Mechanisms and Kinetics of Thermal Degradation of Poly(butylene succinate-*co*-propylene succinate)s

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ABSTRACT: Poly(butylene succinate) (PBSu) and two PBSu-rich poly(butylene succinate-co-propylene succinate)s were studied. Copolyesters were characterized as random copolymers, based on ^{13}C-NMR spectra. TGA-FTIR was used to monitor the degradation products at a heating rate of 5°C/min under N_2. FTIR spectra revealed that the major products were anhydrides, which were formed following two cyclic intramolecular degradation mechanisms by the breaking of the weak O-CH$_2$ bonds around succinate groups. Thermal stability at heating rates of 1, 3, 5, and 10°C/min under N_2 was investigated using TGA. The model-free methods of the Friedman and Ozawa equations are useful for studying the activation energy of degradation in each period of mass loss. The results reveal that the random incorporation of minor propylene succinate units into PBSu did not markedly affect their thermal resistance. Two model-fitting mechanisms were used to determine the mass loss function $f(\alpha)$, the activation energy and the associated mechanism. The mechanism of autocatalysis nth-order, with $f(\alpha) = \alpha^m(1 - \alpha)^n$, fitted the experimental data much more closely than did the nth-order mechanism given by $f(\alpha) = (1 - \alpha)^n$. The obtained activation energy was used to estimate the failure temperature (T_f). The values of T_f for a mass loss of 5% and an endurance time of 60,000 h are 160.7, 155.5, and 159.3°C for PBSu and two the copolyesters, respectively. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3610–3619, 2012

Key words: degradation; FTIR; polyesters; thermogravimetric analysis

INTRODUCTION

Plastic products are part of daily life because of their wide range of applications and extreme usefulness. Imagining modern civilization without these products is difficult. However, they have led to the problem of the need to deal with a rapidly growing amount of solid waste. Scientists and engineers are considering solving problems of waste management by replacing bio-resistant synthetic polymers with biodegradable polymers. Aliphatic polyesters are among the most interesting candidate biodegradable materials because they are readily susceptible to attack by enzymes or microorganisms. Bio-synthetic aliphatic polyesters are generally regarded as one of the most important classes of biodegradable polymers. Some of them, such as bacterial poly(3-hydroxy butyrate) (P3HB), are of particular interest.

Chemosynthetic aliphatic polyesters, including poly(ethylene succinate) (PESu), poly(butylene succinate) (PBSu), and poly(butylene adipate) (PBA), as well as their copolymers, have been commercialized because of their environmental compatibility.

PBSu is no doubt a highly promising biodegradable polyester. It has a high melting temperature ($T_m \approx 113°C$) and excellent mechanical properties which are similar to the most extensively used polymers, such as low-density polyethylene (LDPE).[1] Many studies of PBSu have been published to elucidate its crystalline structure.[2–4] The crystallization, spherulite morphology, and melting behavior of PBSu have also been extensively investigated.[5–13] Copolymers have higher degradation rates than homopolymers, basically because they have lower crystallinity. Therefore, some tests on PBSu and its various copolyesters have been conducted to examine their morphologies, crystallization kinetics, and melting behaviors.[9,14–17] Poly(propylene succinate) (PPSu), with an odd number of methylene groups in the diol monomer, has low crystallinity. It has attracted increasing attention, because it has a higher biodegradation rate than that with an even number of methylene groups in the diol monomer. To reduce the crystallinity of PBSu, PBSu-rich aliphatic copolyesters that combine the properties of the homopolyesters—the high melting point of PBSu and the

TABLE I
Basic Properties of the Polyesters

Sample code	Composition mol % of PS units	$[\eta]$ (dL/g)	$M_n \times 10^4$ (g/mol)	$M_w \times 10^4$ (g/mol)	M_w/M_n	T_g (°C)	T_m (°C)
PBSu	–	1.27	3.0	7.5	2.5	−41.1	113.2
PBPSu 95/5	7.0	1.29	3.4	13.3	3.9	−40.1	107.9
PBPSu 90/10	11.5	1.62	9.8	17.7	1.8	−39.5	103.3

high biodegradability of PPSu—were synthesized. Hence, the synthesis, crystallization kinetics, morphology, melting behavior, and enzymatic degradation of biodegradable poly(butylene succinate-co-propylene succinate) (PBPSu) copolymers have been explored in recent years.[18–22]

Besides the biodegradability, the thermal stability and thermal degradation behavior of biodegradable polymers are important for their processing, application, and thermal recycling. Some studies have explored the thermal degradation of PESu, PPSu, and PBSu,[23–26] including their activation energies, kinetic parameters, and degradation mechanisms. However, to the best of the authors' knowledge, no study has addressed on the thermal stability of PBPSu. In a previous study,[21] high-molecular weight PBSu and PBSu-rich copolymers were synthesized by a direct polycondensation reaction in the presence of titanium tetraisopropoxide. The aim of this research is to characterize the thermal degradation of PBPSu copolyesters and PBSu by using TGA-FTIR. This approach involves a simultaneous coupling of thermogravimetric analyzer (TGA) and a Fourier transform infrared spectrometer (FTIR). The thermal degradation kinetics were studied by TGA with heating at various rates. The kinetic parameters were analyzed and compared with each other using the model-free methods of Friedman[27] and Ozawa[28] equations. The mass loss function, $f(\alpha)$, of degradation was determined and then discussed with reference to model-fitting methods. Finally, the life-time and failure temperatures of these polyesters were evaluated.

