of the synthesized copolyesters.
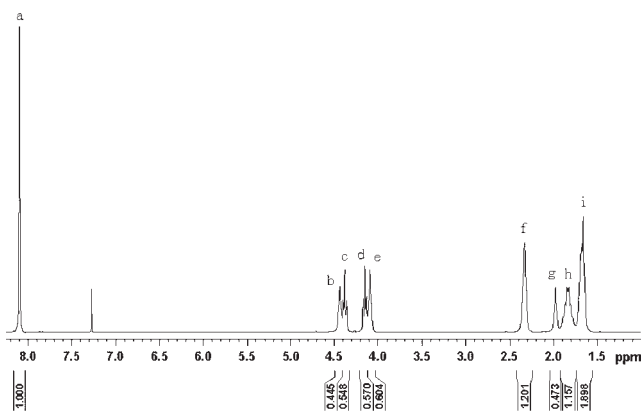[d] Polydispersities of the synthesized copolyesters.

Figure 2 ^{1}H-NMR spectra of a copolyester BA55BT45.

ence of a tetrabutylorthotitanate (TBOT) catalyst (Fig. 1). All copolyesters prepared in this work, were used without further purification for the measurement. Molecular weights and thermal properties of the synthesized copolymers are listed in Table I.

Sample identification

The copolyesters, investigated by ^{1}H-NMR spectroscopy and GPC, are abbreviated as P(BA-*co*-BT) (poly[butylene adipate-*co*-butylene terephthalate]). ''A'' and ''T'' indicated the adipate and terephthalate unit respectively. ''BA'' and ''BT'' is denoted to butylene adipate and butylene terephthalate unit respectively. The numbers at the end of each ''BA'' or ''BT'' is noted as the mole fractions (%) of the two acid components. For example, BA60BT40 represents a copolyester component with 60 mol % adipic acid and 40 mol % terephthalic acid.

Polymer characterization

The molecular weights and polydispersities of the copolyesters were measured by GPC. Melting points T_m and glass transition temperature T_g were examined using DSC.

To observe the copolyester formation, sample composition was investigated by ^{1}H-NMR. As an example, the ^{1}H-NMR spectra for a copolyester BA55BT45 are shown in Figure 2 and assignment of proton signals and their chemical shifts showed in ^{1}H-NMR spectra are listed in Table II.

The compositions, average sequence length, and the degree of randomness were calculated by the relation of the four types of peak integrals at $\delta = 4.09$–4.44 ppm. The results clearly show differences in chemical shifts of tetramethylene proton signals, ^{1}H-NMR spectroscopy enable a detailed analysis copolyesters microstructure.

For each sample, the integrated intensities of the peaks of protons are abbreviated with ''I.'' I_b, I_c, I_d, and I_e represent the integrated intensities of the correspond-

ing peaks of the two side protons of tetramethylene glycol because of homolikages and heterolinkages.

For P(BA-*co*-BT) copolyesters, molar fractions of butylene adipate unit (MF_A) and butylene terephthalate unit (MF_T) are determined by eqs. (1) and (2):[11,12]

$$MF_A(\text{mol \%}) = \frac{I_e + \frac{(I_c + I_d)}{2}}{I_b + I_c + I_d + I_e} \times 100 \qquad (1)$$

$$MF_T(\text{mol \%}) = \frac{I_b + \frac{(I_c + I_d)}{2}}{I_b + I_c + I_d + I_e} \times 100 \qquad (2)$$

The number-average sequence length of butylenes adipate units (SL_A) and butylene terephthalate units (SL_T) are determined of by eqs. (3) and (4) respectively:[11,12]

$$SL_A = 1 + \frac{I_e}{\frac{(I_c + I_d)}{2}} \qquad (3)$$

$$ST_T = 1 + \frac{I_b}{\frac{(I_c + I_d)}{2}} \qquad (4)$$

The degree of randomness (R) is defined by eq. (5):[11]

$$R = \frac{1}{SL_A} + \frac{1}{SL_T} \qquad (5)$$

Based on the eqs. (1)–(5) above, the analytical results for four samples of P(BA-*co*-BT) copolyesters are shown in Table III.

