

# Synthesis and Biodegradation of Aliphatic Polyesters from Dicarboxylic Acids and Diols

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**ABSTRACT:** Poly(butylene succinate) (PBS) and its copolymers, poly(butylene succinate-co-adipate) (PBSA) and poly(butylene-co-hexylene succinate) (PBHS), were synthesized by direct polyesterification of corresponding diols and dicarboxylic acids. Dimethyl benzene was used as solvent and water-removing agent. Several catalysts were used to study the esterification of butanediol and succinic acid. Among them, SnCl<sub>2</sub> demonstrated superior catalysis behavior. Kinetic behaviors of the synthesis of PBS, PBSA, and PBHS were investigated using SnCl<sub>2</sub> as catalyst. By using a water trap containing a 4-Å molecular sieve, a relatively faster reaction rate was achieved and the molecular weight of some polyesters surpassed 30,000. The variation of mo-

lecular weight distribution during the polymerization was monitored by GPC and  $M_w/M_n$  demonstrated a trend of decrease with the reaction time. The melting point ( $T_m$ ) and the glass-transition temperature ( $T_g$ ) were measured by DSC technique. The results show that the incorporation of a third monomer unit to PBS lowered  $T_g$  and  $T_m$ . The biodegradation test was carried out both in the laboratory and in outdoor soil burial. The copolyesters displayed a faster degradation rate than that of PBS. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 982–990, 2003

**Key words:** aliphatic polyester; polyesterification; biodegradation; diol; dicarboxylic acid

## INTRODUCTION

Since the last half of the 20th century, the plastics industry has experienced rapid development and plastic products have been used universally. Nowadays, annual production of synthetic plastics is about 150 million tons, and production and consumption continue to increase.<sup>1</sup> At the same time, however, the problem of environmental pollution caused by plastic waste also has become increasingly serious. Many countries have put forth much effort and emphasis on recycling plastic waste and, at the same time, on developing alternative degradable materials.<sup>2,3</sup> Several synthetic polymers have been identified as degradable in the natural environment or in animal bodies.<sup>4</sup> Among them, the family of aliphatic polyesters appears to be the most attractive and promising.<sup>5,6</sup> Apart from the high molecular weight polyesters produced by microorganisms<sup>7</sup> and by ring-opening polymerization of lactones or lactides,<sup>8,9</sup> aliphatic polyesters from the condensation of hydroxycarboxylic acid or the condensation of diols with dicarboxylic acids have also attracted the attention of many researchers.<sup>10–14</sup> Properties of these polyesters, such as melting point, crystallinity, mechanical strength, as well as biodegradability, greatly depend on the chemical structure and the molecular weight of the polyester and it has

been recognized that polyesters from butanediol and succinic acid possess a high melting point.<sup>15</sup> Therefore, much research had been conducted to study the synthesis, modification, and properties of poly(butylene succinate) and/or its corresponding copolymers.<sup>16–20</sup>

In this study, we report our work on the synthesis of poly(butylene succinate) (PBS) and its copolyesters, poly(butylene-co-hexylene succinate) (PBHS) and poly(butylene succinate-co-adipate) (PBSA). To synthesize the polyesters with relatively high molecular weight, we designed a new water trap that contains a 4-Å molecular sieve. The kinetics of polyesterification using this apparatus was studied. The biodegradation of these polyesters both in the laboratory and in natural soil burial was investigated.

## EXPERIMENTAL

### Materials

Adipic acid and succinic acid were provided by Tianjin Chemical Co. (China) and used as received. Hexanediol and butanediol (Shanghai Chemical Co., China) were analyzed as to their the exact content by GC before use. *p*-Toluene sulfonic acid (P-TS; Beijing Chemical Co., China) was used as received. Sn powder was prepared from granulated tin. SnCl<sub>4</sub>, SnCl<sub>2</sub>, dimethyl benzene, and Na<sub>2</sub>CO<sub>3</sub> (all from Tianjin Chemical Co.) were used as received. A 4-Å molecular sieve (Dalian Molecular Sieve Plant, China) was activated at 500°C before use.

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TABLE I  
Synthesized Polyesters and Their Abbreviations

Monomer	Molar ratio	Polyester	Abbreviation
Butanediol + succinic acid	1:1	Poly(butylene succinate)	PBS
Butanediol + hexanediol + succinic acid	4:1:5	Poly[butylene- <i>co</i> -hexylene (4:1) succinate]	PBH(4:1)S
Butanediol + hexanediol + succinic acid	2:1:3	Poly[butylene- <i>co</i> -hexylene (2:1) succinate]	PBH(2:1)S
Butanediol + hexanediol + succinic acid	1:1:2	Poly[butylene- <i>co</i> -hexylene (1:1) succinate]	PBH(1:1)S
Butanediol + succinic acid + adipic acid	3:2:1	Poly[butylene succinate- <i>co</i> -adipate (2:1)]	PBSA(2:1)
Butanediol + succinic acid + adipic acid	2:1:1	Poly[butylene succinate- <i>co</i> -adipate(1:1)]	PBSA(1:1)