EXPERIMENTAL

Materials and specimen preparation

PBSu, PBPSu 95/5, and PBPSu 90/10 were synthesized using a two-step esterification reaction in the melt state. The authors' recent studies have provided details of the synthesis and characterization.[21] Table I summarizes their properties. The second column lists the compositions of the copolyesters that were analyzed by ^{1}H-NMR. These polyesters had intrinsic viscosity values $[\eta]$ between 1.27 and 1.62 dL/g, measured in phenol/1,1,2,2-tetrachloroethane (3/2, w/w) at 30°C using an Ubbelohde viscometer. The number average molecular weights (M_n) in relation to poly(methyl methacrylate)

for PBSu, PBPSu 95/5, and PBPSu 90/10 were 3.0 × 10^4, 3.4 × 10^4, and 9.8 × 10^4 g/mol, respectively, as presented in the fourth column. Columns 5 and 6 tabulate the weight average molecular weights (M_w) and molecular weight distributions (M_w/M_n), which were obtained by gel permeation chromatography. The last two columns present the glass transition temperatures (T_g) and T_ms. The incorporation of minor propylene succinate (PS) units into PBSu slightly increases T_g, but markedly reduces T_m.[21]

All of the polyester sheets were prepared in a hot press machine. They were formed by compression molding for 5 min at 115°C, and then allowed to cool slowly to room temperature. Compressed sheets with a thickness of around 0.2 mm were thus formed, and then dried in vacuo overnight at room temperature before use.

NMR measurements

NMR spectra of d-chloroform solutions were obtained using tetramethylsilane as the reference standard, on a Varian UNITY INOVA-500 NMR at 295.5 K. ^{13}C-NMR was used to determine both the composition and the distribution of esters in these two copolyesters.

Thermogravimetric analysis

Thermal stability experiments were performed using a TA 2050 TGA. The sample (10 ± 1.0 mg) was placed in a platinum crucible, and was heated from 30 to 800°C in a 50 mL/min flow of nitrogen. Heating rates of 1, 3, 5, and 10°C/min were used. Percent of original sample mass was recorded throughout the heating process, and then the first derivative of the mass curve was obtained. These thermal curves were analyzed according to ASTM E 1641.[29]

Measurements of TGA-FTIR

The sheet specimen was heated from 30 to 800°C at a heating rate of 5°C/min. Gases that were evolved from TGA were sent to a FTIR spectrometer through a heated line. This transfer line and the gas measurement cell were maintained at 225°C. FTIR spectra were obtained using a BIO-RAD FTS3000MX
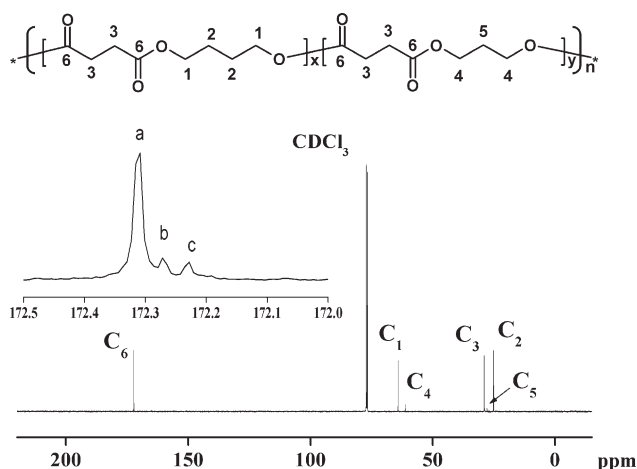
Figure 1 ^{13}C-NMR spectrum of PBPSu 90/10 (solvent: *d*-chloroform at 295.5 K) and its peak assignments.

spectrometer at a resolution of 4 cm^{-1}, with an accumulation of 32 scans.

RESULTS AND DISCUSSION

Copolymer composition and sequence distribution

Figure 1 presents the ^{13}C-NMR spectrum of PBPSu 90/10 and the peak assignments. The two chemical shifts at 64.10–64.17 (C$_1$) and 25.13–25.21 (C$_2$) ppm are associated with the methylene carbons that are α and β bonded to the ester oxygen in the butylene succinate (BS) groups. The carbon atoms of the PS groups yield peak at 61.17–61.25 (C$_4$) and 27.81–27.87 (C$_5$) ppm. The chemical shifts of the ethylene carbons and the carbonyl carbons of the succinic moiety yield peaks at 28.94-29.00 (C$_3$) and 172.22–172.29 (C$_6$) ppm, respectively. Magnification of the ^{13}C-NMR spectrum reveals that the signals of the carbonyl carbons (C$_6$) are in three peaks, as shown in the inset in Figure 1. Peaks a–c are associated with the carbonyl carbons of BSB, the BSP-B side structure and the BSP-P side structure, respectively, (where B, S, and P represent the groups that are derived from 1,4-butanediol, succinic acid, and 1,3-propanediol, respectively). The normalized areas under these three peaks can be used to calculate the probabilities of three triads, composition, randomness, and the sequence distribution of BS and PS units of this copolyester.[21,30,31] PBPSu 90/10 is characterized as having 89.5% BS units and 10.5% PS units, which finding differs slightly from that of ^{1}H-NMR (see Table I). BS and PS units have average-number sequence lengths of 8.5 and 1.0, respectively. The randomness, *B*, is 1.12, which is consistent with the value $B = 1.0$ for a random copolyester, to within experimental error. Therefore, the distributions of BS and PS units in this copolyester are random, given that a single value T_g of $-39.5°C$ applies.[21]

For brevity, the ^{13}C-NMR spectrum of PBPSu 95/5 is not presented here.[21] It revealed 92.7% BS units and 7.3% PS units. BS and PS units have average-number sequence lengths of 12.8 and 1.0, respectively. This copolyester can be considered to be random, given the presence of a single T_g at $-40.1°C$ and a randomness value of 1.07.[21]

