

Hydrolytic degradation of biobased poly(butylene succinate-co-furandicarboxylate) and poly(butylene adipate-co-furandicarboxylate) copolyesters under mild conditions

Shuangbao Peng,¹ BinShuang Wu,¹ Linbo Wu,¹ Bo-Geng Li,¹ Philippe Dubois^{1,2,3}

¹State Key Laboratory of Chemical Engineering at ZJU, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

²Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials and Polymers (CIRMAP) University of Mons, 7000, Belgium

³Materials Research and Technology Department (MRT), Luxembourg Institute of Science and Technology (LIST), Esch-sur-Alzette 4362, Luxembourg

Correspondence to: L. Wu (E-mail: wulinbo@zju.edu.cn) and P. Dubois (E-mail: philippe.dubois@list.lu)

ABSTRACT: It is indispensable to investigate hydrolytic degradation behavior to develop novel (bio)degradable polyesters. Biobased and biodegradable copolyesters poly(butylene adipate-co-butylene furandicarboxylate) (PBAF) and poly(butylene succinate-co-butylene furandicarboxylate) (PBSF) with BF molar fraction (ϕ_{BF}) between 40 and 60% were synthesized in this study. The hydrolytic degradation of film samples was conducted in a pH 7.0 PBS buffer solution at 25 °C. Slight mass loss (1–2%) but significant decrease in intrinsic viscosity (35–44%) was observed after 22 weeks. The apparent hydrolytic degradation rate decreased with increasing ϕ_{BF} and initial crystallinity. Meanwhile, PBAFs degraded slightly faster than PBSFs with the same composition. The ϕ_{BF} and crystallinity increased slowly with degradation time, suggesting the aliphatic moiety and the amorphous region are more susceptible to hydrolysis. And high enough tensile properties were retained after hydrolysis degradation, indicating PBAF and PBSF copolyesters are hydrolytically degradable, with tunable hydrolytic degradation rate and good balance between hydrolytic degradability and durability. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2017**, *134*, 44674.

KEYWORDS: biodegradable; biopolymers and renewable polymers; degradation; polyesters

Received 20 May 2016; accepted 14 November 2016

DOI: 10.1002/app.44674

INTRODUCTION

Due to increasing environmental awareness and depletion of fossil oil reserves, biodegradable polymers derived from renewable biomass have attracted more and more attention from scientists in the last decades.^{1–6} Production and applications of biobased and biodegradable polymers are effective ways to realize the life-to-death carbon-neutral circle^{7,8} and to solve the problem of white pollution.⁹ So, biobased and biodegradable polymers are deemed as real green and sustainable materials from cradle to grave. Polylactic acid (PLA) is the most representative biobased and (bio)degradable polymers. PLA is produced from lactic acid obtained by fermentation of (poly)saccharides derived from corn, rice, sugar beets. PLA is aliphatic polyester known to be degraded through hydrolysis of the ester functions. It also degrades into industrial compost conditions. PLA has been successfully commercialized in large scale and it is more and more used into a variety of fields from disposable to

durable items.^{10,11} However, some inherent shortcomings like brittleness, low heat resistance limit some of its applications.^{12,13} Research and development of new biobased and biodegradable polymers with satisfactory performance are still very desirable.

2,5-Furandicarboxylic acid (FDCA) is one of the 12 top value-added platform chemicals derived from biomass.¹⁴ It is a very important diacid monomer for synthesizing new biobased polymers, especially polyesters and copolyesters.^{15–24} Synthesis, thermo-mechanical properties, enzymatic and compost degradation of FDCA-based copolyesters such as poly(butylene adipate-co-furandicarboxylate) (PBAF) and poly(butylene succinate-co-furandicarboxylate) (PBSF) have been reported in recent years.^{18–21} As FDCA has a molecular structure similar to terephthalic acid (TPA),^{15,25} these biobased copolyesters have thermo-mechanical properties comparable to their petroleum-issued (TPA-based) counterparts, namely, poly(butylene adipate-co-terephthalate) (PBAT) and poly(butylene-co-succinate

terephthalate) (PBST).^{18–21} In fact, PBAT is biodegradable only within a given composition^{26–28} and has been commercialized at a much lower scale when compared to PLA.²⁹ Importantly, recent research proved that PBAFs with an aromatic unit content maintained below 50% are enzymatically degradable in the presence of lipase from porcine pancreas¹⁹ and PBSFs with an aromatic unit content limited to <20% possess good compost biodegradability as well.²¹ Therefore, PBAF and PBSF copolyesters appear to be promising biobased and biodegradable polymers with attractive performance and potentially wide applications.

For biodegradable (co)polyesters, hydrolytic degradation usually plays a key role in a variety of biodegradation manners including enzymatic or compost degradation.^{9,30} Hydrolytic degradation also happens unavoidably in practical use in storage and applications due to absorption of moisture from the air, leading to deterioration of mechanical properties.³¹ So, knowledge of hydrolytic degradation is helpful not only to understand the (bio)degradability but also to predict and tune the lifetime of the materials. Therefore, it is indispensable to investigate hydrolytic degradation behaviors to develop novel biobased and biodegradable copolyesters.

Hydrolytic degradation behaviors of some FDCA-based copolyesters have been reported.^{22–24} Matos *et al.*²² and Wu *et al.*²³ studied the hydrolytic degradation of poly(ethylene furandicarboxylate)-*co*-poly(lactic acid) in a neutral PBS buffer solution and found that the degraded rate is related to copolymer composition. Hbaieb *et al.*²⁴ reported that there was no obvious weight loss of poly(1,3-propylene adipate-*co*-furandicarboxylate) and poly(1,3-propylene succinate-*co*-furandicarboxylate) when hydrolyzed in an acidic PBS buffer solution for 4 weeks. However, the hydrolytic degradation behaviors of PBAFs and PBSFs have not been reported so far, and the effect of hydrolytic degradation on mechanical properties of FDCA-based copolyesters was not reported yet. So, further studies are still needed to understand the hydrolytic degradation of FDCA-based copolyesters.

