Synthesis and Characterization of High-Molecular Weight Aliphatic Polyesters from Monomers Derived from Renewable Resources

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ABSTRACT: A series of high-molecular weight aliphatic polyesters have been synthesized, at temperatures of $< 200°C$, through a polycondensation reaction between 1,4-butanediol and three diacids of different chain length (succinic acid, azelaic acid, and sebacic acid). All the polyesters obtained have a bio-based content of 100% and number average molecular weight in the range of 28,000–116,000 Da. These average molecular weights are about 5–10 times higher than those of most reported aliphatic polyesters synthesized through similar reaction routes but at temperatures $> 230°C$. The over-heating phenomenon, i.e., the observation of thermal degradation behavior of these polyesters at 230°C is reported. The crystallization behavior, mechanical properties, and enzymatic hydrolysis rate of the polyesters obtained are characterized. Poly(butylene succinate) (PBSu) shows the highest crystallinity and melting temperature, but the lowest thermal stability and slowest potential rate of enzymatic biodegradation rate compared with poly(butylene azelate) and poly(butylene sebacate). © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40579.

INTRODUCTION

The family of polyesters comprises all polymers with ester functional groups in the polymer backbone. The chemistry of the structural units connecting the ester groups can be varied over a broad range, making the polyesters a diverse group covering fibers, films, and coatings. Polyesters are typically synthesized by stepwise polymerization of difunctional monomers of the AB type, i.e., hydroxy acids, or from a combination of AA and BB di-hydroxy and di-acid monomers.[1,2] Such polymerization reactions are commonly referred to as polycondensation[3] because they involve the formation of a small byproduct, e.g., water. Generally, polycondensation is more difficult to fulfill than chain polymerization, because high molecular weights are only achieved at very high degree of monomer conversions (98%–99%). To facilitate these high conversion efficiencies, long reaction times and high temperatures are needed. Usually, higher molecular weight polyesters (i.e., $M_n > 30,000$ Da) are made in two steps. The first step involves the preparation of a polyester precondensate either by transesterification reactions or by esterification of the diacids with excess diols. The second step is the further removal of condensation byproducts from the molten precondensate under vacuum at high temperatures (i.e., 230°C).[4]

Aliphatic polyesters such as poly(L-lactic acid), poly(ε-caprolactone), poly(butylene succinate) (PBSu), poly(3-hydroxy butyrate), poly(3-hydroxy valerate), and so forth make up a very important class of biodegradable polymers. The inherent degradability of these aliphatic polyesters makes them especially suitable for applications where the environmental impact is a concern, e.g., packaging, disposable items, and agricultural mulch films. For this reason, aliphatic polyesters have been discussed in many reports, especially polyhydroxyalkanoates.[5–8] In addition, numerous articles on making aliphatic polyesters from diols and diacids (mainly succinic acid) have recently appeared in the literature.[9–13] Studies on the crystallization, melting behavior, and enzymatic degradation of these polyesters have been reported.[9,10,12,14–16] However, the polymers produced by these researchers[12,14–16] generally have relatively low molecular weight (number average molecular weight, M_n, in the range of 1000–10,000 Da) and lack structural regularity, resulting in

materials with poor mechanical properties. Until now, the only commercial homopolyesters that are synthesized through polycondensation and have high molecular weight ($M_n > 35{,}000$ Da) is PBSu, made under the trade name of Bionolle® from the Japanese company Showa High Polymers.[17] In their process, the polycondensation reaction involves chain extension of the ester oligomers by the use of diisocyanate coupling compounds to achieve sufficiently high molecular weights.[18] Overall, there are few reports describing the synthesis of high molecular weight aliphatic polyesters directly through polycondensation process without chain extension.[19]

Long reaction times and high temperatures are necessary to achieve high-molecular weight polymers through polycondensation process.[4] However, esterification is thermodynamically a reversible reaction. During the polycondensation process, heating at high temperature for long time can cause side reactions such as the decomposition of the glycol to form aldehydic products,[20] or thermal decomposition of the polymer to form oligomers, H_2O and CO_2 through random degradation of ester chains.[21,22] These side reactions may result in decreasing, rather than increasing, the molecular weight of the polyester prepared. This over-heating issue somehow has been overlooked because most reports of the polycondensation process were performed at temperatures of over 250°C, at which point any over-heating side reaction might have already occurred. In this study, the over-heating phenomenon is discussed through the observation of thermal degradation behavior of these polyesters at 230°C. A series of high-molecular weight aliphatic polyesters, in the range of 28,000–116,000 Da, were synthesized directly from 1,4-butanediol and various diacids (i.e., succinic acid, azelaic acid, and sebacic acid) under mild conditions (< 200°C) and without the involvement of other chain extending compounds. These average molecular weights were about 5–10 times higher than those aliphatic polyesters synthesized through similar reaction routes but at temperature > 230°C as summarized above. An important consideration in selecting 1,4-butanediol, succinic acid, azelaic acid, and sebacic acid is that all these monomers can be produced from renewable starting materials. For example, 1,4-butanediol can be produced by direct fermentation of glucose,[23] succinic acid can be produced through fermentation and metabolism by microorganisms such as *Anaerobiospirillum succiniciproducens* and *Actinobacillus succinogenes*,[24,25] azelaic acid is industrially produced by the ozonolysis of oleic acid[26] and sebacic acid is a derivative of castor oil.[27] Hence, polyesters produced primarily from monomers derived from renewable resources could have a biomass content approaching 100%. This makes them attractive, as "green polymers" that are derived from renewable resources and are potentially biodegradable, minimizing waste disposal problems. The chemical structures of the polyesters obtained were confirmed by ^1H nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy. Their physical properties were characterized by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). We also reported on the mechanical properties, thermal degradation, and enzymatic degradation of these polyesters.