FTIR spectra changes during thermal degradation

Figure 2 plots the mass percentages retained and the derivatives of the mass (DTG) traces as a function of temperature for PBSu (solid curves), PBPSu 95/5 (dashed curves) and PBPSu 90/10 (dotted curves) in flowing nitrogen at a heating rate of 5°C/min. At temperatures below 220°C, these three polyesters appear to be stable. The rate of mass loss slowly increased to a maximum at $\sim 390°C$, which was determined from the DTG curves. After deconvolution of the DTG curves (Supporting Information Figure S1), two stages of mass loss were evident. Continuous online identification of evolved gases without intermediate trapping or an isolation step prevents gas condensation and side reactions before detection and characterization. Figure 3 presents the online FTIR spectrum obtained from the gas products that evolved at the temperature at which the decomposition of PBPSu 90/10 was the fastest. It reveals several main absorptions which are enumerated from 1 to 10 in order of decreasing band area. Table II presents the assignments of the FTIR bands to the vibration modes of the functional groups: released carbon dioxide at 2300–2400 cm^{-1}; the anhydride functional group, which is the dehydration product of succinic acid, at 1050, 1757, and 1818 cm^{-1};[32,33] the methyl ester of carboxylic acid in the gas phase, produced by pyrolysis of the PBSu ester functions, at 1158 cm^{-1}; and alkene groups at 3000–3100 cm^{-1} (C—H stretch), 1650 cm^{-1} (C=C stretch), and 910 cm^{-1} (C—H out-of-plane bend).
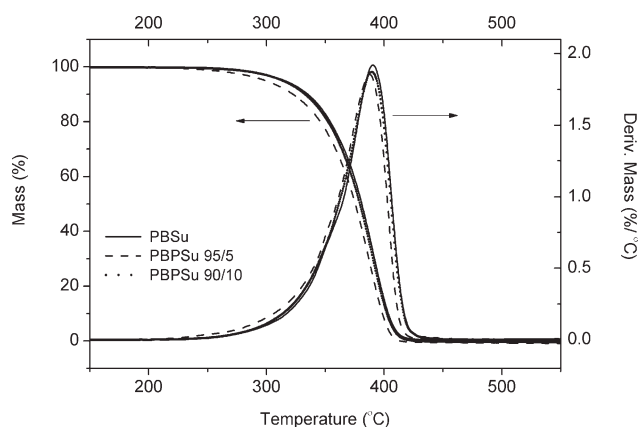

Figure 2 Mass retained (%) and derivative mass (DTG) traces at a heating rate of 5°C/min for PBPSu copolyesters as well as PBSu under nitrogen.
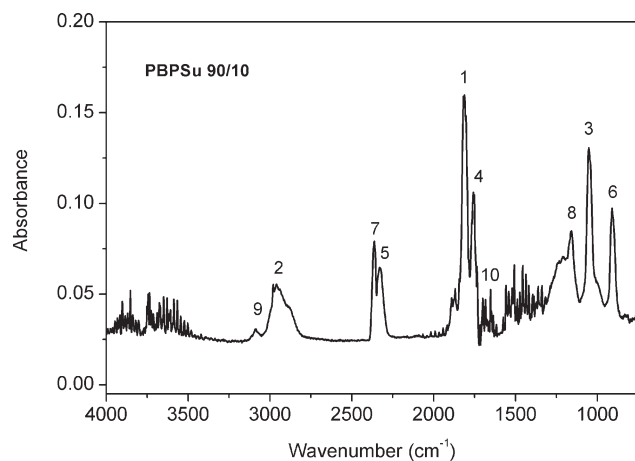
Figure 3 FTIR spectrum for the evolved gases of PBPSu 90/10 at the temperature of the maximum rate of decomposition during the heating at 5°C/min.

Figure 4 presents the temperature-dependent FTIR spectra of PBPSu 90/10 recorded over a temperature range from 350 to 420°C at a heating rate of 5°C/min. The absorbance intensity of the decomposition products of PBPSu 90/10 increased from those peaks detected at 350°C, to a maximum at 390°C, and then fell smoothly as the temperature increased further to 420°C. PBSu and PBPSu 95/5 yielded similar results. Figures 5 and 6 compare the areas of ten absorption bands of FTIR spectra and the DTG trace (dash curve) from PBPSu 90/10 and PBSu, respectively, over decomposition temperatures from 350 to 420°C. All curves reach a maximum at ~ 390°C. The band areas of the anhydride functional group are more intense than those of the other degradation products, because free or end-group succinic acid in the polymer chain is easily dehydrated by the cyclization decomposition mechanism.[34] The anhydride compound was identified by GC-MS from the thermal
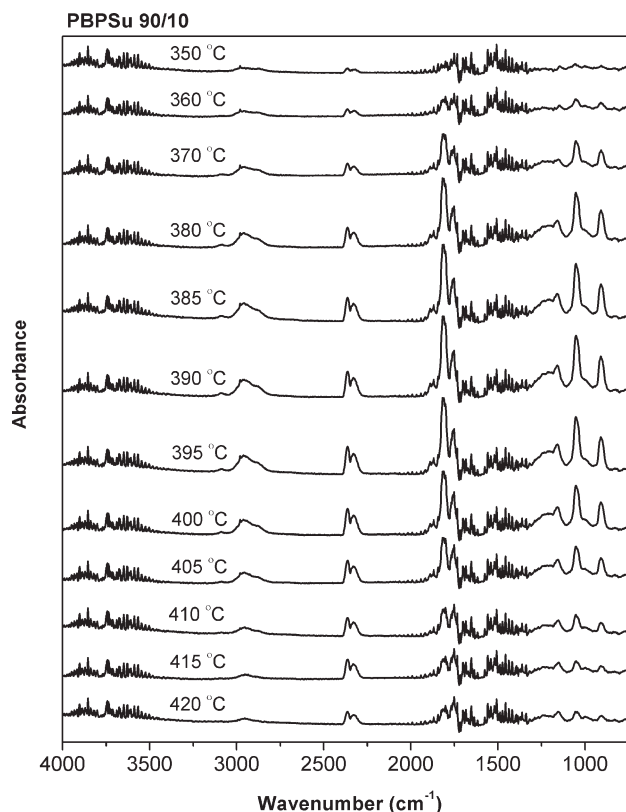

Figure 4 FTIR spectra of PBPSu 90/10 during the thermal degradation at the heating rate of 5°C/min.

degradation of homopolyesters (such as PPSu).[25] In this study, the anhydride functional group of the evolved gases is identified more conveniently and quickly by FTIR. Similar results in Figures 5 and 6 reveal that PBSu and PBSu-rich (PBPSu) copolyesters exhibit similar decomposition mechanisms.