In our previous studies, we reported the synthesis and thermo-mechanical properties of PBSF and PBAF copolyesters.^{18,20} In this study, we aim to investigate their hydrolytic degradation behaviors. High molecular weight semicrystalline PBAFs and PBSFs with BF unit molar fraction 40–60% were synthesized and characterized with GPC, ¹H NMR and DSC, and the hydrolytic degradation was conducted under mild conditions (25 °C, PBS buffer solution with pH 7.0) for a period as long as 22 weeks. The mass loss and change of molecular weight, composition, thermal transition, and mechanical properties with degradation time were tracked. The results indicate that these copolyesters are hydrolytic degradable and interestingly the hydrolysis rate can be tuned by copolymer composition and crystallinity. However, they retain sufficient mechanical properties after hydrolysis for 22 weeks, suggesting good balance between hydrolytic degradability and durability.

EXPERIMENTAL

Materials

Succinic acid (SA, Anhui Sanxin Chem, China), adipic acid (AA, Shanghai Dibo Chem, China), 1,4-butanediol (BDO,

Sinopec Yizheng Chem Fibre, China), and tetrabutyl titanate (TBT, ≥99.0%, Aladdin) were all used as received. FDCA (98%, Satar Chem., China) was purified by a modified reflux purification method as described previously.²⁰ A phosphate buffer solution (PBS, pH 7.0) was prepared from Na₂HPO₄ and NaH₂PO₄ (Sinopham, China). The solution was sterilized at 100 °C for 3 h and then used for hydrolytic experiments.

Synthesis of PBSFs and PBAFs

PBSF and PBAF copolyesters with butylene furandicarboxylate (BF) unit content ranging from 40 to 60 mol % were synthesized from SA (or AA), FDCA, and BDO via a two-step melt polycondensation procedure. In brief, the three monomers (FDCA representing 40–60 mol % of the diacid feed, diol/diacid molar ratio 2:1) were added into a 500 mL four-necked round flask under mechanical stirring and N₂ inlet and then heated to the esterification temperature (170–190 °C for PBSFs, 200–220 °C for PBAFs). TBT (0.1 mol % with respect to the diacid) was added and the esterification reaction was conducted for 3–4 h up to over 98% esterification degree. Finally, the polycondensation reaction was performed under vacuum (50–300 Pa) at 230 °C for 1 h and 240 °C for 2–5 h until Weissenberg effect emerged. The products were vacuum-dried at 40 °C for more than 24 h and stored in a desiccator before characterization and testing. The copolyesters were named as PBSF ϕ_F or PBAF ϕ_F where ϕ_F is the molar ratio of FDCA in the diacid feed.

Film Preparation and Hydrolytic Degradation

PBSF or PBAF was dissolved in chloroform to form a 4 g/dL solution. The solution was cast into a polytetrafluoroethylene mould and then volatilized slowly at room temperature. The so-formed film was further dried in a vacuum oven at 40 °C to remove residual solvent. Finally, a film with thickness of 100 ± 10 μm was obtained and cut into dumbbell-shaped specimens using a punch machine. The specimens were stored in a desiccator for about one month before starting the hydrolysis experiments. As PBSF40 was too sticky to get a good film with stable shape and uniform thickness, erucamid (0.5 wt % of PBSF40) was added to improve crystallization and demoulding. Thus, obtained sample was name as PBSF40e.

For each sample, 15*6 film specimens were placed in 15 Schott bottles (50 mL) containing 40 mL 0.2M PBS buffer solution. All the bottles were placed in a shaking table at 25 °C with an agitation frequency of 180 rpm. The hydrolytic experiments lasted for 22 weeks. The PBS solution was monitored by pH meter and replaced with fresh PBS every week to keep constant pH. Every 1–2 week(s), 6 specimens in one bottle of each sample were taken out. The specimens were washed by deionized water, dried at 40 °C in a vacuum oven for 48 h and stored in a desiccator before characterization.

Characterization

The copolymer composition of PBSFs and PBAFs was determined by ¹H NMR. The ¹H NMR spectra were recorded with an AC-80 spectroscopy (400 MHz, BRUKER). Deuterated chloroform was used as solvent and tetramethylsilane as internal reference. The molecular weight and its distribution of original PBAF and PBSF samples were measured at 30 °C by a gel permeation chromatography (GPC, Waters 1525/2414) equipped

Table I. Chain Characteristics and Thermo-mechanical Properties of PBAF and PBSF Copolyesters Used for Hydrolytic Experiments

Sample	M_w (g/mol)	PDI	$[\eta]$ (dL/g)	ϕ_{BF} (mol %)	$L_{n,BA(S)}$	$L_{n,BF}$	R
PBAF40	99 000	1.91	1.46	38.4	2.29	1.59	1.07
PBAF45	128 500	1.87	1.80	44.9	1.97	1.76	1.07
PBAF50	109 300	2.17	1.37	48.0	1.83	2.01	1.04
PBAF55	/	/	1.15	53.6	1.71	2.17	1.05
PBAF60	110 300	2.18	1.45	58.3	1.52	2.53	1.05
PBSF40	162 100	2.07	1.43	39.8	2.32	1.66	1.03
PBSF45	165 400	2.00	1.53	43.2	2.13	1.84	1.01
PBSF50	167 200	1.95	1.34	49.1	2.02	2.20	0.95
PBSF55	162 800	2.05	1.36	53.8	1.81	2.34	0.98
PBSF60	/	/	1.12	58.8	1.63	2.56	1.01

with a differential refractive index detector (DRI, Water 2414) and an UV-vis light detector (Water 2487). Chloroform was used as eluent. The concentration of sample solution was about 3 mg/mL, and the eluent flow rate was 1.0 mL/min. Polystyrene standards were used for calibration. The intrinsic viscosity was measured at 25 °C by an automatic viscosity tester (ZONWON IVS300, China) equipped with a Ubbelohde viscometer with a diameter of 0.88 mm. Mixture of phenol and tetrachloroethane (3/2 w/w) was used as solvent. The solution concentration was 5 mg/mL. The intrinsic viscosity was calculated via Billmeyer empirical formula $[\eta] = (\eta_{sp} + 3\ln\eta_r)/4C$.³² The thermal transition was recorded with a differential scanning calorimetry (DSC) on a Q200 thermal analyzer (TA Instruments). First heating scans of the as-prepared (original) and the as-degraded samples were recorded from room temperature to 150 °C at a heating rate of 10 °C/min. The tensile properties were measured with a Zwick Roell testing machine according to ASTM D638. The crosshead speed was 100 mm/min. For each sample, at least five specimens were tested in parallel.