### Synthesis of the polyesters

The polyesters were synthesized from equivalent moles of corresponding dicarboxylic acid and diol in the presence of catalyst. Dimethyl benzene was used as solvent and water-removing agent. The amount of catalyst was 0.2 mol % to monomer and the monomer concentration was 1.66 mol/L. The reaction was accomplished in a four-neck flask equipped with an agitator, a thermometer, a nitrogen inlet, and a water trap connected with a condenser. At the first stage, the byproduct water was removed from the flask by azeotropic distillation of dimethyl benzene with water and then fractionated by the Dean–Stark trap. When the extent of the reaction was over 0.95, a water trap that contained a 100-mL 4-Å molecular sieve was mounted to replace the Dean–stark trap. Using this equipment, the azeotrope of dimethyl benzene with water was condensed, then passed through the molecular sieve and then recycled into the flask. By this process, the water was successively absorbed by the molecular sieve and the extent of reaction increased. The poly-

esters synthesized in this study and their abbreviations are listed in Table I.

### Characterization

The number-average molecular weights ( $M_n$ ) of the polyesters were monitored by taking samples from the contents of the flask during polymerization and casting them onto watch glasses. After drying, the samples were weighed and dissolved in chloroform, then titrated using standard KOH ethanol solution.  $M_n$  was calculated as follows:

$$M_n = \frac{W}{C V}$$

where  $W$  is the weight of the sample, and  $C$  and  $V$  are the molar concentration and volume of the KOH solution, respectively. The degree of polymerization ( $X_n$ ) and the extent of reaction ( $P$ ) were calculated according to the following equations:

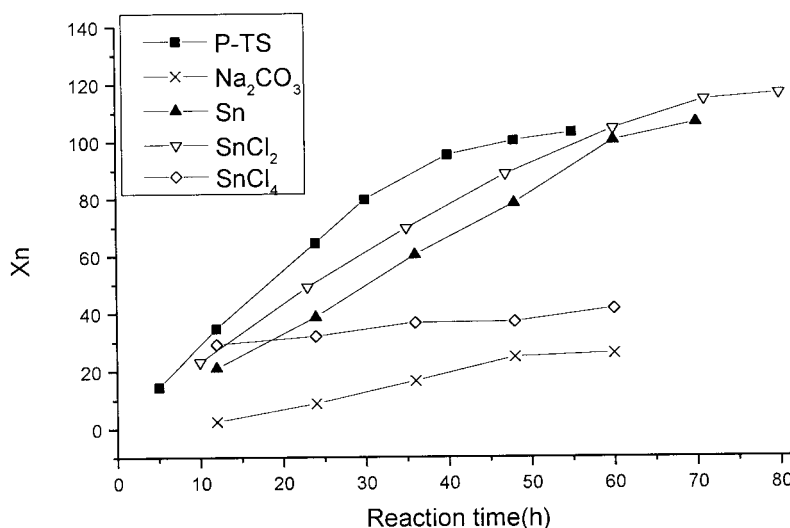
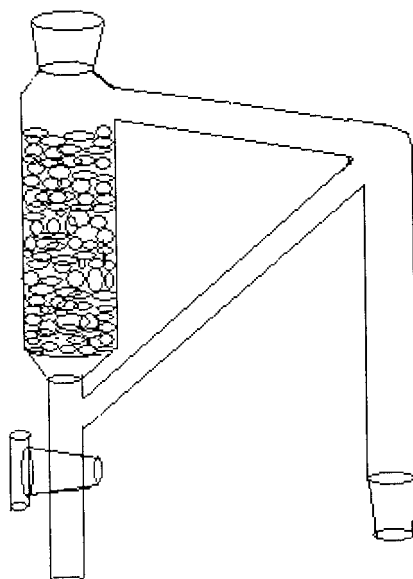


Figure 1 Polyesterification of succinic acid with butanediol in the presence of different catalysts (amount of catalyst, 0.2 mol % to monomer; monomer concentration, 1.66 mol/L).



**Figure 2** Illustration of the water trap containing 4-Å molecular sieve.

$$X_n = \frac{M_n}{M} \quad P = 1 - \frac{1}{X_n}$$

where  $M$  is the average molecular weight of the structural unit of the corresponding polyester.

The molecular weight distribution was determined using a Waters 208 gel permeation chromatography instrument (Waters Chromatography Division/Millipore, Milford, MA). Samples were run in THF at 25°C with a flow rate of 1.0 mL/min. Polystyrene standards were used to make the calibration.

The glass-transition temperature ( $T_g$ ) and melting point ( $T_m$ ) of the polyesters were measured using a differential scanning calorimeter (DSC 204, Netzsch Co., Germany)

### Biodegradation test

The polyester was dissolved in chloroform and then cast onto a plate of polypropylene to prepare films of either 1 or 0.1 mm thickness. Then the films were cut into pieces of about 0.5 g for the biodegradation test.