TABLE II
Assignment of Proton Signals and Chemical Shifts in the ^{1}H-NMR Spectra of the Copolyester

Structural unit	Chemical shift (δ in ppm)	
$-OOC-\overset{a}{\bigcirc}-COO-$	a	8.10
$T-\overset{b}{CH_2}(CH_2)_2\overset{b}{CH_2}-T$	b	4.44
$T-\overset{c}{CH_2}(CH_2)_2CH_2-A$	c	4.38
$A-\overset{d}{CH_2}(CH_2)_2CH_2-T$	d	4.15
$A-\overset{e}{CH_2}(CH_2)_2CH_2-A$	e	4.09
$-OOC-\overset{f}{CH_2}(CH_2)_2\overset{f}{CH_2}-COO-$	f	2.33
$T-\overset{g}{CH_2CH_2CH_2CH_2}-A(T)$	g	1.98
$A-\overset{h}{CH_2CH_2CH_2CH_2}-A(T)$	h	1.83
$-OOC-\overset{i}{CH_2}\overset{i}{CH_2}CH_2CH_2-COO-$	i	1.68

TABLE III
Molar Fractions, Sequence Distribution Parameters of P(BA-*co*-BT) Copolyesters

No.	Feeding composition (MF_A/MF_T) (mol %)	Integrated intensities of relevant signals				Average sequence length		Copolyester composition (MF_A/MF_T) (mol %)	Randomness (R)
		I_b	I_c	I_d	I_e	SL_A	SL_T		
1	60/40	0.401	0.594	0.635	0.832	2.35	1.65	58.8/41.2	1.03
2	55/45	0.445	0.548	0.570	0.604	2.08	1.79	53.7/46.3	1.04
3	50/50	0.477	0.509	0.497	0.466	1.93	1.95	49.7/50.3	1.03
4	40/60	0.600	0.395	0.376	0.228	1.59	2.56	38.4/61.6	1.02

Biodegradation study

Biodegradation of copolyesters was tested by composting in laboratory scale, based on GB/T19277-2003, which is a standard test method for determining biodegradability of plastic materials. The degradation in compost also take place in soil, so it can be considered to be synonymous with degradation in soil conditions, except the degradation rates in composting are higher than in natural conditions because of the higher temperature. To investigate the degradation behavior of copolyesters, we have studied the chemical structure of the degraded copolyesters, including the components and the average sequence length by using ^{1}H-NMR spectroscopy. For comparison purposes, ^{1}H-NMR spectra for a copolyester BA55BT45 after composting are shown in Figure 3. The content of BT and BA, and the degree of randomness of P(BA-*co*-BT) copolyesters after composting were given by eqs. (1), (2), and (5) from solution ^{1}H-NMR spectra, respectively. The number-average sequence lengths of BA units (SL_A) and those of BT units (SL_T) were obtained from eqs. (3) and (4) respectively, which are corresponding to peak integrals from solution ^{1}H-NMR spectra. Those results are shown in Table IV. Visible changes, weight loss, molecular weights less, and SEM micrograph of the surface of the degraded copolyesters were observed. Based on these findings, an indication of the biodegradation behavior could be received. The changes of molecular weights of copolyesters after composting are listed in Table V. Figure 4 shows the weight loss of the degraded copolyesters.

Under practical composting conditions, many degradation induced cracks and disintegrations on the surfaces of the copolyester sample are visible. The morphology of each inner crack is shown in Figure 5. This figure shows that the distinct zones of microbial attack and a beginning crack of a film derived from BA55BT45, which are found for all the copolyesters investigated.

The aim of this work was a thorough investigation of the change of microstructure of copolymer chain after composting and biodegradation behavior of P(BA-*co*-BT) copolyesters, consisting of aromatic poly(butylene terephthalate) units (PBT), and aliphatic poly(butylene adipate) units (PBA). These kinds of copolyester were synthesized by polycondensation in bulk. Table I lists

the glass transition temperature T_g and the melting temperatures T_m of the four P(BA-*co*-BT) copolyesters with different compositions. Figure 6 shows the melting curves of the four copolyesters by DSC. Copolyester contains more aromatic repeating units, showing higher melting temperature and glass transition temperature. This is due to the aromatic repeating unit of BT is more stable and more rigid than the aliphatic repeating unit of BA. Thus, making easier maintenance of the polymer crystalline structure. Therefore, aromatic unit enhance the thermal stability of these copolyesters. To observe the copolymer formation, the ^{1}H-NMR spectra for a copolyester BA55BT45 is shown in Figure 2. ^{1}H-NMR spectra for a copolyester BA55BT45, after degradation is shown in Figure 3. The chemical shift and assignment of proton signed of all copolyester structural unit are listed in Table II, and their coincident characteristic peaks are assigned in Figure 2. As we can see from Figures 2 and 3, the characteristic peaks site of degraded sample is the same as original sample.