EXPERIMENTS

Materials

1,4-butanediol ($> 99\%$), succinic acid ($> 99\%$), azelaic acid (98%), sebacic acid (99%), and titanium (IV) butoxide ($Ti(OBu)_4$) catalyst of analytical grade were all purchased from Aldrich Chemicals. Chloroform (ACS grade) and methanol (ACS grade) were obtained from Fisher Scientific. All the other solvents used for the analytical methods were of analytical grade.

Polyester Synthesis

The synthesis of aliphatic polyesters was performed following the two-stage melt polycondensation method (esterification and polycondensation) (Supporting Information Scheme 1) in a glass batch reactor using a driving gas-melt process,[28] i.e., continuously flushed with nitrogen gas. Synthesis was performed in a 100 mL round-bottomed three-neck flask with reactant stoichiometry of 1 : 1.1 of diacid to diol. The flask was charged with diacids (0.05 mol) and was heated to 180°C for succinic acid, 100°C for azelaic acid, and 140°C for sebacic acid. After the solid diacids were melted completely, the diol (0.055 mol) was added to the flask, followed by $Ti(OBu)_4$ (0.25 mol % based on diacid). To minimize the loss of diol during this process, the reaction mixture was heated step-by-step to 180°C within 2 h for azelaic acid and sebacic acid systems; with succinic acid, the reaction mixture was dropped to 160°C for the first hour, then heated to 180°C for the second hour. In all cases, reaction was then kept running at 180°C for a further 2 h. During this process, H_2O and excess diol were removed from the reaction mixture by evaporation. In the second step of polycondensation, the temperature was slowly increased to 200°C and held for 12 h for all the three reaction systems. The synthesized polyesters were purified by dissolving them in chloroform, then precipitating them in ice-cold methanol (10-fold amount to chloroform). The products were dried at room temperature for 72 h under vacuum and stored in desiccators. In this way, white or yellowish aliphatic polyesters of poly(butylene succinate) (PBSu), poly(butylene azelate) (PBAz), and poly(butylene sebacate) (PBSe) were obtained.

Following synthesis of the polymer, films were prepared for measurements of enzymatic degradation and mechanical properties. The films were compressed in a stainless steel mold of dimensions $100 \times 100 \times 0.5$ mm^3 at a temperature of 150°C for PBSu, and 100°C for PBAz and PBSe, immediately followed by rapid cooling to room temperature.

Polyester Characterization

^1H-NMR spectra for the synthesized polyesters were recorded with a Varian Inova spectrometer (Varian, CA) at 400 MHz and performed at ambient temperature with 5% (w/v) polymer solution in deuterated chloroform ($CDCl_3$).

The molecular weight distributions of the polyesters were determined by GPC. The chromatograms were acquired using an isocratic Agilent 1100 pump (Agilent Technologies; CA) equipped with an evaporative light scattering detector (Alltech ELSD 2000, Mandel Scientific Company, Canada). A column (300 $\times$ 7.8 mm^2 i.d.) with particle size of 5 μm (Styragel HR1, Waters Corporation) was used under the following conditions:

Table I. Physical Properties of Aliphatic Polyesters

Sources	M_n (×10⁴ Da)	M_w (×10⁴ Da)	DP	T_g (°C)	T_m (°C)	ΔH (J/g)	ΔH_m (J/g)	X_c (%)	Yield strength (MPa)	Elongation (%)	Tensile strength (MPa)
PBSu	11.6	19.9	1.71	−32	106/113	87.6	210[a]	46	39 ± 1	51 ± 5	29 ± 1
PBAz	3.7	5.6	1.54	−62	47	42.6	150[b]	28	15 ± 1	158 ± 13	14 ± 2
PBSe	2.8	3.7	1.33	NA	64	45.5	155[a]	29	–	–	–

[a] From Ref. 7.
[b] From Ref. 29.

chloroform as the mobile phase; flow rate of 1 mL/min; sample concentrations of 0.4 mg/mL; and injection volumes of 10 μL. Polystyrene standards with known molecular weight were used to generate a calibration curve.

A DSC Q100 (TA Instruments, DE) equipped with a refrigerated cooling system was used to measure the thermal behavior of all the polyester samples. The samples were heated under a dry nitrogen gas atmosphere at a rate of 10°C/min from 25°C to 180°C to erase thermal history, then cooled down to −80°C at a cooling rate of 0.5°C/min. To study the double melting behavior, the crystallization experiment was also performed at 20°C/min for one of the PBSu sample. Modulated differential scanning (MDSC) measurements were performed with a modulation amplitude of 1°C/min and a modulation period of 60 s at a heating rate of 2°C/min from −80°C to 180°C. The second heating stage was selected for the analysis of heating data. For crystallinity determination, the polyester films were cooled down to −80°C first, followed by heating using the MDSC procedure described above. The crystallinities of each polyester film were calculated from the ratio of the heat fusion measured to the equilibrium heat of fusion, and the results are listed in Table I. All the DSC measurements were performed following the ASTM E1356-03 standard procedure.