In the laboratory, the microbial degradation tests were carried out with *Penicillium chrysogenum* (fungi). Each sample was put into a 250-mL conical flask that contained an aerated liquid medium and the above microbial. The medium consisted of 100 mL boiled and then cooled potato-water solution. The pH value was 5.5. The conical flasks were then affixed to a shaking bed and the temperature was kept at 37°C. At certain time intervals, the samples were removed from the flask, gently washed, dried, and weighed. The weight loss was recorded and the molecular weight was determined.

The outdoor biodegradation test was accomplished by burying the samples in natural soil at a depth of 20 cm. The samples were removed from the soil at specific times, after which they were treated as in the laboratory test.

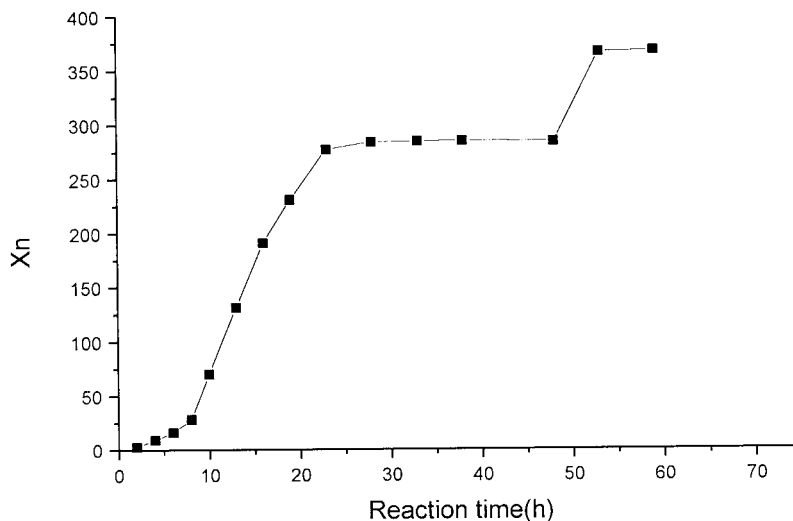
## RESULTS AND DISCUSSION

### Influence of catalyst on the polyesterification of butanediol with succinic acid

Five catalysts, *p*-toluene sulfonic acid (P-TS),  $\text{Na}_2\text{CO}_3$ , Sn powder,  $\text{SnCl}_2$ , and  $\text{SnCl}_4$  were used to catalyze the polyesterification of succinic acid with butanediol. A normal Dean–Stark trap was used to fractionate the water carried by dimethyl benzene through azeotropic distillation. Figure 1 shows the variation of number-average degree of polymerization ( $X_n$ ) with reaction time. We can see that  $\text{Na}_2\text{CO}_3$  and  $\text{SnCl}_4$  showed poor catalysis behavior, especially  $\text{Na}_2\text{CO}_3$ , which demonstrated a very slow reaction rate. The maximum  $X_n$  was only 22 after 48 h. Although  $\text{SnCl}_4$  displayed a fast reaction rate at the early stage ( $X_n$  reached 30 at 10 h), the reaction rate slowed considerably after 10 h. In the case of P-TS as catalyst, at the first stage of the reaction, the reaction rate was faster and  $X_n$  reached 80 when the reaction time reached 30 h. However, after this, the reaction rate slowed down and nearly stopped at 55 h. The maximum  $X_n$  was 103. In the case of Sn powder as catalyst,  $X_n$  increased steadily from the beginning to 60 h ( $X_n$  reached 102 at this time), although after this time it increased very slowly. For  $\text{SnCl}_2$  as catalyst, just before 60 h, the reaction behaved

**TABLE II**  
Kinetic Results of the Synthesis of PBS

Time (h)	2	4	6	8	10	13	16	19	23
$M_n$	210	773	1377	2408	6020	11,267	16,388	19,817	23,815
$X_n$	2.44	8.98	16.01	28.00	70.00	131.0	190.6	230.4	276.9
$P$ (%)	59.0	88.86	93.75	97.64	98.68	99.23	99.47	99.57	99.63
Time (h)	28	33	38	48	53	59			
$M_n$	24,370	24,424	24,467	24,412	31,457	31,586			
$X_n$	283.4	284.0	284.5	283.9	365.8	367.2			
$P$ (%)	99.65	99.65	99.65	99.65	99.72	99.72			



**Figure 3** Variation of  $X_n$  in the synthesis of PBS catalyzed by  $\text{SnCl}_2$  (amount of  $\text{SnCl}_2$ : 0.2 mol % to monomer; monomer concentration: 1.66 mol/L).

like that of Sn powder. After 60 h, however,  $X_n$  further increased to 120 at 71 h, then the increase of  $X_n$  slowed significantly. The maximum  $X_n$  was 123. Based on these results, we chose  $\text{SnCl}_2$  as catalyst for subsequent kinetic investigations.