With the clear ^{1}H-NMR measurements presented in this paper, each copolyester composition and structural data are easier to be calculated by the relation of corresponding peak integrals. Tables III and IV summarizes the quantitative data of the copolyesters, before and after composting from the ^{1}H-NMR measurements respectively. Theoretically, the peak intensities I_c and I_d should be equal, but deviations in the range of 1.2 to 3.3%, from the mean were observed. Based on a proba-
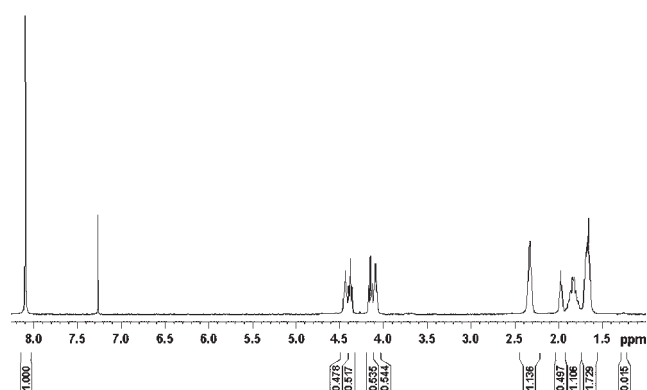

Figure 3 ^{1}H-NMR spectra of a copolyester BA55BT45 after composting.

TABLE IV
Molar Fractions, Sequence Distribution Parameters of P(BA-*co*-BT) Copolyesters After Degradation

No.	Copolyester composition before degradation (MF_A/MF_T) (mol %)	Integrated intensities of relevant signals				Average sequence length		Copolyester composition after degradation (MF_A/MF_T) (mol %)	Randomness (R)
		I_b	I_c	I_d	I_e	SL_A	SL_T		
1	58.8/41.2	0.460	0.560	0.620	0.690	2.17	1.78	54.9/48.4	1.02
2	53.7/46.3	0.478	0.517	0.535	0.544	2.03	1.91	51.6/48.4	1.02
3	49.7/50.3	0.510	0.466	0.455	0.353	1.77	2.11	45.6/54.4	1.04
4	38.4/61.6	0.612	0.388	0.372	0.210	1.55	2.61	37.3/62.7	1.03

ble error of ±10% for the integration intensities, the deviations between I_c and I_d are within the experimental error. The monomer compositions derived from the NMR-data in the copolymers are close to the ratio of the educts. The maximum deviations in the composition are not more than 2%. This shows that the copolyester composition can be controlled by its initial feed ratio. Based on the previous studies,[8,9] the biodegradability of the aliphatic-aromatic copolyester actually depends on the exact monomer composition and monomer sequence distribution in the copolymer. To investigate the block length distribution within the copolymer chain, many scientists adopt the concept of degree of randomness.[13] Degree of randomness is used for the description of a statistical copolymer, in which the probability of finding in a given monomer unit at any site in the chain is independent of neighboring units in nature. It should be unity for an ideal random copolymer. As can be seen in the Table III, degree of randomness of the copolymer is close to unity of entire composition range, indicating that random copolyesters were obtained. Besides that, the average block length of aromatic unit and aliphatic unit are less than 3. The results in Table III also exhibits more BT contents to copolymer leading to an increase, for the average sequence length of aromatic unit, but a decrease for the average sequence length of aliphatic unit.