Thermogravimetric analysis (TGA) was performed on a TGA Q50 (TA Instruments, DE) following the ASTM D3850-94 standard. Approximately 10 mg of the specimen was loaded in the open platinum pan. The samples were heated from 25°C to 600°C under dry nitrogen with 100 mL/min purging flow at constant heating rates of 5°C/min. For isothermal degradation, the samples were heated to 230°C under dry nitrogen and kept at this temperature for 400 min.

Mechanical properties were tested using an Instron (MA) tensile testing machine (model 4202). A 500 Kgf load cell was used for all the tests. Specimens were cut out from the polyester films using an ASTM D638 Type V cutter. As suggested by the aforementioned ASTM standard, the measurements were performed at room temperature with crosshead speed of 100 mm/min. The data presented are an average of five different measurements, and the errors reported are the associated standard deviations.

Enzymatic Degradation
The polyester films were cut into pieces of dimension 10 × 20 × 0.5 mm³ with a weight of ∼100 mg. All the samples were immersed into 10 mL of buffer solution (pH = 7.0) containing *Pseudomonas cepacia* lipase (0.2 mg/mL).[30] The vials were placed in an oven at 30°C. The buffer/enzyme solution was

changed every day to restore original level of enzymatic activity. After a specific period of incubation, the films were removed from the vials, washed with distilled water, and freeze dried at room temperature for 24 h and weighted.

RESULTS AND DISCUSSION

Characterization of Polyesters
High molar masses are an essential requisite to achieve good mechanical properties in polymeric materials such as good filmability. However, there is an intrinsic difficulty in synthesizing high molar mass aliphatic polyesters through a conventional polycondensation process. During the polycondensation, a high reaction temperature and long reaction time are necessary to make up for the decrease in the concentration of reactive end groups as the polymerization reaction proceeds and the molar mass increases.

Preliminary experiments were performed to synthesize aliphatic polyester by reacting 1,4-butanenol with succinic acid at high temperatures (over 230°C) during the polycondensation step as reported.[12–14,30] The resultant polymer had two peaks in its GPC spectrum. The M_n of the first polymer peak is around 13,500 Da, and M_n of the second oligomer peak is ∼3000 Da. After purification following the procedure described in the experimental section, the oligomers were removed, but the resulting purified polymer still has a low molecular weight of M_n less than 15,000 Da, as well as a yellow color. To overcome
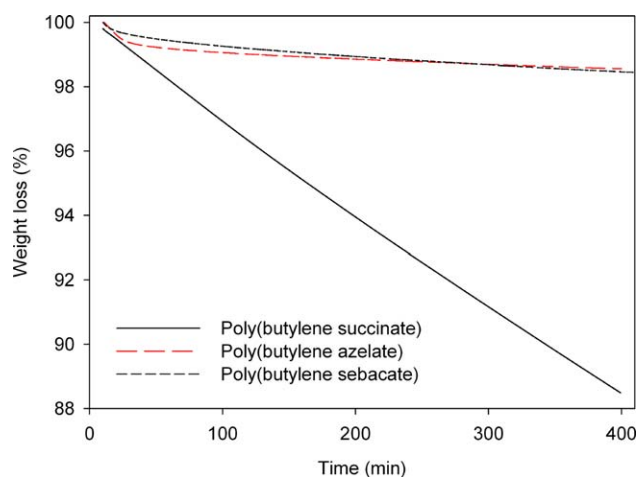
Figure 1. Weight loss of poly(butylene succinate), poly(butylene azelate), and poly(butylene sebacate) during TGA scanning at 230°C for 400 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
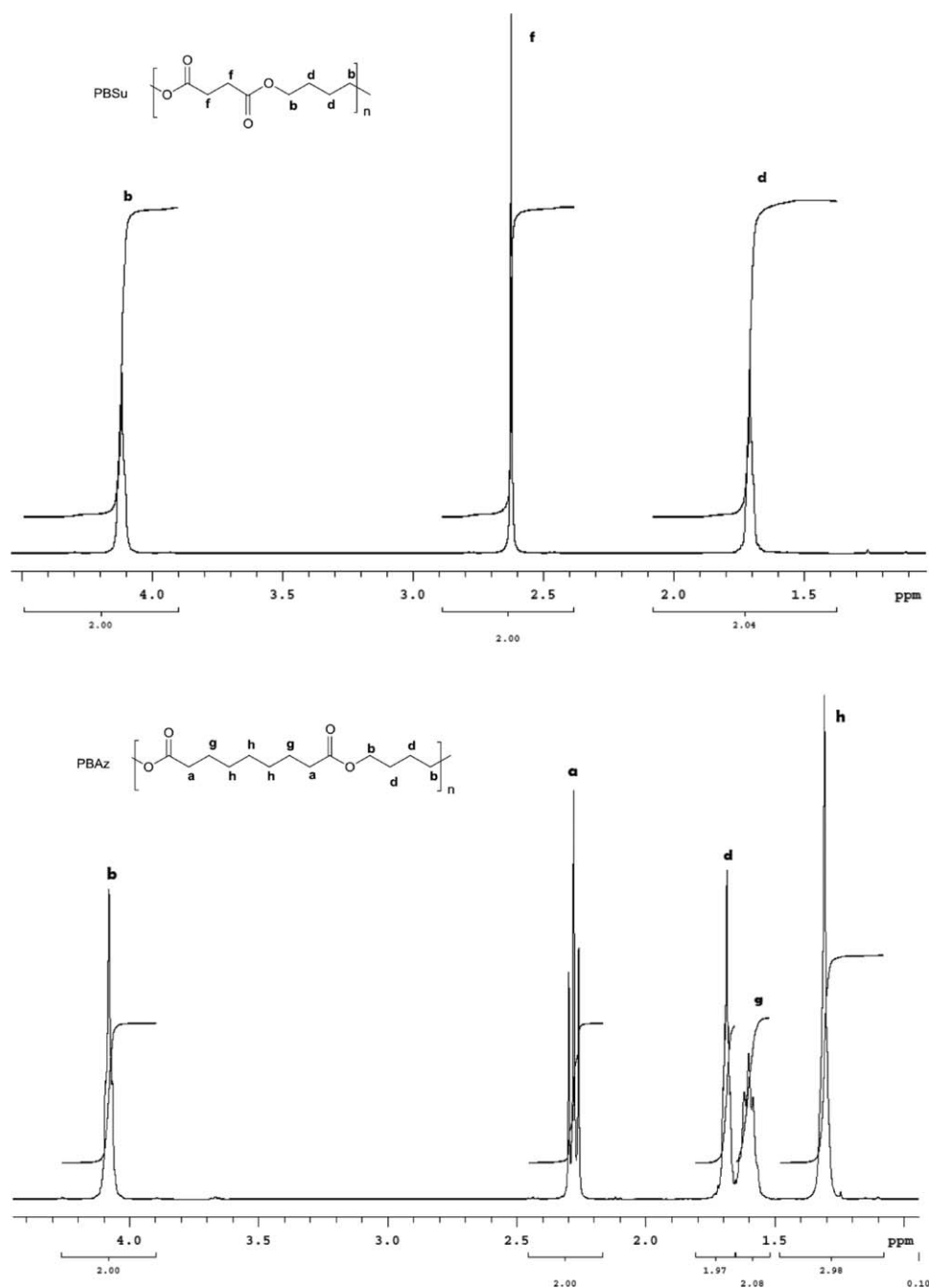
Figure 2. ^{1}H-NMR spectra of poly(butylene succinate), poly(butylene azelate), and poly(butylene sebacate).