RESULTS AND DISCUSSION

Characterization of Copolyesters and Films

PBAF and PBSF copolyesters with BF unit content of 40–60 mol % were synthesized from AA or SA, FA, and BDO by a two-step melt polycondensation procedure. The chain structures were characterized with GPC and ¹H NMR and the results are summarized in Table I. The weight average molecular weights (M_w) of the copolyesters are all above 95,000 g/mol and the polydispersity (PDI) is around 2.0. The intrinsic viscosity measured in phenol/tetrachloroethane (3/2 w/w) mixture solvent at 25 °C was over 1.1 dL/g. So, high molecular weight copolyesters were successfully synthesized.

The composition or molar fraction of BF repeat unit (ϕ_{BF}), number-average sequence length of repeat units ($L_{n,BA}$ or $L_{n,BS}$, $L_{n,BF}$) and randomness degree (R) of the copolyesters were calculated from ¹H NMR spectra as previously reported.^{18,20} The composition agrees well with the molar percentage of FDCA in diacid feed (ϕ_F). The randomness degrees are all about 1.0, indicating the copolyesters are random copolymers. The $L_{n,BF}$

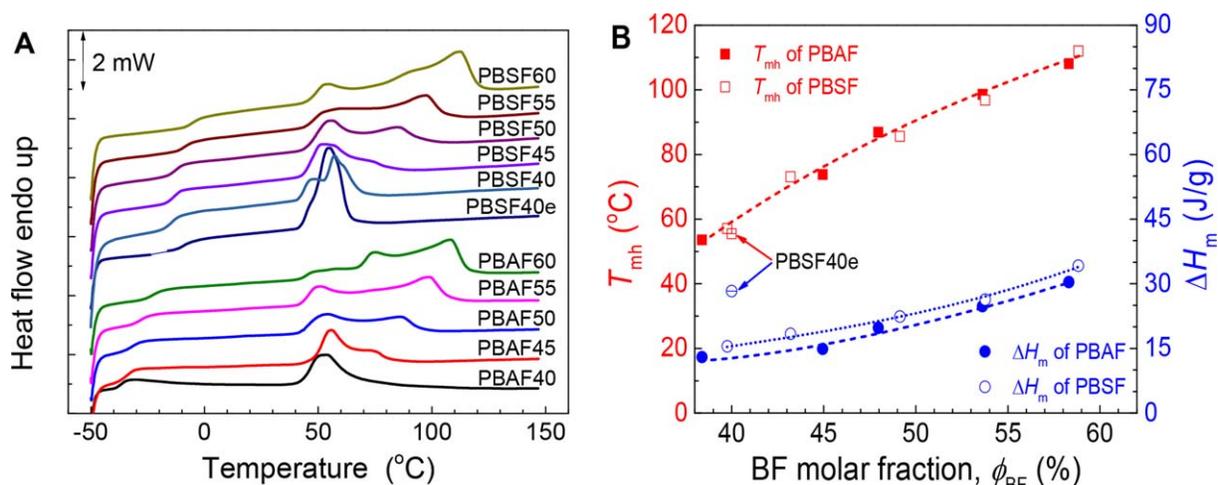


Figure 1. (A) DSC curves (first heating scan) and (B) composition dependence of melting temperature (T_{mh}) of high melt peak and enthalpy (ΔH_m) of PBAF and PBSF copolyesters. (PBSF40e is a film sample made of PBSF40 and 0.5 wt % erucamid). [Color figure can be viewed at wileyonlinelibrary.com]

Table II. Thermal Transition and Tensile Properties of PBAF and PBSF Films Used for Hydrolytic Experiments

Samples	T_m (°C)	ΔH_m (J/g)	E (Mpa)	σ_b (Mpa)	ϵ_b (%)
PBAF40	53.6	13.0	34 ± 1	28 ± 1	940 ± 70
PBAF45	73.8	14.9	47 ± 3	28 ± 1	896 ± 46
PBAF50	86.9	19.8	73 ± 2	35 ± 1	943 ± 34
PBAF55	98.6	24.8	117 ± 1	26 ± 2	800 ± 69
PBAF60	108.1	30.4	185 ± 6	43 ± 4	798 ± 32
PBSF40	57.1	15.5	/	/	/
PBSF40e ^a	55.5	28.3	143 ± 1	51 ± 6	782 ± 41
PBSF45	73.1	18.4	64 ± 1	56 ± 3	758 ± 17
PBSF50	85.6	22.4	99 ± 3.6	46 ± 3	758 ± 31
PBSF55	96.8	26.3	167 ± 5	49 ± 1	706 ± 22
PBSF60	112.0	34.2	300 ± 7	27 ± 1	434 ± 25

^aThe film sample PBSF40e contains 0.5 wt % erucamid.

increases from 1.6 to 2.6 with increasing ϕ_{BF} from 40 to 60%. According to Rantze *et al.*,³³ TPA-derived aliphatic-aromatic copolyesters PBAT and PBST are biodegradable when the number-average sequence length of aromatic unit is no more than 2. So, as the counterparts of PBAT and PBST, the PBAF and PBSF copolyesters having similar composition and number-average sequence length in this study may be biodegradable polymers.

Film samples with thickness of about 100 μm were prepared via solution casting and used for hydrolytic experiments. According to our previous studies, PBAFs and PBSFs with ϕ_{BF} of 40–60% did show weak crystallization in first heating scan though no clear crystallization was observed during cooling and second heating scans at 10 °C/min.^{18,20} As the crystallization will affect the hydrolysis behaviors of these copolyesters, the thermal transitions of the film samples were recorded with DSC just before hydrolysis experiments. Figure 1(A) shows the DSC first heating scans of PBAFs and PBSFs. The film samples exhibited from 1 to 3 melting peaks when heated at 10 °C/min, indicating that these copolyesters retained certain crystallizability and did crystallize during film forming and storing. The temperature of the high melting peak (T_{mh} , 55–110 °C) and the total enthalpy (ΔH_m , 13–34 J/g) increased with increasing ϕ_{BF} , see Figure 1(B) and Table II. The melting temperatures of PBAF and PBSF are almost the same at the same composition, but the melting enthalpy of PBSF is slightly higher than that of PBAF. As PBSF40 is sticky at room temperature, 0.5 wt % erucamid was added as it is usually employed as a slip agent for film processing. As expected, the addition of erucamid was helpful for film demolding. The resultant film named “PBSF40e” showed unchanged T_m but clearly higher ΔH_m suggesting that the presence of erucamid promoted the crystallization of PBSF40. This was an unexpected result and implied that erucamid might have certain nucleation or plasticization effect on PBSF40. The mechanism involved needs further study yet. The effect of such improved crystallinity on hydrolytic degradation will be discussed later.