To investigate the complex degradation behavior of such copolyesters, the change of the microstructure and composition of the copolymer detail is listed in Table IV. Table IV shows data of the sample after 8–10 weeks in compost, excluding a copolyester BA60BT40 (about two weeks). In Table IV, a noticeable change in composition is observed. The BT content of degraded sample was more than initial sample, while the BA content of the degraded sample was lower than initial sam-

ple. On the other hand, the aromatic chain length of the degraded sample increases, but the aliphatic chain length decreases. However, the parameter R is also close to unity in all cases. This is due to the aliphatic chain sequence is preferentially attack and cleaved by microorganisms. It has been reported that the P(BA-*co*-BT) copolyester decomposed rapidly by degradation even, even though amount of aromatic terephthalic acid in these copolyesters was high, up to 60 mol %.[8] Thus, we can conclude that both aromatic chains and aliphatic chains of such copolyesters can be degraded. However, aliphatic units showed higher biodegradation rate resulting in a faster change for the aliphatic sequence length, in contrast to the aromatic chains in the degradation stage in compost. Molecular weights analysis are listed in Table V, and we found that the number average-molecular weight (M_n) and weight-average molecular weight (M_w) of the degraded sample drastically dropped, and polydispersities are larger than original polyester sample. This indicates that high molecular copolyesters are converted to low molecular polymer due to the polymer chain cracked by biodegradation in compost. As presented in Figure 4, we observed that all samples have weight loss during composting. We also found an obvious stains and cracks, which provide supportive evidence that these copolyesters are degraded by the attack of microorganisms.

TABLE V
Molecular Weights of the Degraded Copolyesters

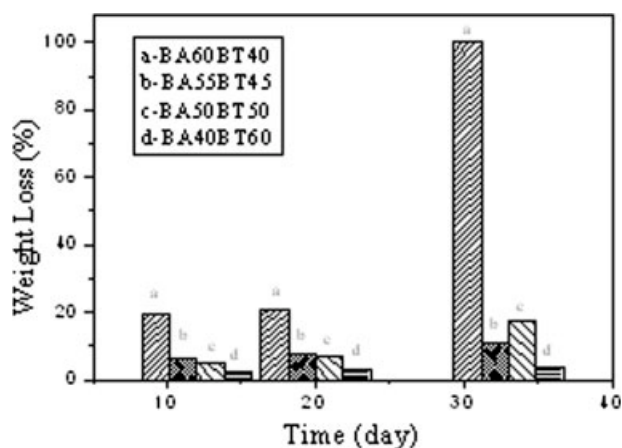| No.	Initial feeding composition (mol %)	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_z}$	PD
1	BA60BT40	150,00	33,000	56,000	2.30
2	BA55BT45	160,00	29,000	47,000	1.77
3	BA50BT50	8,400	17,000	28,000	2.01
4	BA40BT60	10,000	17,000	27,000	1.64