this problem, the reaction temperature for the polycondensation reaction was decreased to 200°C and the reaction time was increased from 8 h to 16 h. In this way, PBSu with an M_n of 116,000 Da and polydispersity distribution index of 1.7 was obtained, as determined by GPC (Table I). As well as finding the optimum reaction temperature, the use of a 10% molar excess of 1,4-butanediol over the carboxylic diacid was necessary to increase the polymer molecular weight. The use of excess diol was justified by the observation that during the reaction some diol was removed from the flask by the stream of nitrogen, limiting the polymerization reaction from proceeding. A similar procedure was applied to the azelaic acid and sebacic

acid systems, and PBAz and PBSe with M_n in the range of 28,000–37,000 Da were obtained. By comparison, in a recent report of PBAz synthesis, a PBAz polymer with molecular weight of 7200 Da was obtained.[31] Related work by Cao et al.[32] succeeded in synthesizing a range of copolymers by copolymerizing caprolactone with PBSu. In that work, PBSu homopolymer was also synthesized at an M_n of ~62,000 Da. Also, Papageorgiou et al.[16] synthesized PBSe and again only low molecular weights were obtained with an M_n of ~19,000 Da.

To demonstrate the effect of over-heating on the polycondensation step, thermal degradation of the three polyesters was
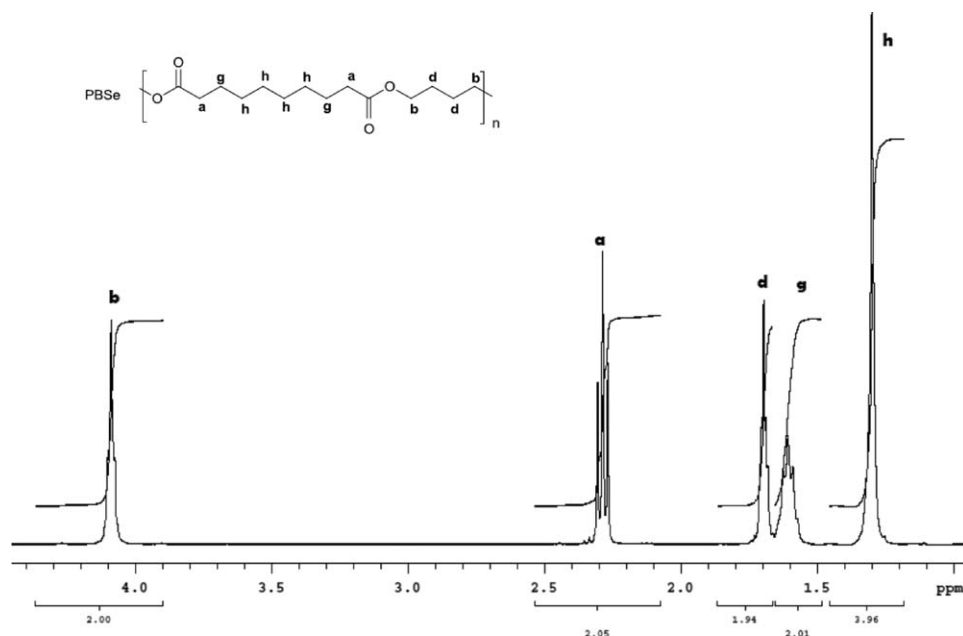
Figure 2. Continued