The tensile properties were measured and summarized in Figure 2 and Table II. The modulus (E) increases and the

elongation at break (ϵ_b) decreases with ϕ_{BF} but there is not clear composition dependence of break strength (σ_b). The PBSF40e film has abnormally high E (143 MPa) because of the crystallization promotion effect of erucamid as aforementioned. The PBSF60 film has relatively lower strength and elongation at break possibly due to the relatively lower intrinsic viscosity (1.12 vs. 1.34–1.53 dL/g). In comparison with PBAF, PBSF exhibits higher modulus and strength but lower elongation at break as a result of its higher crystallizability [see Figure 1(B)] and weaker chain flexibility. When compared with our previous results,^{18,20} all the tensile properties (E , ϵ_b , ϕ_{BF}) were significantly improved, more likely due to the higher molar weight as well as different sample preparation methods (solution-casting vs. injection molding).

Hydrolytic Degradation

Hydrolytic degradation experiments were conducted in 0.2M PBS buffer solution at 25 °C for 22 weeks. The pH value of the PBS solution, the mass, intrinsic viscosity, composition, thermal transitions, and mechanical properties of the copolyesters were tracked. The pH kept almost unchanged and only 1–2% mass loss was observed after 22 weeks. However, clear variation in intrinsic viscosity, composition, thermal transitions, and mechanical properties was observed. The results are discussed as follows.

Change of Chain Length. As aliphatic-aromatic polyesters have hydrolysis-sensitive ester bonds and certain hydrophilicity, they usually absorb water and then hydrolyze by self-catalysis in random chain scission way if the polymerization degree is high enough.^{34–36} The direct consequence of hydrolysis is decrease in chain molecular weight. Hence, the intrinsic viscosity [η] was tracked to indirectly monitor the molecular weight change of the copolyesters. The results are shown in Figure 3. The value of intrinsic viscosity decreased by 40–44% and 35–39% after 22 weeks for PBAFs and PBSFs (expect PBSF60), respectively. The intrinsic viscosity of PBSF60 decreased much more slowly than the others. Only 18% decrease in [η] was observed. These results validate that the hydrolytic degradation did occur in PBS solution at room temperature.

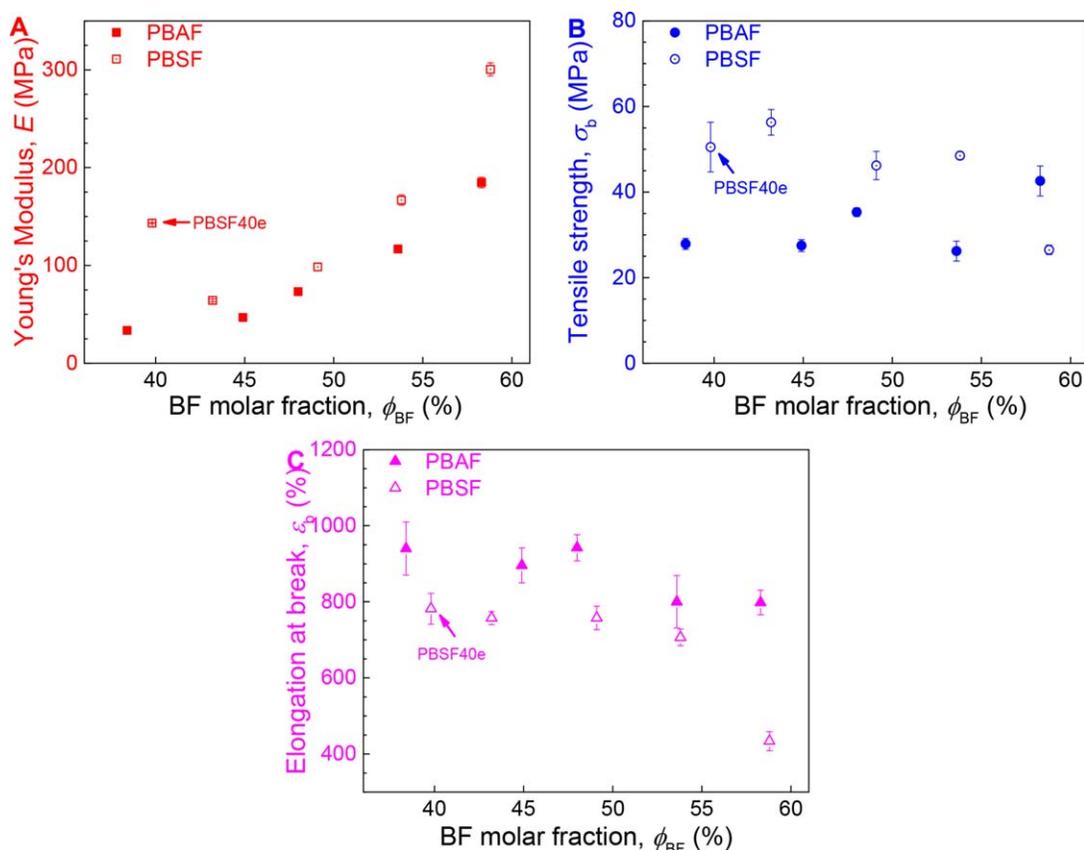


Figure 2. Composition dependence of (A) modulus, (B) strength at break, and (C) elongation at break of PBAF and PBSF copolyesters in tensile testing. (The film sample PBSF40e contains 0.5 wt % erucamid). [Color figure can be viewed at wileyonlinelibrary.com]

According to a random chain scission mechanism, an exponential decrease of molecular weight can be deduced [eq. (1)].³⁵ So, from eq. (1) and the Mark-Houwink equation ($[\eta] = KM_\alpha$), an exponential decrease of intrinsic viscosity can also be deduced [eq. (2)]. Clearly, the results of the semi-logarithmic plots $[\eta]$ versus degradation time shown in Figure 4 support such a hydrolysis mechanism. From these plots, the apparent hydrolysis rate constant (k) can be calculated. Then, the half period ($t_{1/2}$), namely, the time at which the $[\eta]$ value decreases by 50% can

be further calculated from eq. (3). These two quantities can be used to express the apparent hydrolysis rate of the materials. The results are summarized in Figure 5. It can be seen that the apparent hydrolytic degradation rate constant decreases and the half period increases with ϕ_{BF} of PBAF and PBSF copolyesters, except that PBSF40e and PBSF60 exhibit unusually low k or high $t_{1/2}$ value. Interestingly enough, the PBAF copolyesters hydrolyze slightly faster than PBSF ones with the same composition.