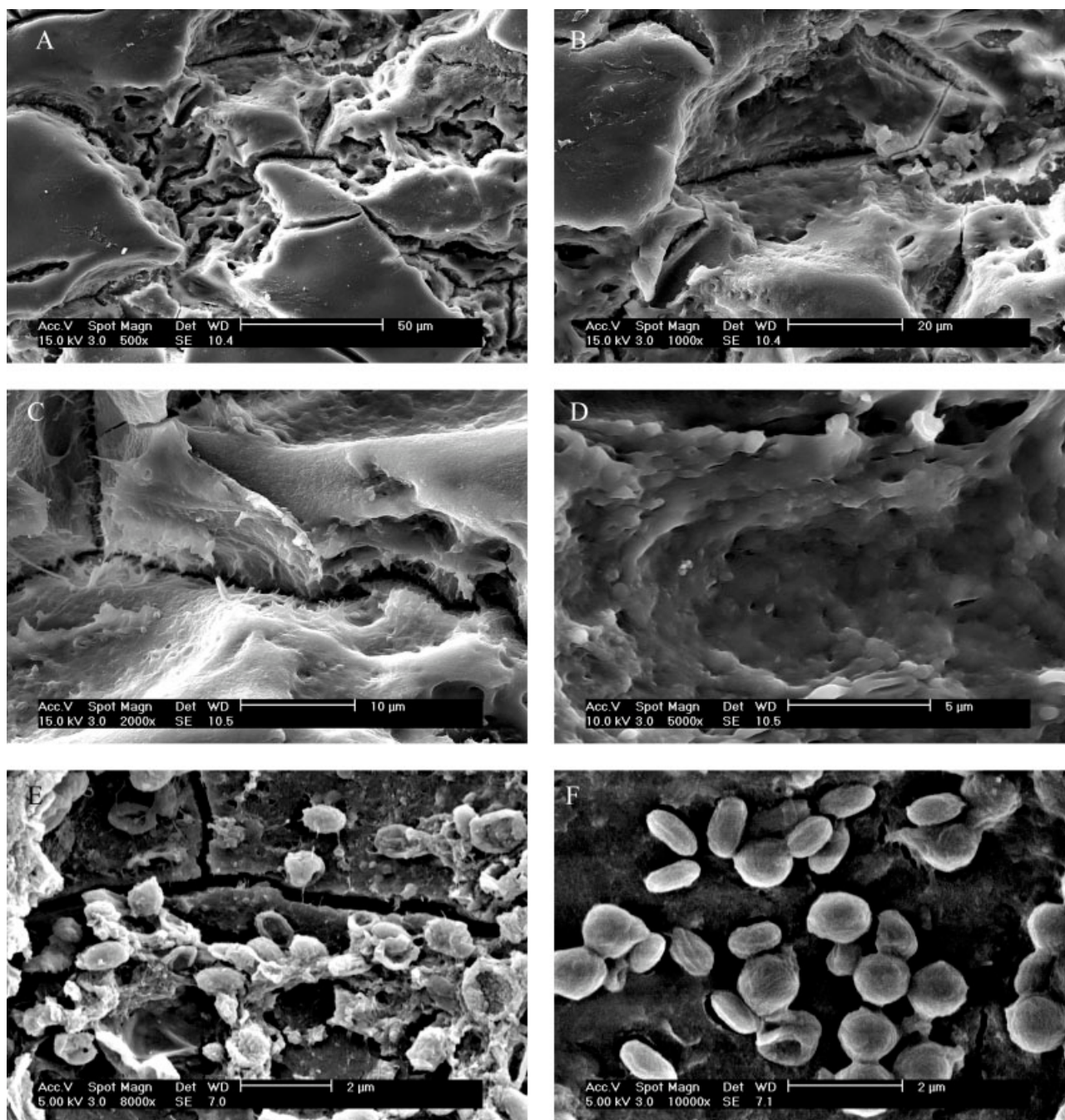**Figure 4** Weight loss of the copolyesters during compost tests.

Figure 5 Surface morphology of the copolyester film after 10 weeks composting.

Figure 5 shows stains traces of growing microorganisms on the surface of each sample. In addition, it can be observed that severe surface degradation is caused by microorganisms.

CONCLUSIONS

Four biodegradable aliphatic-aromatic random copolyesters were synthesized through the polycondensation with BT (40–60 mol %). Their melting

temperature and glass transition temperature increase with composition of BT. Biodegradation behavior was investigated by composting, based on GB/T19277-2003. In ^{1}H-NMR analysis, we found that the average sequence length of aliphatic chains reduced and aromatic chains increased, after degradation. The composition, weight and molecular weight change with the composting time. It indicated that the biodegradation of aliphatic-aromatic copolyester occurs, and aliphatic unit degraded much rapidly than the aromatic unit. It is evidence
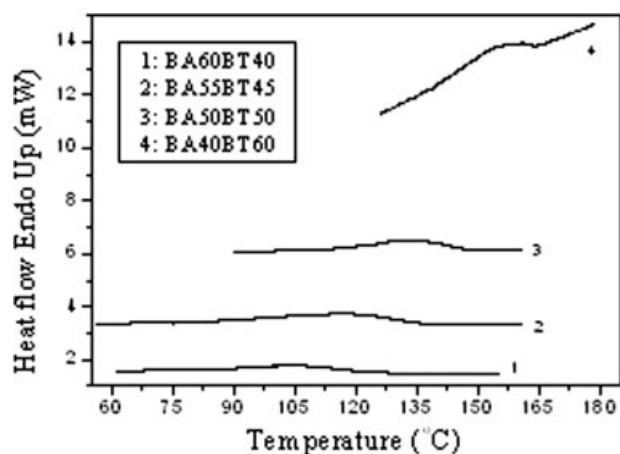
Figure 6 Melting curves of P(BA-*co*-BT) copolyesters with different composition.

that ^{1}H-NMR method is a valuable tool to obtain composition and microstructure of copolymer. It is essential to investigate the biodegradation behavior and degradation stage of copolymer in compost. GPC and SEM images show clear evident elucidation of copolyesters biodegradation behavior.

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