studied by determining their weight loss during heating at 230°C as shown in Figure 1. From the thermogravimetric curves, it can be seen that PBSu loses almost 12% of its original weight over 400 min, whereas PBAz and PPSe only lose about 1.5% of theirs, suggesting that thermal degradation occurred at 230°C, particularly for PBSu. The differences in thermal degradation behavior between PBSu and PBAz, PBSe might be due to the differences between their ester bond densities, and/or the diacid chain length, as discussed in detail later. The occurrence of thermal degradation at 230°C implies that polycondensation should be run at lower temperatures to achieve polyesters with a molecular weight that is high enough to yield the required properties. Thus, the use of excess temperatures that cause thermal decomposition of polyesters, may explain the lower molecular weights of polyesters in previous reports.[16,29,31]

The chemical structure of PBSu, PBaz, and PBSe were also characterized by ^{1}H-NMR spectra and shown in Figure 2. The ^{1}H-NMR spectrum of PBSu is very simple, containing only three characteristic peaks at 2.65, 1.7, and 4.1 ppm attributed to the **f** protons of the succinic acid residue and the **b** and **d** proton of the 1,4-butanediol residue. In the case of PBAz, a triplet at 2.25–2.35 ppm, a multiplet at 1.55–1.65 ppm and a singlet at 1.3 ppm are attributed to **a**, **g**, and **h** protons from the azelaic acid residue, respectively. The PBSe ^{1}H-NMR spectrum is similar to that of PBAz, except that the integration for peak **h** in the two spectra are different as they arise from different diacids of different chain length. The successful of synthesis polyesters was also confirmed by FTIR measurements, as reported in the Supporting Information.

Thermal Properties of Polyesters

It is important to understand the thermal behavior of the polymers developed in this work as they relate to the physical properties of these materials. The MDSC traces for the polyester samples (Figure 3) indicate that the melting points are $T_m = 113°C$ for PBSu, $T_m = 47°C$ for PBAz and $T_m = 64°C$ for PBSe. As expected, the greater chain flexibility that results from the longer chain length of the monomeric unit facilitates the melting process and therefore the melting temperature of the polymers decreases. However, the T_m of PBSe is 17°C higher than that for PBAz even though the chain length of sebacic acid is one carbon longer than azelaic acid. This can be explained by an odd–even effect on crystal packing, i.e., chains with an odd numbers of carbon atoms pack less effectively compared with even-numbered chains.[30] This result is in agreement with thermal studies on other types of polyesters, for which T_m is higher for even–even polyesters than for odd–even ones.[30]