#### Synthesis of PBS, PBH(2 : 1)S, and PBSA(2 : 1) catalyzed by $\text{SnCl}_2$

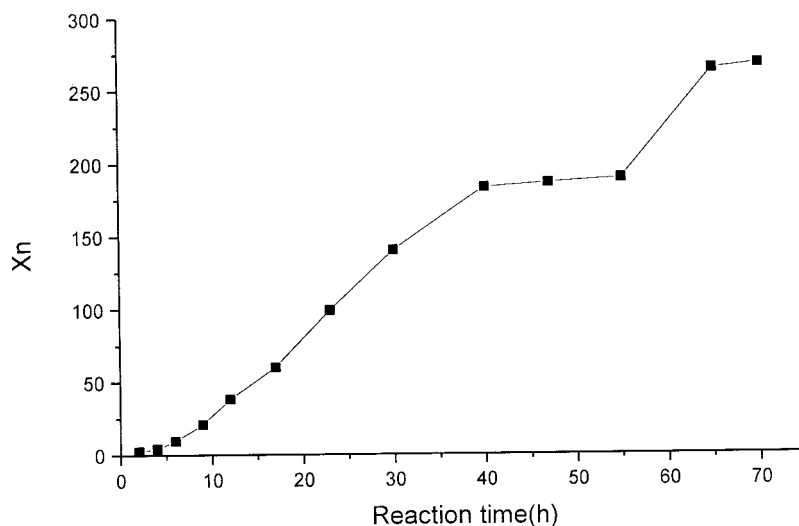
In the above study, we discovered that the polyesterification rate was rather slow and the molecular weight of the polyester was limited to within 10,000 when using a normal Dean–Stark trap to fractionate the water carried by the solvent. To synthesize aliphatic polyesters Ajioka et al.<sup>12</sup> used a tube containing a 3-Å molecular sieve. The molecular weight of the polyesters were over 100,000. In this present work, we designed a new type of water trap, illustrated in Figure 2. When the reaction proceeded to about 8–10 h, by which time the extent of reaction ( $P$ ) reached  $>0.95$ , this water trap, which contained a 100-mL 4-Å molecular sieve, was mounted to replace the normal Dean–Stark trap. The condensed azeotrope of dimethyl benzene with water passed through the molecular sieve and then returned to the reaction flask. By this pro-

cess, the water was successively absorbed by the molecular sieve. Table II presents the kinetic results of the polyesterification of butanediol with succinic acid using  $\text{SnCl}_2$  as catalyst. Figure 3 is the plot of  $X_n$  versus reaction time using the data from Table II. One can see that after 8 h, by which time  $P$  had reached 0.970 and the normal Dean–Stark trap was replaced by the new water trap,  $X_n$  increased rapidly and reached 276.9 and  $P$  reached 99.63% by 23 h. After 23 h, the increase of  $X_n$  slowed considerably and nearly stopped increasing by 38 h. At this time, another water trap that contained a new activated molecular sieve was used to replace the former one. As can be seen from Table II and Figure 3,  $X_n$  increased further to 365.7 within 5 h, after which the increase slowed. The maximum  $X_n$  of PBS was 367.3 and the molecular weight was 31,586 (see Table II).

Using this technique, the synthesis of PBH(2 : 1)S and PBSA(2 : 1) were also studied. Table III presents the kinetic results of the synthesis of PBH(2 : 1)S. Figure 4 is the plot of  $X_n$  versus time from the data in Table III. As can be seen the trend of the curve is very much like that in Figure 3, except that the slope of the curve was smaller and the corresponding  $X_n$  is lower.

**TABLE III**  
Kinetic Results of the Synthesis of PBH(2:1)S

Time (h)	2	4	6	9	12	17	23	30	40
$M_n$	209	372	859	1925	3534	5582	9207	13,038	17,919
$X_n$	2.25	4.00	9.24	20.70	38.01	60.02	99.00	140.1	183.3
$P$ (%)	55.6	75.0	89.1	95.17	97.37	98.33	98.99	99.29	99.45
Time (h)	47	55	65	70					
$M_n$	17,298	17,577	24,514	24,831					
$X_n$	185.9	189.0	263.7	267.0					
$P$ (%)	99.46	99.47	99.62	99.63					



**Figure 4** Variation of  $X_n$  in the synthesis of PBH(2:1)S catalyzed by  $\text{SnCl}_2$  (amount of  $\text{SnCl}_2$ : 0.2 mol % to monomer; monomer concentration: 1.66 mol/L).