Thermal degradation mechanisms

Figures 3–6 and Table II reveal that the evolved gases are anhydride, olefin, esters, and carbon

TABLE II
Assignments of the FTIR Bands to the Vibration Modes of Functional Groups

Denoted number[a]	Assigned wavenumber (cm^{-1})	Functional group and vibration mode
1	1818	Anhydride (C=O, stretch)
2	2960	Alkane (C—H, stretch)
3	1050	Anhydride (C—O—C, stretch)
4	1757	Anhydride (C=O, stretch)
5	2330	Carbon dioxide, CO_2
6	910	Alkene (C—H, out-of-plane bend)
7	2360	Carbon dioxide, CO_2
8	1158	Methyl esters of alphatic acids (C—O, stretch)
9	3088	Alkene (C—H, stretch)
10	1650	Alkene (C=C, stretch)

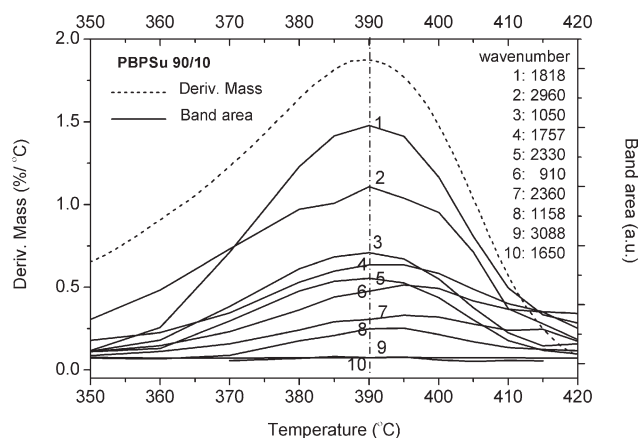[a] In order of decreasing band area, see Figure 3.

Figure 5 Plots of band areas from FTIR spectra and DTG trace from TGA for PBPSu 90/10 during the thermal degradation at the heating rate of 5°C/min.
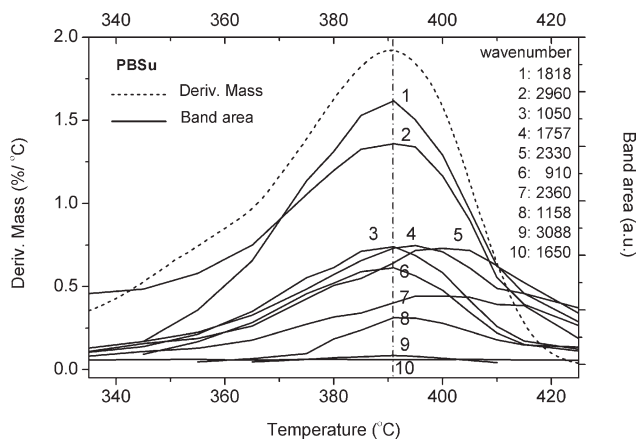
Figure 6 Plots of band areas from FTIR spectra and DTG trace from TGA for PBSu during the thermal degradation at the heating rate of 5°C/min.
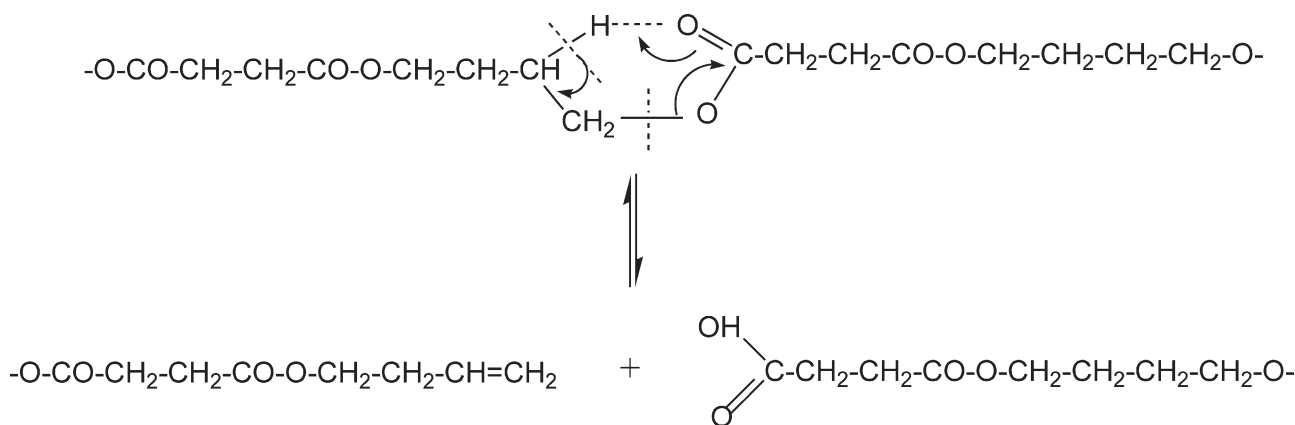
dioxide. With respect to the degradation mechanism of the polyesters in the gas phase,[35–37] the β-hydrogen next to the oxygen linkage of the ester transfers to the carbonyl oxygen of the succinate and this phenomenon results in the selective cleavage of the —O—CH$_2$— bonds, with the formation of two chains, one of which has a carboxylic acid end group and the other of which is an alkenyl group. Therefore, the backbone of the polymer chains degrades at the weak O—CH$_2$ bonds by a cyclic intramolecular rearrangement (Scheme 1).