From the polyester MDSC traces in Figure 3, multiple melting points were observed for PBSu after crystallization from the melt, whereas only one melting temperature was observed in PBAz and PBSe. Multiple melting endotherms in DSC traces of semicrystalline polymers, including polyesters, are often encountered.[33–38] The most common interpretations of multiple melting behaviors in polymers are that they result from the melting of crystals with different stability (dual morphology mechanism)[39] or the melting–recrystallization remelting process (reorganization mechanism).[40] The multiple endotherm behavior of polyesters has been described as a reorganization process taking place during the DSC scan. Yasuniwa and Satou[41] studied the double melting behavior of PBSu by monitoring its endotherms on crystallizing nonisothermally from the melt at a constant cooling rate. They concluded that this behavior is due to melting–recrystallization remelting process. Yoo and Im[42] also reported the multiple melting behavior of PBSu crystallized isothermally from the melt using DSC. However, using wide angle X-ray diffraction, they found that there was no crystal
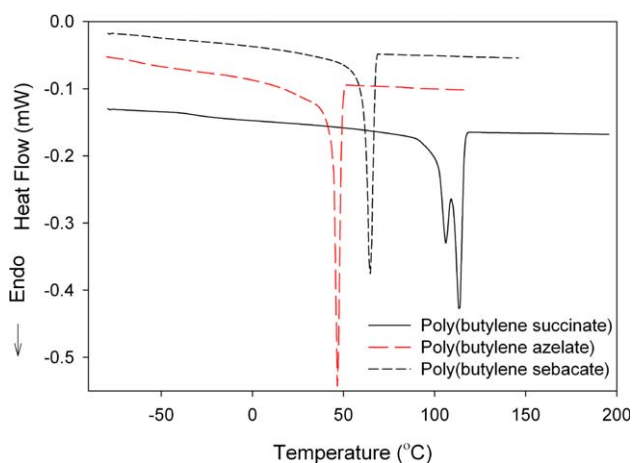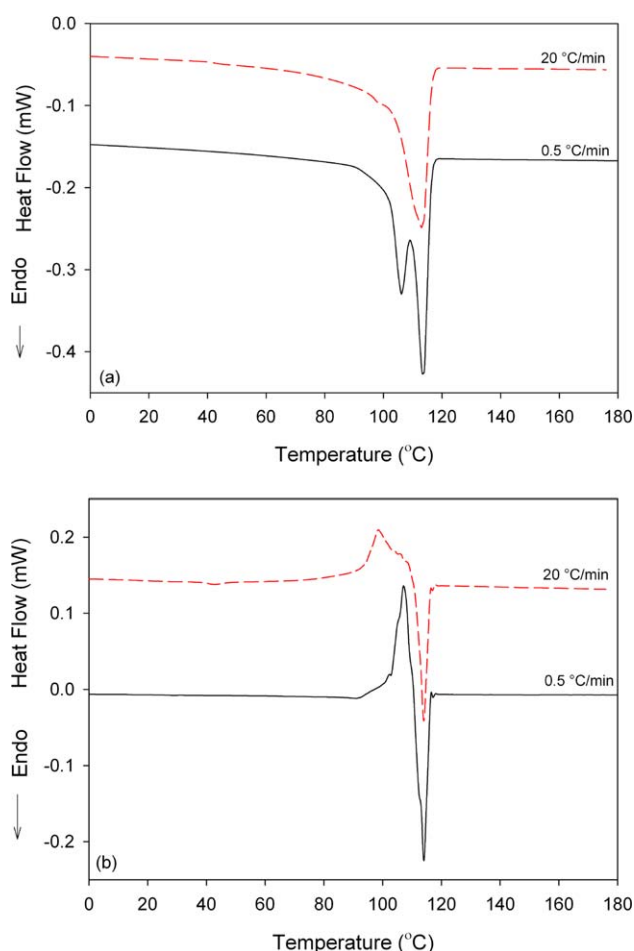
Figure 3. MDSC traces of poly(butylene succinate), poly(butylene azelate), and poly(butylene sebacate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modification occurring when PBSu crystallized at different temperatures. As a result, they concluded that the multiple melting behavior of thermally formed PBSu does not originate from the crystal modifications. Consistent with this finding, in this work, we provide direct evidence in support of the applicability of the melting and recrystallization model through MDSC measurements.

MDSC is a relatively new thermal analysis technique, which superimposes a sinusoidal temperature oscillation (modulation) onto the linear heating/cooling ramps of conventional DSC. This not only provides the total heat flow signal but also the heat capacity (the component relates to heating rate) and its kinetic components (the component relates to time at a constant temperature). The total heat flow is separated into the components of reversing heat flow (heat capacity-related) and nonreversing heat flow (kinetic-related). Thus, the endothermic signals can be detected in both reversible and nonreversible scans, whereas the crystallization exotherms only contribute to the nonreversible signal. This makes MDSC a very powerful technique for the separation of exotherms (including crystallization and recrystallization) from glass transitions, reversible melting, or other heat capacity related events.[43–45] To investigate the origin of the double melting peak appearing in the heating scans of PBSu crystallized from the melt, nonisothermal crystallization experiments were performed at crystallization rates of 0.5°C/min and 20°C/min. In these cooling traces, the crystallization peak moved to lower temperatures (12°C shifting) at faster cooling rates (Supporting Information Figure S2). The reversible heating traces [Figure 4(a)] from the crystallized PBSu samples display a double melting peak with the higher melting point component being independent to the cooling rate and the lower one decreasing in intensity at faster cooling rates. In the nonreversible curves [Figure 4(b)], the crystallization exotherm shifts to lower temperatures for the sample cooled at cooling rate of 20°C/min compared with that observed at cooling rate of 0.5°C/min. Thus, clearly only the lower melting point structure is sensitive to cooling rate. So, they must be the crystals originally formed during cooling process. These crystals have low

thermal stability. The high melting endotherm corresponds to the melting of the crystallites formed through the recrystallization of the melt of the crystallites of the low melting endotherms. All the facts mentioned above confirm the occurrence of a reorganization process, i.e., through the whole heating scan the material melts at low temperature (first peak), recrystallizes immediately and remelts in the second peak.

Plots from TGA and its derivative (DTGA) for all three polyesters are shown in Figure 5(a,b). For all samples, decomposition starts at ∼ 230°C and ends at 500°C. DTGA curves reveal either one or two main degradation processes, with noticeable differences across the whole temperature range. For example, for PBSu the temperature for a 5% mass loss is 300°C and the fastest rate of mass loss is observed at 390°C. In contrast, PBAz and PBSe show higher thermal stability, both having temperatures for 5% mass loss and fastest rate mass loss of 350°C and 400°C, respectively. From the above, it can be concluded that PBAz and PBSe with longer diacid chain lengths compared with PBSu, have better thermal stability, although they have lower melting points.