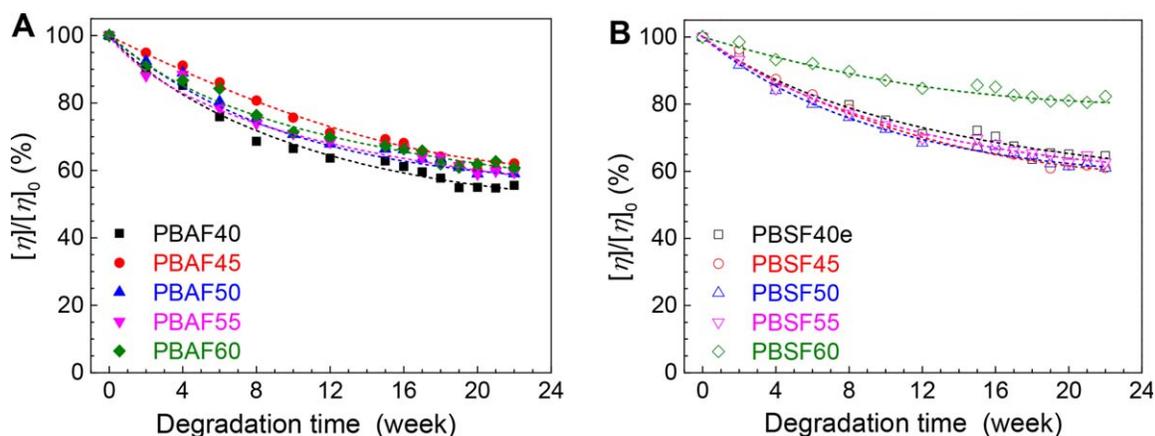


Figure 3. Change of intrinsic viscosity ratio $[\eta]/[\eta]_0$ of (A) PBAF and (B) PBSF copolyesters during hydrolytic degradation in a pH 7.0 PBS buffer solution at 25 °C for 22 weeks. [Color figure can be viewed at wileyonlinelibrary.com]

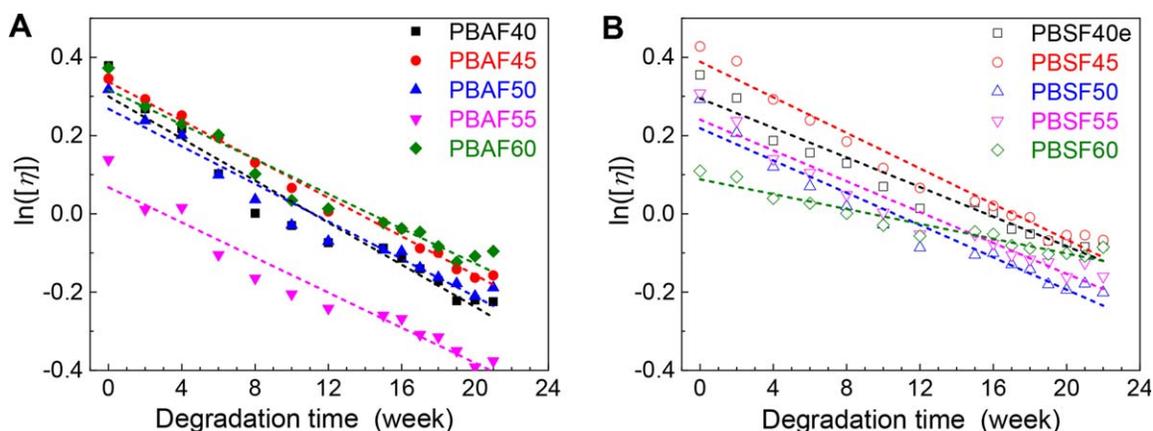


Figure 4. Change of logarithm of intrinsic viscosity $\ln([\eta])$ of (A) PBAF and (B) PBSF copolyesters during hydrolytic degradation in a pH 7.0 PBS buffer solution at 25 °C for 22 weeks. [Color figure can be viewed at wileyonlinelibrary.com]

$$\ln(M/M_0) = -k't \quad (1)$$

$$\ln([\eta]/[\eta]_0) = -k't = -k'\alpha t \quad (2)$$

$$t_{1/2} = \ln 2/k \quad (3)$$

In general, hydrophilicity of macromolecular chains and hydrolysis sensitivity of ester bonds are the two main internal factors determining the hydrolytic degradation rate of polyesters. The aromatic BF unit has weaker hydrophilicity and hydrolysis sensitivity than the aliphatic counterparts. Therefore, the hydrolysis rate slows down with increasing the molar fraction of BF unit. Besides, hydrolysis of polyester can be depressed by crystallization as crystalline region has much slower water absorption and diffusion than amorphous region. Therefore, the composition dependence of crystallization (Figure 1) also contributes to the composition dependence of hydrolysis rate. The higher crystallinity also accounts for the unusually slower hydrolysis of PBSF40e and PBSF60 than other PBSF samples. PBSF has higher crystallinity but more hydrophilic chains than PBAF as it has shorter $(\text{CH}_2)_n$ chains ($n=2$ vs. $n=4$) and higher ester bond density. These two factors will lead to opposite results in hydrolysis rate as aforementioned. Therefore, the slower hydrolysis of PBSFs than PBAFs suggests that the crystallinity plays a more significant role in influencing the hydrolytic degradability of these copolyesters.