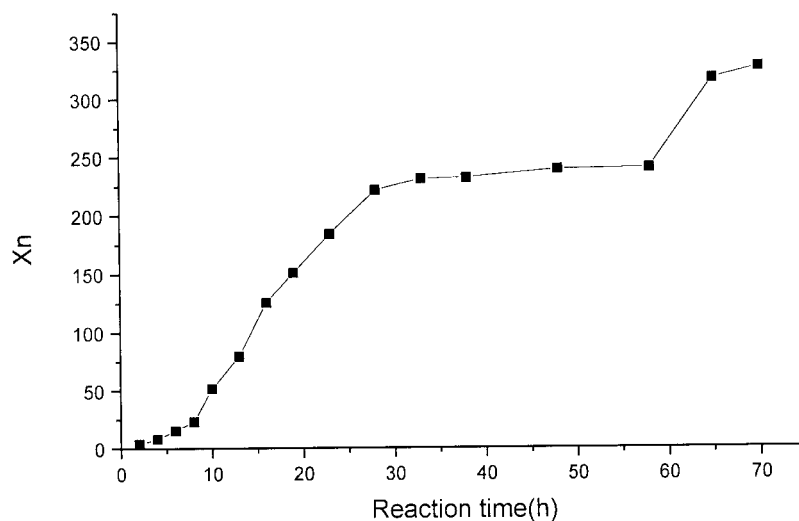
It also reveals a sharp increase of  $X_n$  after the molecular sieve was replaced at 55 h by the fresh one. The final molecular weight was 24,831 and the  $X_n$  was 267 (see Table III), lower than that in the case of PBS,

perhaps because the reactivity of hexanediol is lower than that of butanediol at this reaction condition.

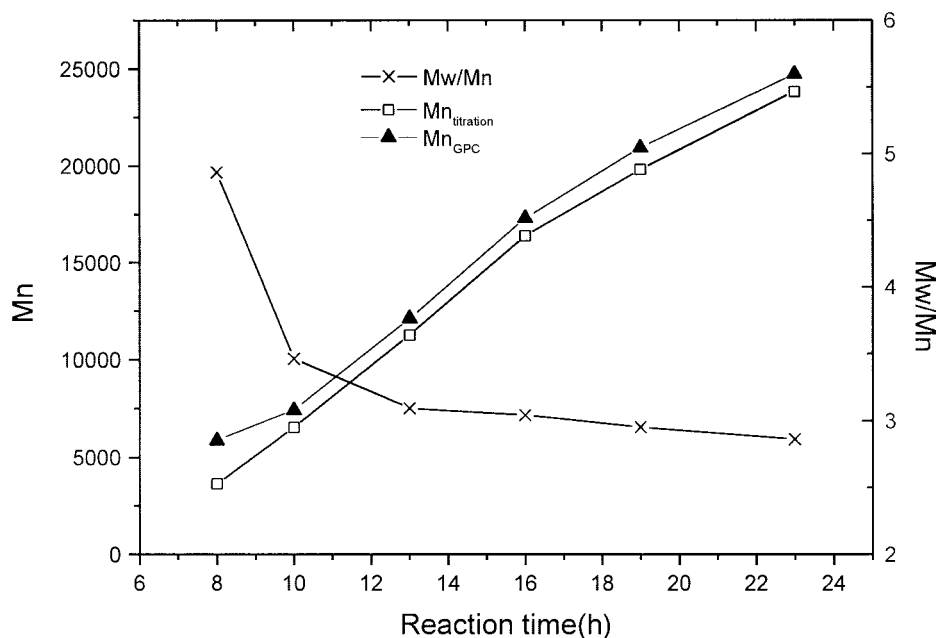
Table IV and Figure 5 show the kinetic results and kinetic plot of the synthesis of PBSA(2:1), respec-

**TABLE IV**  
Kinetic Results of the Synthesis of PBSA (2:1)

Time (h)	2	4	6	8	10	13	16	19	23
$M_n$	365	759	1449	2187	4891	7547	11,945	14,377	17,515
$X_n$	3.74	7.96	15.20	22.94	51.32	79.20	125.3	150.9	183.8
$P$ (%)	73.3	87.4	93.42	95.64	98.05	98.73	99.20	99.34	99.45
Time (h)	28	33	38	48	58	65	70		
$M_n$	21,061	21,974	22,074	22,740	22,829	30,145	31,070		
$X_n$	221.0	230.6	231.6	238.6	239.5	316.3	325.9		
$P$ (%)	99.55	99.57	99.57	99.58	99.58	99.68	99.69		



**Figure 5** Variation of  $X_n$  in the synthesis of PBSA(2:1) catalyzed by  $\text{SnCl}_2$  (amount of  $\text{SnCl}_2$ : 0.2 mol % to monomer; monomer concentration: 1.66 mol/L).



**Figure 6** Variation of number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of PBS with reaction time.

tively. From Figure 5 we can also see that the trend of the variation of  $X_n$  is like that in Figure 3. After using the water trap containing a molecular sieve at 8 h, it also displayed a fast reaction rate.  $X_n$  increased rapidly and reached 221 by 28 h, then it increased to 230.6 by 33 h. After this time,  $X_n$  increased very slowly. At 58 h, when the molecular sieve was replaced a second time, it also demonstrates a sharp increase of  $X_n$ . The final molecular weight of the polyester was 31,070;  $X_n$  was 326 (see Table IV).