The FTIR spectra in Figure 4 and the band areas in Figures 5 and 6 reveal that anhydride was the dominant product of the thermal degradation of these polyesters. Scheme 2 presents the main mechanisms of thermal degradation. Following scission of the nearest β-hydrogen bond from the end of the polymer chain with carboxylic acid, alkenyl-terminated chain, and succinic acid are formed (Path 1). Then, dihydrofuran-2,5-dione (anhydride) is produced by the dehydration of succinic acid. After scission of the nearest β-hydrogen bond from the alkene end of the
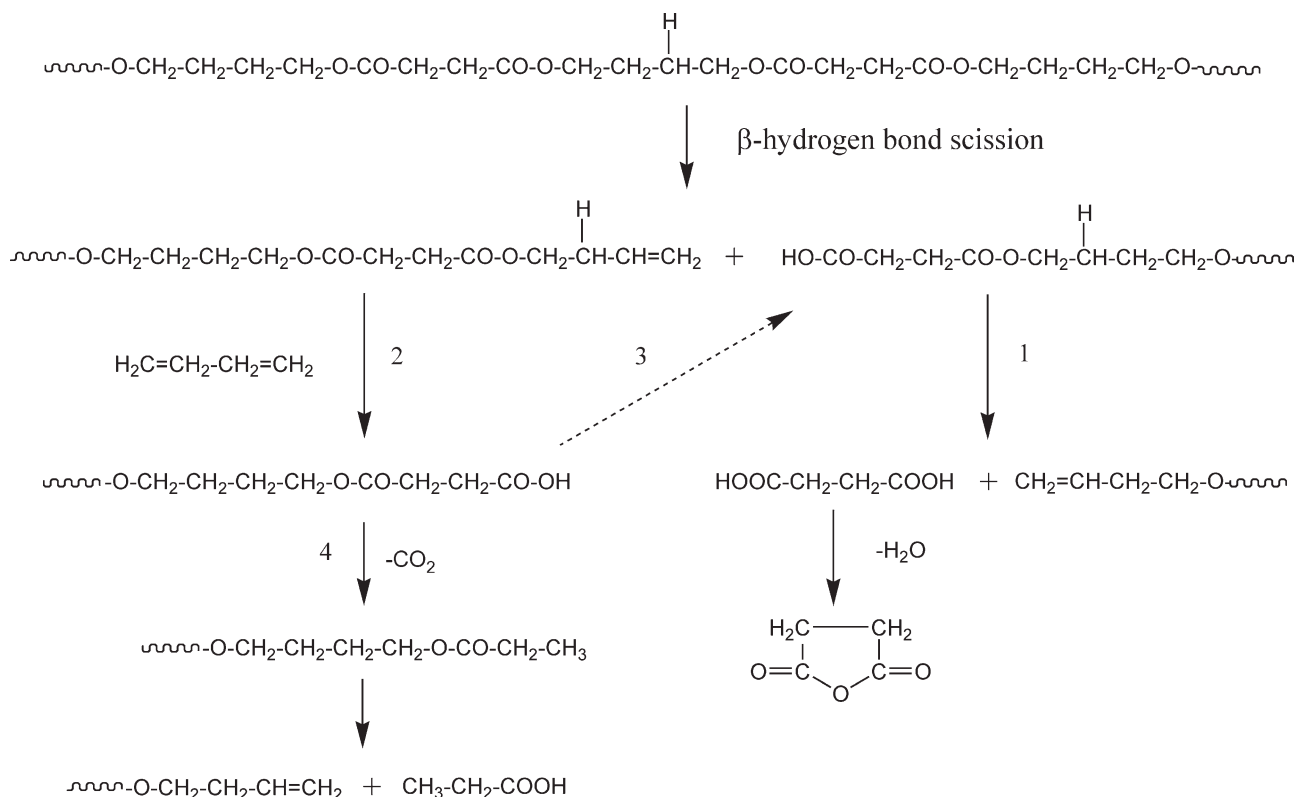
polymer chain, 1,4-butadiene and carboxylic acid-terminated chains are produced (Path 2). Then, the carboxylic acid-terminated chains may decompose to yield anhydride via Path (3 and) 1 in Scheme 2, or eliminate carbon dioxide (CO$_2$) to form acetate, which, in turn, yield an acid molecule (Path 4). In this study, PBSu and PBSu-rich PBPSu copolyesters underwent the same thermal decomposition mechanisms, according to the FTIR spectra.

Thermal degradation kinetics

In Figure 2, the TGA curves monotonously decreased with temperature and there is no divergence from the peak regularity in each DTG curve. This DTG result differs from that of Bikiaris et al. This discrepancy may arise from the difference in the molecular weight: 3.0×10^4 versus 6,820 g/mol (M_n).[26] Figure S1 (Supporting information) presents two curves deconvoluted from each DTG curve. It can be assumed that these three polyesters proceeded in a two-stage degradation mechanism. The peak of the first stage locates at $\sim$ 360°C. This first stage is relatively easy because it has relatively low activation energy (described later in Table IV). Table III presents the temperatures at 2 and 98 wt % mass loss, and the temperature of maximal loss rate for these three polyesters, heated at four rates. PBPSu 95/5 has a lower decomposition temperature than PBSu, because of the incorporation of minor amounts of PS units into PBSu. However, the degradation temperatures of PBPSu 90/10 are close to those of PBSu, perhaps because PBPSu 90/10 has a higher molecular weight. The decomposition temperatures of these three aliphatic polyesters were comparable with those of aromatic polyesters, such as poly(trimethylene terephthalate)[38] ($\sim$ 410°C) and poly(butylene terephthalate)[39] ($\sim$ 424°C), since they decomposed first at the weak O—CH$_2$ bonds of polyester chains.