Change of Composition. The copolyester composition was an influencing factor of hydrolysis and the same time, the hydrolysis also led to change of the composition. Figure 6 illustrates the composition change of PBAFs and PBSFs during the 22 weeks of hydrolysis. It can be seen that the molar fraction of BF increased slowly with degradation time for all copolyester samples. This result further validates that the aliphatic BS or BA unit is more susceptible to hydrolysis than the aromatic BF unit. Because of higher hydrophilicity and hydrolysis reactivity, the ester bonds in the aliphatic units are more vulnerable to be attacked by water molecules. Similar results have also been found in TPA-based aliphatic-aromatic copolyesters such as PBAT^{37,38} and PBST.³⁹ It should be noted that the composition change during the whole hydrolysis process is small ($<5\%$) and no clear dependence of composition growth rate (the slope of the lines) on the initial composition of the copolyesters was observed.

Change of Thermal Transition. The thermal transition was tracked with first heating DSC scan of the hydrolyzed samples. The samples experienced different hydrolysis periods and then same drying thermal history (40 °C, 48 h), therefore the DSC results can reflect the effect of hydrolysis thermal history. Figures 7 and 8 show the change of melting temperature (T_{mh}) of

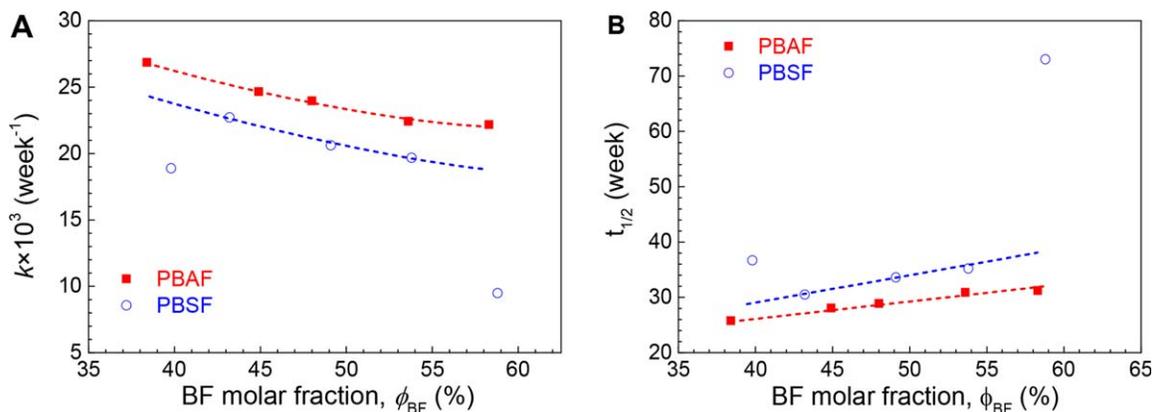


Figure 5. A: Apparent hydrolysis rate constant (k) and (B) half period ($t_{1/2}$) as a function of BF molar fraction. [Color figure can be viewed at wileyonlinelibrary.com]

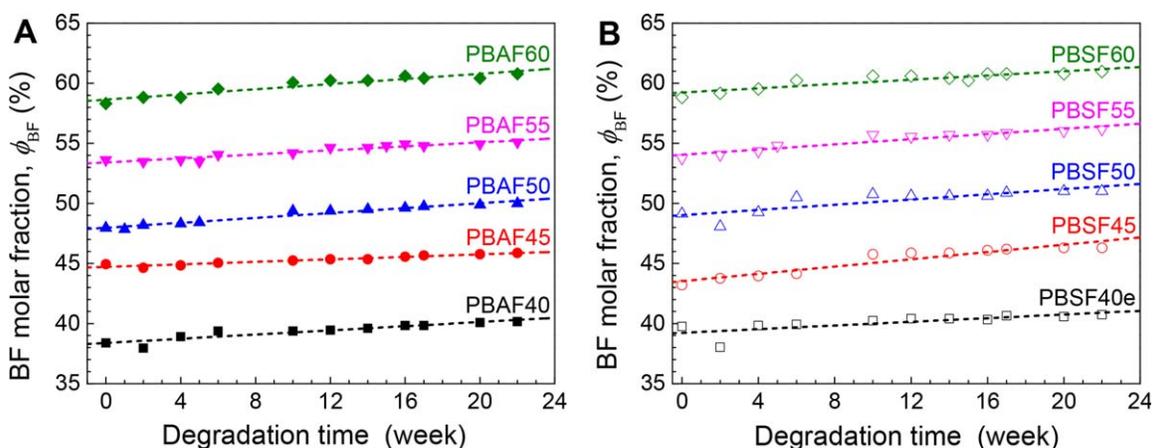


Figure 6. Change of copolyester composition (BF molar fraction, ϕ_{BF}) of (A) PBAF and (B) PBSF copolyesters during hydrolytic degradation in a pH 7.0 PBS buffer solution at 25 °C for 22 weeks. [Color figure can be viewed at wileyonlinelibrary.com]

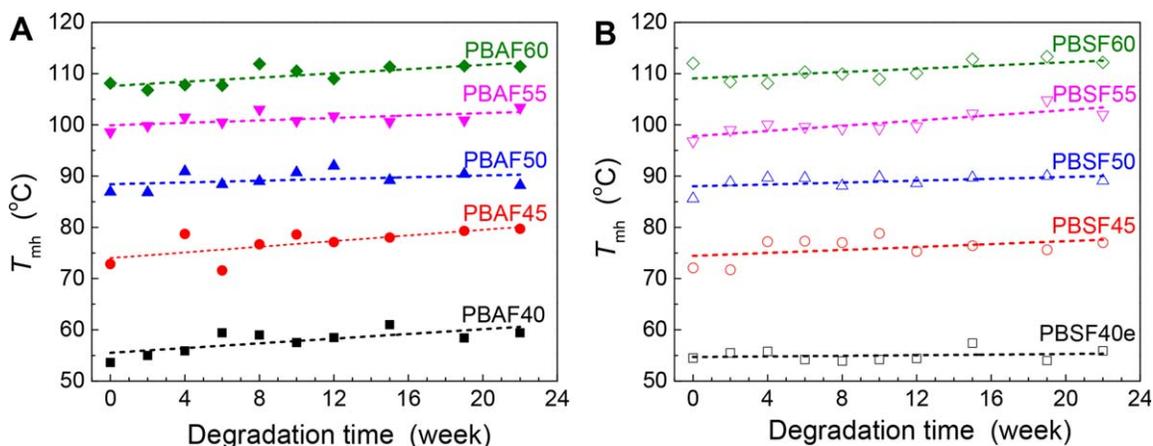


Figure 7. Change of melting temperature of (A) PBAF and (B) PBSF copolyesters during hydrolytic degradation in a pH 7.0 PBS buffer solution at 25 °C for 22 weeks. [Color figure can be viewed at wileyonlinelibrary.com]

high melt peak) and enthalpy (ΔH_m) of the hydrolyzed samples with degradation time. Increasing trend was observed in T_{mh} and ΔH_m during hydrolytic degradation though the growth of T_{mh} (1.4–6.9 °C) and T_{mh} (2.8–7.2 J/g) is not high and there is

certain data fluctuation, especially in melting enthalpy. During the hydrolytic degradation of crystalline copolyesters, further crystallization often occurred. In addition, the increase in BF unit fraction (see Figure 6) promoted the crystallization as