Figure 4. (a) Reversible heating flow, (b) nonreversible heating flow of poly(butylene succinate) crystallized with cooling rates of 0.5°C/min and 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
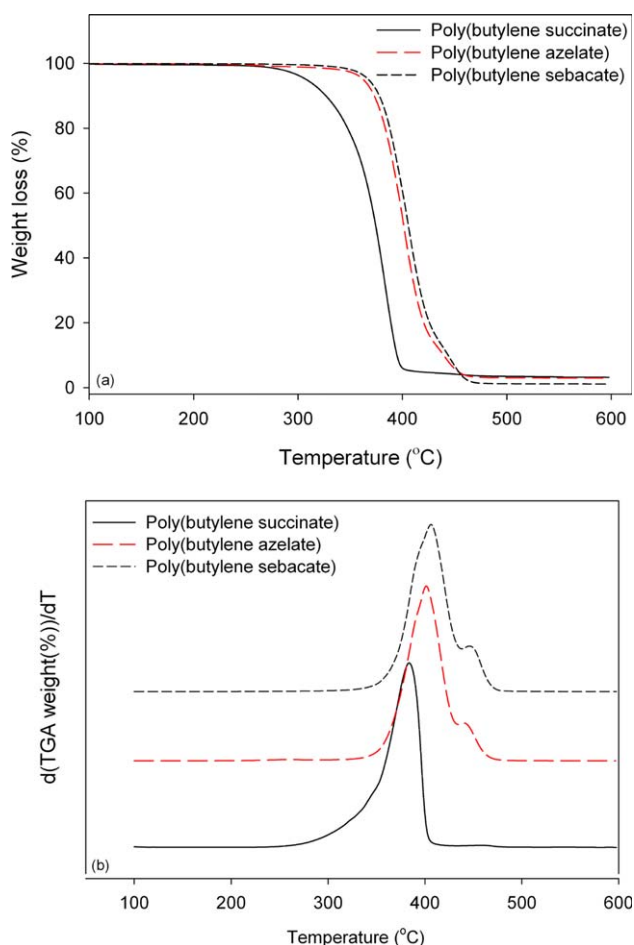
Figure 5. (a) TGA curves of poly(butylene succinate), poly(butylene azelate), and poly(butylene sebacate) and (b) DTGA curves of poly(butylene succinate), poly(butylene azelate), and poly(butylene sebacate). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to the thermal degradation mechanism described for poly(ε-caprolactone),[46,47] poly(propylane azelate), and poly(propylane sebacate),[48] which have similar structure to the polyesters synthesized in this work, the first stage of degradation is attributed to the random ester bond decomposition which produces H_2O, CO_2 and corresponding monomers, dimers, trimers, and oligomers. In the case of PBAz and PBSe, the appearance of a second stage of degradation, at considerably higher temperature (ca., 440°C) might be due to C—C bond cleavages. The observed differences of the thermal stabilities between these polyesters in the first stage may be due to the ester bond density difference of the polyesters, as PBSu has a higher ester bond density than the other two for the same molar fraction. The differences in the second stage arising from the C—C bond cleavages are due to the structural differences between the diacids used, i.e., the chain length of succinic acid is shorter than the other two. The observation of C—C bond cleavages has been previously reported in various polymer systems such as polyethylene, polypropylene,[49] and other polymers derived from long chain starting materials including polyurethanes[50] and poly(nonanolactones).[22] For example, Grassie and Mendoza[50] found

that ethylene appeared in the residue of polyurethanes prepared from high-molecular weight poly(ethylene glycols), which was attributed to the cleavage of C—C bond. Overall, the thermal stabilities of PBAz and PBSe polyesters synthesized in this work are slightly better than other aliphatic polyesters such as poly(L-lactide).

Enzymatic Biodegradation of Polyesters

It is well known that aliphatic polyesters are more susceptible to enzymatic degradation compared with aromatic polyesters, and therefore they are currently proposed commercially as biodegradable materials. There are many structural factors affecting the enzymatic hydrolysis rates of aliphatic polyesters. These include the distance between ester groups, the steric hindrance for the attachment of the enzyme on the hydrolyzing groups, the hydrophilic/hydrophobic balance within the main chain, the molecular weight,[30] the degree of crystallinity,[51] and the melting point.[30]

Before the polyesters prepared in this work could be subjected to enzymatic degradation, a preliminary test was necessary to choose the temperature to use during the biodegradation tests. For aliphatic polyesters, as the temperature increases, approximating the melting temperature, some crystals with imperfect crystalline structure may melt into an amorphous state and therefore enzymatic hydrolysis is accelerated as the amorphous material is more easily hydrolyzed than is crystalline material.[30] Thus, quite satisfactory hydrolysis rates are obtained when the temperature is 10°C–20°C lower than the polymers melting point. The most commonly used temperature for enzymatic hydrolysis studies is that of 37°C. In this study, it was decided to study the kinetics of hydrolysis at 30°C, as PBAz melts at a relatively low temperature ($T_m = 47$°C).