#### Molecular weight distribution

The molecular weight and molecular weight distribution of PBS were monitored by GPC technique. Figure 6 shows the plot of  $M_n$  and  $M_w/M_n$  versus reaction time. For comparison, the molecular weight determined by terminal titration is also included in Figure 6. We can see that  $M_w/M_n$  decreased with the increase of molecular weight, which indicates that the functional group on the molecules with different size possessed different reaction probability and the reaction probability decreased with the increase of molecular weight. Thus the esterification between small molecules or oligomers was predominant, resulting in the decrease of  $M_w/M_n$ . We also can see from Figure 6 that the molecular weight determined by GPC was higher than that determined by terminal titration. This is because no proper polyester standard was available; the calibration was made by polystyrene standards in GPC analysis. Nevertheless, the trend of variation of these two curves with reaction time is similar, indicating that terminal titration is reliable.

#### Melting point and glass-transition temperature of the polyesters

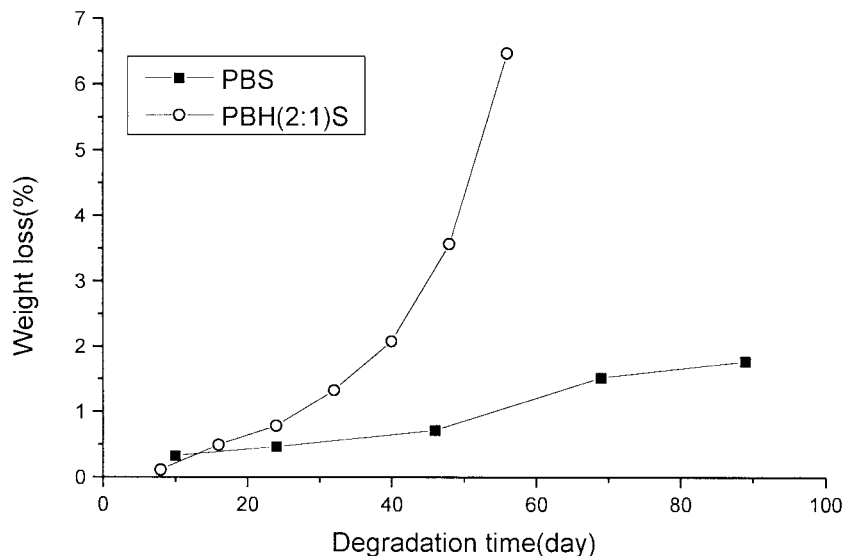
The melting point ( $T_m$ ) and glass-transition temperature ( $T_g$ ) of the polyesters were measured by DSC technique. Table V summarizes  $T_m$  and  $T_g$  of six polyesters. One can see that PBS displayed a higher  $T_m$  (117.1°C) and relatively higher  $T_g$  (-0.5°C), which is consistent with the results from the literature.<sup>11</sup> One also can see from Table V that  $T_g$  and  $T_m$  values of all the copolyesters were lower than those of PBS. For PBHS,  $T_g$  and  $T_m$  increased with the increase of the amount of butylene unit in the copolyester. For PBSA,  $T_g$  and  $T_m$  increased with the increase of the amount of succinic acid and butanediol played an important role in determination of  $T_m$  and  $T_g$  of the polyester.

#### Biodegradation of the polyesters

In the laboratory two polyesters, PBS and PBH(2:1)S, were subjected to biodegradation study. The biodeg-

**TABLE V**  
Melting Point and Glass-Transition Temperature of the Polyesters

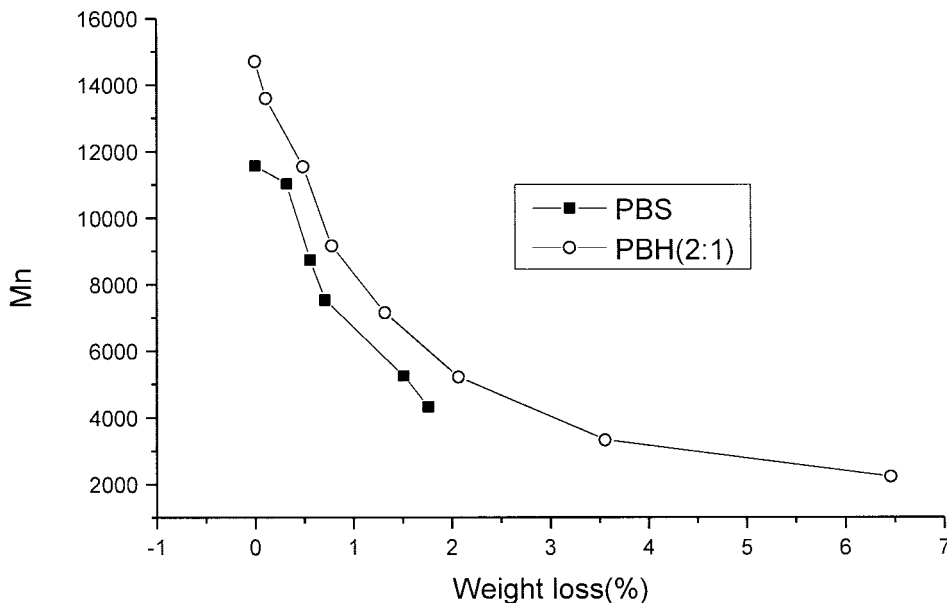
Polyester	$T_m$ (°C)	$T_g$ (°C)
PBS	117.1	0.5
PBH(4:1)S	97.9	-37.9
PBH(2:1)S	65.2	-43.5
PBH(1:1)S	63.8	-51.4
PBSA(2:1)	83.0	-31.1
PBSA(1:1)	61.8	-50.1