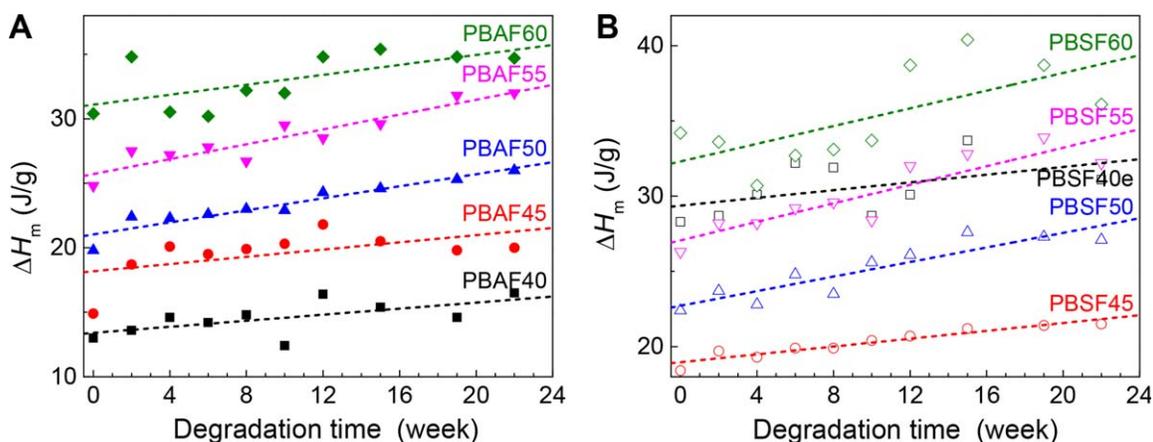


Figure 8. Change of melting enthalpy of (A) PBAF and (B) PBSF copolyesters during hydrolytic degradation in a pH 7.0 PBS buffer solution at 25 °C for 22 weeks. [Color figure can be viewed at wileyonlinelibrary.com]

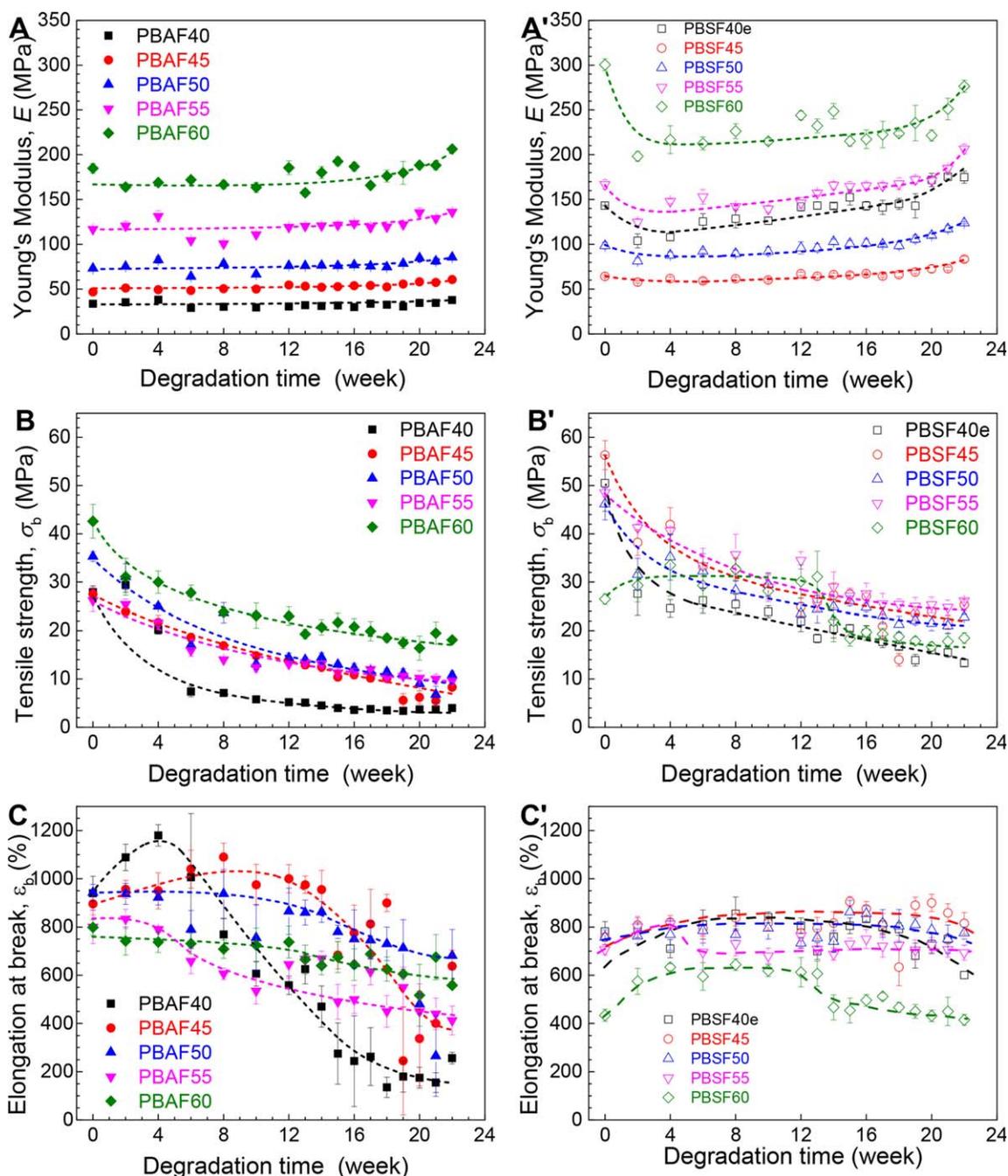


Figure 9. Change of tensile modulus (A,A'), strength (B,B') and elongation at break (C,C') of PBAF and PBSF copolyesters during hydrolytic degradation in a pH 7.0 PBS buffer solution at 25 °C for 22 weeks. [Color figure can be viewed at wileyonlinelibrary.com]

higher BF content is favorable for the crystallization. Therefore, the crystallization during hydrolysis contributed to the increase in melting temperature and enthalpy. Therefore, the PBSF40e sample which was fully crystallized with the aid of erucamid at the beginning exhibited smallest change in both T_{mh} and ΔH_m .