Scheme 1 Cyclic intramolecular degradation mechanism.

wwww-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-CO-CH$_2$-CH$_2$-CO-O-CH$_2$-CH$_2$-CH-CH$_2$-O-CO-CH$_2$-CH$_2$-CO-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-wwww

β-hydrogen bond scission

wwww-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-CO-CH$_2$-CH$_2$-CO-O-CH$_2$-CH-CH=CH$_2$ +   HO-CO-CH$_2$-CH$_2$-CO-O-CH$_2$-CH-CH$_2$-CH$_2$-O-wwww

H$_2$C=CH$_2$-CH$_2$=CH$_2$ 2   3   1

wwww-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-CO-CH$_2$-CH$_2$-CO-OH   HOOC-CH$_2$-CH$_2$-COOH + CH$_2$=CH-CH$_2$-CH$_2$-O-wwww

4   -CO$_2$ -H$_2$O

wwww-O-CH$_2$-CH$_2$-CH$_2$-CH$_2$-O-CO-CH$_2$-CH$_3$ H$_2$C——CH$_2$ / O=C, C=O, O

wwww-O-CH$_2$-CH$_2$-CH=CH$_2$ + CH$_3$-CH$_2$-COOH

Scheme 2 Thermal degradation routes for PBPSu copolyesters and PBSu.

A general kinetic model is as follows:

$$\frac{d\alpha}{dt} = f(\alpha)K(T) \qquad (1)$$

where α is the normalized mass loss, defined as:

$$\alpha = \frac{m_t - m_i}{m_i - m_f} \qquad (2)$$

Here, m_t is the mass at time t, m_i the initial mass, and m_f the final mass of the sample; $d\alpha/dt$ denotes the mass loss rate, and $f(\alpha)$ represents a temperature-independent function of the mass loss. $K(T)$ is a function of temperature of the Arrhenius type:

$$K(T) = Ae^{-E/RT} \qquad (3)$$

where A, E, T, and R are the pre-exponential factor, activation energy (J/mol), temperature (K), and gas

constant (8.314 J/mol K), respectively. Hence, the thermal degradation kinetics is expressed as follows;

$$\frac{d\alpha}{dt} = f(\alpha)Ae^{-E/RT} \qquad (4)$$

For nonisothermal measurements at a constant heating rate ($\varphi = dT/dt$), eq. (4) becomes

$$\varphi\frac{d\alpha}{dT} = f(\alpha)Ae^{-E/RT} \qquad (5)$$

Many researchers have proposed several approaches for evaluating kinetic parameters during thermal degradation. In this study, the model-free methods, Friedman and Ozawa equations, were used to determine the kinetic parameters. The Friedman method derives the following from eq. (4).

$$\ln(d\alpha/dt) = \ln(f(\alpha)) + \ln A - E/RT \qquad (6)$$

TABLE III
Degradation Temperatures (°C) of Polyesters at Different Heating Rates (ϕ) and Mass Losses

Sample code	$\phi = 1°C/min$			$\phi = 3°C/min$			$\phi = 5°C/min$			$\phi = 10°C/min$		
	2%	Peak[a]	98%	2%	Peak[a]	98%	2%	Peak[a]	98%	2%	Peak[a]	98%
PBSu	252	359	383	280	381	408	290	391	414	302	404	428
PBPSu 95/5	222	356	371	266	379	405	270	388	407	290	397	426
PBPSu 90/10	256	358	380	278	379	406	290	390	412	304	403	432

[a] The maximum decomposition rate during thermal heating.
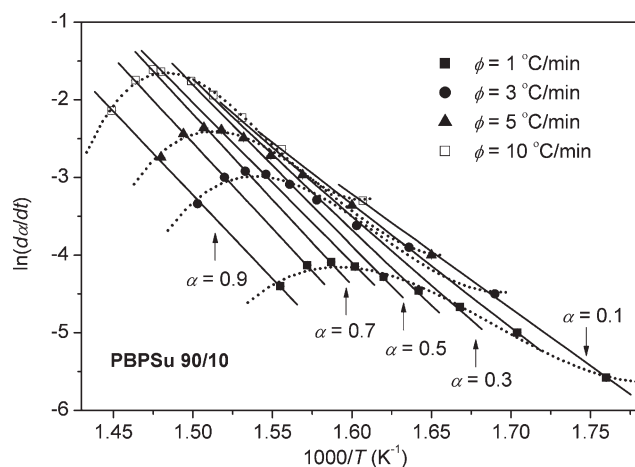
Figure 7 Friedman plots at different mass losses.

Figure 8 Ozawa plots at different mass losses.

Plotting $\ln(d\alpha/dt)$ against $1/T$ directly yields the value of $-E/R$ for a given α, heated at four rates. E is evaluated over a wide range of α in an interval of 0.1. All of these plots are linear for PBPSu 90/10, as shown in Figure 7. PBSu and PBPSu 95/5 yielded similar results. Table IV presents the E values of these three polyesters at various isomass losses. Generally, the E value increases with the mass loss, but E is remarkably small at low mass loss ($\alpha \leq 0.3$). The values of E are distributed between 160 and 190 kJ/mol at high mass loss ($\alpha > 0.3$).