The degree of enzymatic biodegradation of all the three polyesters was estimated from the percentage weight loss and the weight loss per unit of area for several days and was shown in Figure 6(a,b), respectively. As can be seen, the biodegradation rate for PBSu is low over 12 days of enzymatic hydrolysis and the maximum weight loss is very small (about 3.5 wt %). On the other hand, PBAz and PBSe have much higher degradation rates with a weight loss close to 30 and 40 wt %, respectively, over 12 days. In addition, for PBAz and PBSe, a rather abrupt weight loss is observed during the first week of biodegradation (5–8 days), after which the weight loss continues at a slower rate. The fact that PBAz and PBSe hydrolyze much faster than PBSu could be attributed to their lower crystallinity, which in the tested specimens was about 28% for PBAz and PBSe, but much higher, i.e., about 46% for PBSu as listed in Table I. As is well known, enzymatic hydrolysis is a heterogeneous process[14,30,46] in which enzymes tend to attach on the surface of an insoluble substrate and hydrolysis proceeds via surface erosion. In general, the internal parts of polyester specimens are not expected to be attacked until pores are eroded into the polymer surface, allowing enzymes to penetrate. One study reported that for PBSu and its copolymers, the surface initiated enzymatic degradation occurs to a maximum depth of 0.22 mm.[52] Thus, hydrolysis rates may decrease after consumption of the amorphous material of the surface. For material with a high
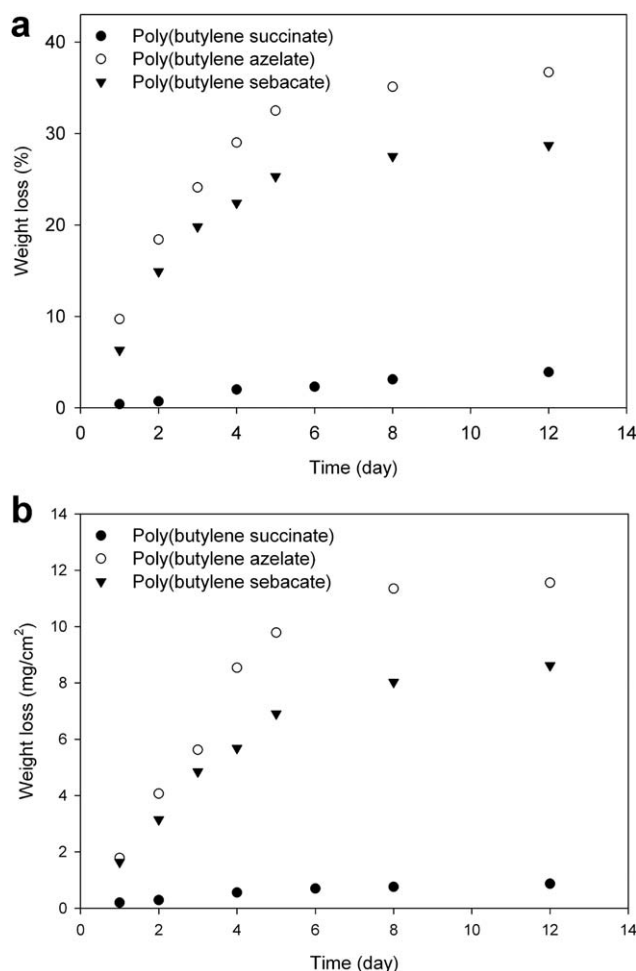
Figure 6. (a) Weight loss percentage, (b) weight loss per surface area, as a function of time of enzymatic hydrolysis of poly(butylene succinate), poly(butylene azelate), and poly(butylene sebacate).

crystalline content such as PBSu, the layer of crystalline domains at the surface is only penetrated by fewer pores as a result of enzymatic hydrolysis. This inhibits further penetration of water into the body of the film leading to decreased rates of hydrolysis. Other factors, such as molecular weights, ester group densities, and melting temperatures of the polyesters also affect the enzymatic degradation rate. However, a systematic detail study of all of these factors is beyond the scope of this article.

Mechanical Properties of Polyesters

As listed in Table I, PBSu has a tensile strength, a yield strength, and an elongation at break of 29 $\pm$1 MPa, 39 $\pm$ 1 MPa, and 51% $\pm$ 5%, respectively. These results are comparable with those reported by Papageorgiou and Bikiaris[15] for PBSu. PBAz has a tensile strength, a yield strength, and an elongation at break of 14 $\pm$ 2 MPa, 15 $\pm$ 1 MPa, and 158% $\pm$ 13%, respectively. Unfortunately, PBSe is too brittle to perform tensile test even with a relatively high molecular weight of 28,000 Da, therefore the mechanical properties for this sample are not given. The PBSu sample demonstrated a significantly higher tensile strength ($+$ 107%) and yield strength ($+$ 160%) but lower elongation at break ($-$ 68%) than the PBAz sample. One expla-

nation for this behavior is due to the difference crystallinity of these two samples, as crystallites appear to serve as an effective stress-bearing phase during deformation. In the case of the PBSu system, the more ordered crystals might be able to absorb more strain energy on deformation through an unfolding of the crystalline lamellae or break up of crystalline segments, as indicated by its higher strength. The explanation for the greater elongation at break for PBAz sample is due to the longer chain diacids incorporated in this polymer which results in a greater unfolding extendibility during deformation.

CONCLUSIONS

A series of high-molecular weight (M_n in the range of 28,000–116,000 Da) aliphatic polyester have been successfully synthesized directly from 1,4-butanediol and diacids of different chain lengths under mild conditions ($<$ 200°C, no vacuum applied) without the addition of chain extending compounds. The observation of thermal degradation at 230°C for all of the polyesters studied, indicates that too high a reaction temperature (over-heating) can cause a decrease in the molecular weight rather than an increase. The polyesters produced show different crystallization behavior for the different chain lengths of diacids used. PBSu gives the highest crystallinity and melting temperature, but the lowest thermal stability and potentially the slowest rate of enzymatic biodegradation rate compared with PBAz and PBSe.

ACKNOWLEDGMENTS

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