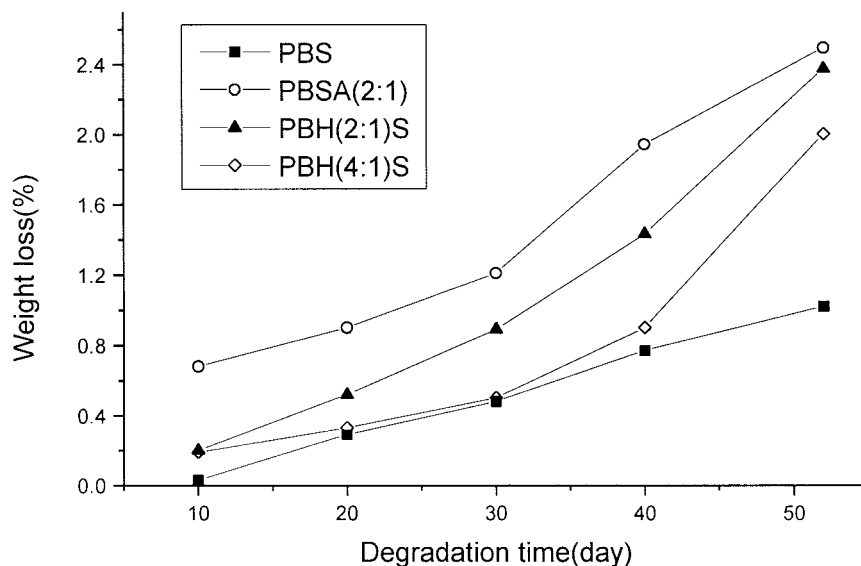
**Figure 7** Weight loss of PBS and PBH(2 : 1)S in the presence of *Penicillium chrysogenum* [original molecular weight of the samples: PBS, 11,576; PBH(2 : 1)S, 14,697].

radation test was carried out in the presence of *Penicillium chrysogenum*, a kind of fungi. It produces esterase during its growth, which is a specific catalyst for the degradation of esters. Figure 7 is the plot of weight loss versus time of PBS and PBH(2 : 1)S. One can see that the weight loss of these two polyesters increased with time. However, the degradation rate of the copolyester PBH(2 : 1)S was much faster than that of PBS. The weight loss reached 6.46% after 58 days, whereas the weight loss of PBS was only 1.76% after 89 days. This is probably because incorporation of the hexylene unit decreased the regularity and increased the flexibility of the polyester, so it was more easily

subject to attack by the enzyme. Our research group studied the biodegradation of poly(hexylene adipate) under the same conditions. The weight loss was 9.1% after 30 days,<sup>14</sup> faster than that of either PBS or PBH(2 : 1)S. These data show that the biodegradation behavior is greatly dependent on the chemical structure of the polyester. The variation of molecular weight of PBS and PBH(2 : 1)S during the degradation was monitored by terminal titration. Figure 8 is the plot of the variation of molecular weight ( $M_n$ ) with weight loss. At the first stage, the molecular weight decreased rapidly for both polyesters. This indicates that the degradation occurred randomly at any of the ester



**Figure 8** Variation of molecular weight with weight loss of PBS and PBH(2 : 1)S in the presence of *Penicillium chrysogenum*.