The Ozawa method measures temperatures that correspond to fixed values of α determined experimentally at four heating rates. Therefore, the thermal degradation kinetics can be transformed from eq. (5) to eq. (7),

$$\ln(\varphi) = \ln\left[\frac{Af(\alpha)}{d\alpha/dt}\right] - \frac{E}{RT} \qquad (7)$$

The E value can be obtained from a plot of $\ln(\varphi)$ versus $1/T$ for a fixed α. Figure 8 fits straight lines to the data for PBPSu 90/10, described by the Ozawa equation. The E values of these three polyesters are comparable, as shown in Table IV. The random incorporation of minor PS units into PBSu did not markedly affect their thermal resistance because
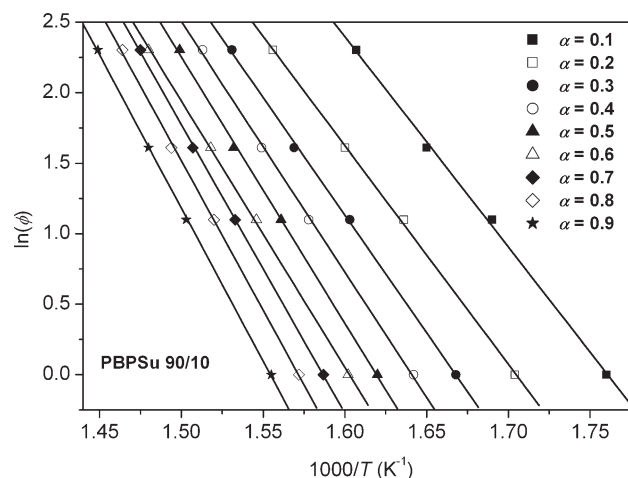
these three polyesters decomposed firstly at the weak O—CH$_2$ bonds.

To elucidate the thermal degradation mechanism, a suitable $f(\alpha)$ function is obtained by fitting theory to the experimental results. $f(\alpha)$ was estimated using several methods, which were based on geometric factors, diffusion, or both.[40] The model-free method is convenient for determining the mechanism, because it does not depend on *a priori* assumptions of a kinetic model. The Friedman equation is commonly used to obtain the conversion function $f(\alpha)$. In the case of the nth-order reaction mechanism, $f(\alpha)$ is defined as $(1 - \alpha)^n$. Figure 9 presents the fitted $f(\alpha) = (1 - \alpha)^n$ as dashed–dotted lines for PBPSu 90/10. The fitted curves are close to the experimental data for mass losses of over 30 wt %, but they diverge at lower mass losses, especially at low heating rates. Similar results were obtained for PBSu and PBPSu 95/5. The fitted values, obtained at four heating rates from 1 to 10°C/min, are averaged and presented in columns 2–4 in Table V. The activation energy (E), pre-exponential factor ($\ln A$) and exponent value (n) are similar across all three polyesters, indicating that incorporating minor PS units into PBSu does not affect its thermal stability, but does markedly change its crystallization behavior.[21] The exponent (n), 0.98, is very close to unity, indicating a

TABLE IV
Activation Energies of the Polyesters at Various Mass Losses Using Friedman[27] and Ozawa[28] Methods

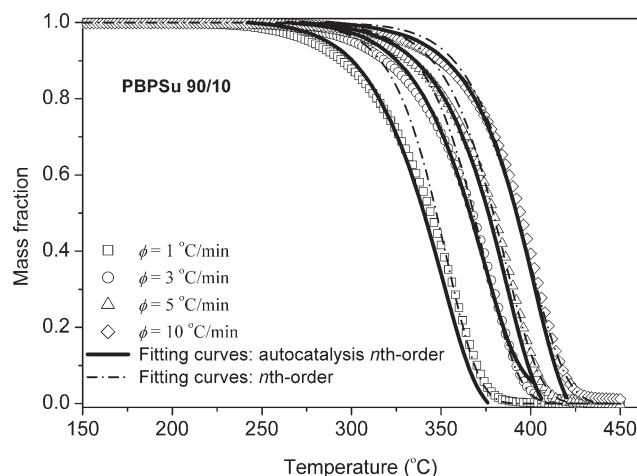| Sample code	Model	Mass loss (α)								
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
PBSu	Friedman method (kJ/mol)	128	141	151	167	176	175	178	182	187
PBPSu 95/5		114	138	160	171	174	176	175	174	157
PBPSu 90/10		123	132	148	161	173	172	183	183	179
PBSu	Ozawa method (kJ/mol)	126	138	143	150	160	163	170	177	180
PBPSu 95/5		115	128	139	152	160	166	171	177	177
PBPSu 90/10		124	129	139	148	157	157	170	176	180

Figure 9 Experimental data and fitted TGA curves for PBPSu 90/10 using the mass loss functions of $f(\alpha) = (1 - \alpha)^n$ and $f(\alpha) = \alpha^m(1 - \alpha)^n$.

first-order thermal degradation reaction. The pre-exponential factor ($\ln A$) is 30.5 $\min^{-1}$. The activation energy obtained by this model fitting method is $\sim$ 174 kJ/mol, which is close to the average value estimated using the model-free method based on the Friedman equation for mass loss values (α) of over 0.3 (Table IV).

Clearly, $f(\alpha) = (1 - \alpha)^n$ must be modified to improve the fitting curves. The conversion function $f(\alpha) = \alpha^m(1 - \alpha)^n$ was adopted to plot the fitting curves according to the mechanism of autocatalysis nth-order.[41] The fitting between experimental and theoretical data was close at all mass losses period during thermal degradation, as revealed by the solid lines in Figure 9. The last three columns in Table V present the fitting values, which for PBPSu 90/10, are $m = 1.20$, $n = 0.75$, and $\ln A = 31.6$ ($\min^{-1}$), at an E value of 174.1 kJ/mol. This result reveals that the un-degraded mass $(1 - \alpha)$ dominates the degradation when the value of α is less than 0.58. PBSu and PBPSu 95/5 exhibited the same phenomenon. In this study, model-free methods were effective for elucidating the activation energy of degradation in each period of mass loss, while the model-fitting method yielded not only the activation energy, but

TABLE VI
Life-Time Parameters (t_f in h) for Polyesters under Nitrogen at Various Temperatures

Temperature (°C)	PBSu	PBPSu 95/5	PBPSu 90/10
150	2.05×10^5	1.13×10^5	1.73×10^5
200	1.07×10^3	6.28×10^2	9.18×10^2
250	1.52×10^1	9.38	1.33×10^1
300	4.55×10^{-1}	2.92×10^{-1}	4.00×10^{-1}
350	2.38×10^{-2}	1.58×10^{-2}	2.12×10^{-2}
400	2.00×10^{-3}	1.33×10^{-3}	1.67×10^{-3}

also the mass loss mechanism and the pre-exponential factor.