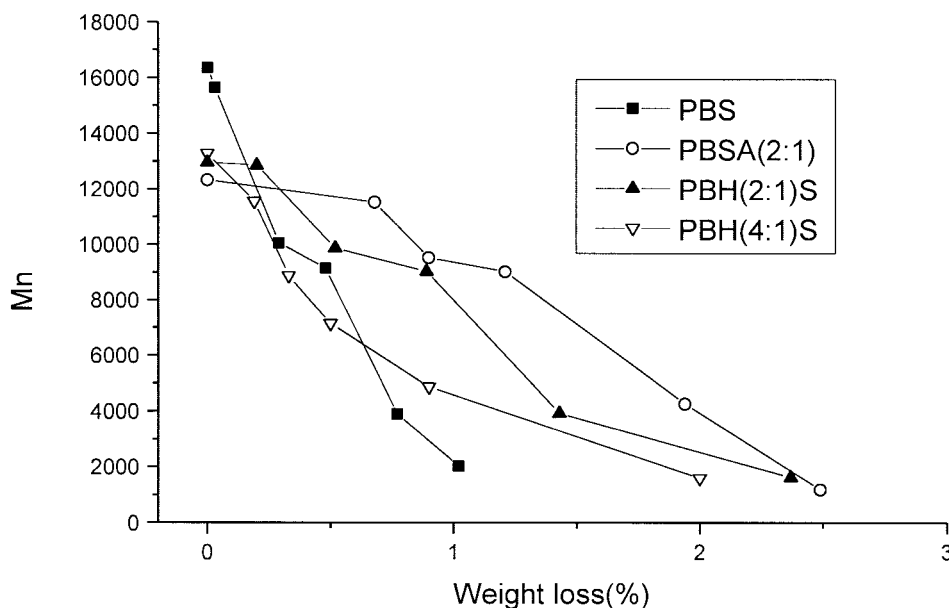


**Figure 9** Weight loss of the polyesters in natural soil burial [original molecular weight of the samples: PBS, 16,395; PBSA(2 : 1), 12,316; PBH(2 : 1)S, 12,955; PBH(4 : 1)S, 13,277].

groups of the macromolecule, resulting in a significant decrease of molecular weight but a negligible weight loss. When the molecular weight decreased to several thousands, the weight loss increased more rapidly, but the decrease of molecular weight slowed (see the curves of PBH(2 : 1)S in Figs. 7 and 8). This indicates that the degradation of the polyesters probably occurred mainly at the terminals at this stage.

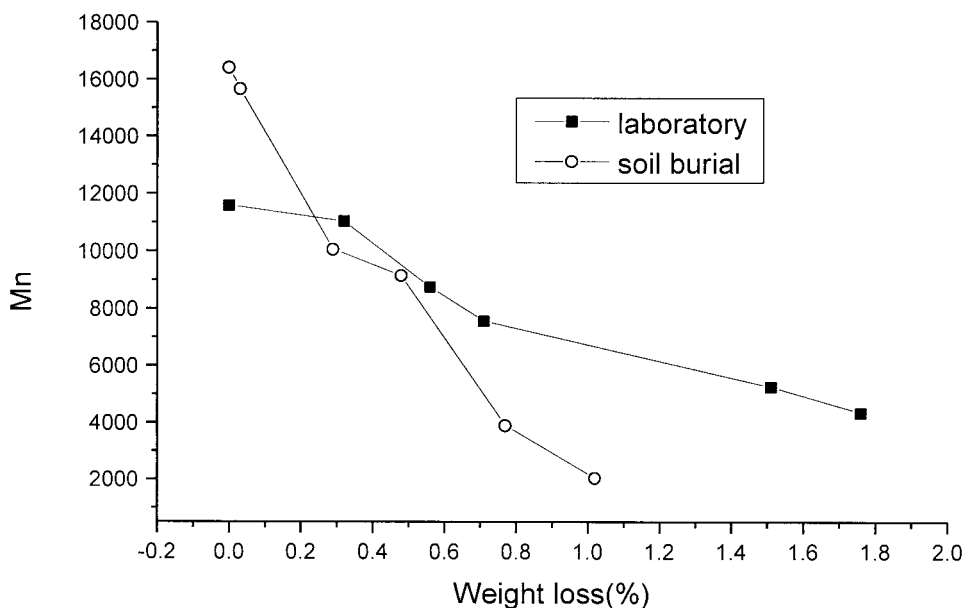
Figure 9 gives the degradation results of four aliphatic polyesters, PBS, PBSA(2 : 1), PBH(2 : 1)S, and PBH(4 : 1)S, in natural soil burial. We can see that all the copolyesters displayed a faster degradation rate than that of PBS. The weight loss of PBS was only

1.02% after 52 days, whereas the weight losses of the copolyesters were all above 2% after the same time period. Among the copolyesters, PBSA(2 : 1) displayed a faster degradation rate than that of either PBH(2 : 1)S or PBH(4 : 1)S. The weight loss reached 2.49% after 52 days, whereas the weight losses of PBH(2 : 1)S and PBH(4 : 1)S were 2.37 and 2.0%, respectively, indicating that the degradation rate decreased with the increase of the amount of butylene unit in the copolyester. Apart from the plasticization effect of copolymerization, this also shows that the adipate unit was more likely to be attacked by microorganisms. Variations of molecular weight were also



**Figure 10** Variation of molecular weight with weight loss of the polyesters in natural soil burial.





**Figure 11** Variation of molecular weight with weight loss of PBS during the degradation in the laboratory (by *Penicillium chrysogenum* attack) and in natural soil burial.

monitored by terminal titration during the degradation and they also decreased with the weight loss (see Fig. 10). However, the rate of decrease of molecular weight in soil was faster than that in the laboratory by single microbial attack, especially for PBS. For comparison, variations of molecular weight with weight loss of PBS in the laboratory and in natural soil are plotted in Figure 11. One can clearly see the significant difference in the rates of decrease of molecular weight in these two cases. We assume that the degradation in natural soil was caused by several kinds of microbes and they attacked any ester groups in the polyester molecule.

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