Life-time and failure temperature

Estimating the life-time and failure temperature of a polymer material from the thermal degradation kinetic parameters is useful, as is predicting aging for quality control. The activation energy is used to calculate the thermal endurance and to estimate the life-time (t_f) of the polymer at a given temperature. The time-to-failure of a polymer structure at a certain temperature has been defined as the time taken for the mass of the sample to decline to 95% of its original value.[23] Integrating eq. (4) yields,

$$t_f = [0.95^{1-n} - 1/(A(n - 1))]e^{E/RT}, \quad n \neq 1 \quad (8)$$

The value of t_f can be evaluated by assuming $f(\alpha) = (1 - \alpha)^n$ according to ASTM E1461 and E1877.[29,42] Table VI presents the values of t_f in unit of h for PBSu and PBPSu copolyesters, calculated using the values of the kinetic parameters (A and n) in Table V and eq. (8). The t_f values of these polyesters declined as the temperature increased. These values also reveal that the life-time of PBSu is slightly longer than that of PBPSu 90/10, which, in turn, is longer than that of PBPSu 95/5. These results follow the same trend as the degradation temperatures in Table III, which were determined experimentally.

The failure temperature (T_f) is the temperature at which a material fails after a specified time. In the absence of reference data, a time-to-failure of 60,000 h was arbitrarily chosen to estimate T_f.[42] Assuming

TABLE V
Kinetic Parameters of Thermal Degradation for the Polyesters Using Two Different Conversion Functions According to the Friedman Method[27]

Sample code	nth-order mechanism[a]			Autocatalysis nth-order mechanism[a,b]		
	E (kJ/mol)	$\ln A$ ($\min^{-1}$)	n	$\ln A$ ($\min^{-1}$)	m	n
PBSu	174.8 ± 0.5	30.45 ± 0.00	0.98	31.66 ± 0.94	1.25 ± 0.04	0.73 ± 0.04
PBPSu 95/5	173.5 ± 1.0	30.47 ± 0.01	0.98	31.57 ± 0.81	1.25 ± 0.04	0.72 ± 0.04
PBPSu 90/10	174.1 ± 0.5	30.45 ± 0.03	0.98	31.56 ± 0.94	1.20 ± 0.01	0.75 ± 0.06

[a] Averaged value for the heating rates from 1 to 10°C/min.
[b] Use the E value of the nth-order mechanism.

$f(\alpha) = (1 - \alpha)^n$ and a 5% mass loss, T_f can be evaluated as follows;

$$T_f = \frac{E}{R \ln[t_f/[0.95^{1-n} - 1]/A(n - 1)]}, \quad n \neq 1 \quad (9)$$

The values of T_f of, PBSu, PBPSu 95/5, and PBPSu 90/10 were 160.7, 155.5, and 159.3°C, respectively. These failure temperatures are reasonable, based on a comparison of life-times at 150°C, presented in the first row of Table VI. Therefore, the values of t_f and T_f are convenient for predicting the aging of polymers, and t_f provides, even more usefully, the service times at different degradation temperatures.

CONCLUSIONS

The compositions of PBPSu 95/5 and PBPSu 90/10 were determined as having 7.3 and 10.5 mol % PS units, respectively, from the split ^{13}C-NMR spectra of the carbonyl carbons. The distribution of minor PS units in these two copolymers was random, as revealed by a randomness value of about 1.1 and a single T_g. The evolved gases from TGA were identified to be anhydride, olefin, esters and carbon dioxide using an online FTIR. The DTG traces reached a maximum at ~ 390°C, and the absorbance intensity of the decomposition products also reached a maximum at 390°C, and then fell smoothly as the temperature increased further. Additionally, the absorption bands of the anhydrides were stronger than those of the other degradation products. Possibly, the β-hydrogen bond scission of the ester groups, along with the breaking of the weak O—CH$_2$ bond, occurred first via a cyclization degradation mechanism; then the succinate group at the polymer chain ends decomposed by the cyclization degradation mechanism again, to yield succinic acid, which dehydrated further to form anhydrides. All of these polyesters yielded similar results. For heating rates from 1 to 10°C/min, the degradation temperatures at 2 and 98 wt % mass loss, and at the maximal loss rate are lower for PBPSu 95/5, while, two model-fitting methods yielded similar activation energy, mass loss mechanism and pre-exponential factor for these polyesters. Based on these results, PBSu, PBPSu 95/5, and PBPSu 90/10 can be assumed to have degraded by the same decomposition mechanisms. Hence, the random incorporation of minor PS units into PBSu did not markedly affect their thermal resistance.

The model-free methods of Friedman and Ozawa were used to estimate the activation energy of thermal degradation. The results reveal that the activation energy increased with the mass loss, and was relatively small at low mass loss ($\alpha \leq 0.3$). At a mass loss of higher than 0.3 ($\alpha > 0.3$), the activation energy was between 150 and 190 kJ/mol. The activation energies of these three polyesters were comparable. Finally, the activation energy was used to calculate the thermal endurance and to estimate the life-time of each polymer at a particular temperature. The estimated life-times of the three polyesters follow the same trend as the degradation temperatures, which were determined from the TGA experiments. The failure temperatures associated with 5% mass loss and an endurance time of 60,000 h were 160.7, 155.5, and 159.3°C, for PBSu, PBPSu 95/5, and PBPSu 90/10, respectively. These failure temperatures are reasonable, by comparison with the life-times at 150°C.

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