Change of Tensile Properties. The change of tensile modulus, strength, and elongation at break (E , σ_b , ϵ_b) of the copolyesters during hydrolytic degradation is shown in Figure 9. Despite of the data fluctuation in mechanical properties, which was often

observed in hydrolytic researches,³¹ some characteristic variation trends can be found. The modulus of PBAFs kept constant in the first 10–15 weeks and increased slightly thereafter. In comparison, the modulus of all PBSF samples decreased in the first two weeks, then increased slightly up to 18–20 weeks, and increased more rapidly thereafter. It seems that the modulus varied more for copolyesters with higher ϕ_{BF} . The initial decrease in modulus may be resulted from plasticization effect caused by water absorption, and the increase in modulus could be attributed to the increase of crystallinity during degradation.

The tensile strength decreased rapidly from the very beginning for both kinds of copolyesters except PBSF60, but the decrease slowed down gradually at the late stage. Clearly, the chain scission or decrease in molecular weight was the main reason responsible for the damping of tensile strength. Water absorption might also contribute to the initial obvious decrease in tensile strength. The elongation of PBAF40, PBAF45 increased slightly in the first 4–8 weeks and then decreased significantly. However, the elongation of PBAFs with higher ϕ_{BF} kept constant for 4–10 weeks and then decreased slowly, and the elongation of for all PBSFs except PBSF60 kept constant during the whole hydrolysis process. It is interesting that PBSF60 exhibited very different variation of tensile strength and elongation: increasing in the first 2–4 weeks, keeping constant up to 10–12 weeks and decreasing gradually thereafter. Clearly, the much slower decrease in molecular weight [see Figure 4(B)] should be responsible for the less deteriorated mechanical properties of PBSF60.

Hydrolytic degradation is usually the basis of biodegradation of polyesters. However, hydrolysis during storage and use often leads to property deterioration and therefore is not desired. Therefore, degradability and durability is a pair of contradiction, and too quick hydrolysis is not desired for biodegradable polyesters. However, when the hydrolysis is slow enough, the polyester can retain certain durability for storage and use. From Figure 9, it can be seen that the copolyesters hydrolyzed slowly so that they retained enough high tensile properties after 22-week (or 5-month) hydrolysis: E 40–210 MPa, σ_b 4–18 MPa and ϵ_b 150–680% for PBAFs, and E 80–280 MPa, σ_b 13–26 MPa, and ϵ_b 420–820% for PBAFs. Such results suggest good balance between hydrolytic degradability and durability. Further studies on accelerated hydrolytic degradation under acid or basic conditions, compost degradation, and storage stability for these copolyesters are under way. The results will be reported later.

CONCLUSIONS

In this study, hydrolytic degradability of PBAF and PBSF copolyesters with copolymer composition (BF unit molar fraction, ϕ_{BF}) of 40–60% was assessed at 25 °C in PBS buffer solution with pH 7.0. Although the mass loss was slight (only 1–2%), the intrinsic viscosity decreased exponentially by 35–44% after hydrolysis for 22 weeks, validating hydrolytic degradability of the copolyesters. PBAFs degraded slightly faster than PBSFs with the same composition. The apparent hydrolytic degradation rate decreased with increasing ϕ_{BF} and initial crystallinity of the copolyesters. Accompanied by decrease in intrinsic viscosity, the ϕ_{BF} and crystallinity increased slowly with degradation time, suggesting that the aliphatic moiety is more susceptible to hydrolysis than the aromatic one and the amorphous region is more vulnerable to hydrolysis than the crystalline region. The variation or deterioration of tensile properties exhibited complicated dependence on the type and composition of the copolyesters as they are affected by many factors including molecular weight, composition, crystallinity as well as water absorption. In brief, the decline degree of tensile properties exhibited such an order: strength > elongation > modulus. After a 22-week

hydrolysis time, the copolyesters retained relatively high tensile properties: E 40–210 MPa, σ_b 4–18 MPa, and ϵ_b 150–680% for PBAFs, and E 80–280 MPa, σ_b 13–26 MPa, and ϵ_b 420–820% for PBAFs. In summary, the PBAF and PBSF copolyesters are hydrolytic degradable under mild conditions, the hydrolysis rate can be tuned by copolymer composition and crystallinity, and they retain sufficient mechanical properties, suggesting good balance between hydrolytic degradability and durability.

ACKNOWLEDGMENTS

This work was supported by the National Nature Science Foundation of China (No. 51373152); 973 Program (No. 2011CB606004); National Key Technology R&D Program of China (No. 2012BAD11B03); the Fundamental Research Funds for the Central Universities (No. 2014FZA4022); State Key Laboratory of Chemical Engineering Opening Project Program (No. SKL-Che-15D01); and 151 Talents Project of Zhejiang Province.

REFERENCES

1. Coombs, J.; Hall, K. *Renew. Energy* **1998**, *15*, 54.
2. Monomers, Polymers and Composites from Renewable Resources; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Amsterdam, **2008**.
3. Bozell, J. J. *Clean–Soil Air Water* **2008**, *36*, 641.
4. Nikolau, B. J.; Perera, M. A. D. N.; Brachova, L.; Shanks, B. *Plant J.* **2008**, *54*, 536.
5. Van Beilen, J. B.; Poirier, Y. *Plant J.* **2008**, *54*, 684.
6. Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1.
7. Rostrup-Nielsen, J. R. *Science* **2005**, *308*, 1421.
8. Fernando, S.; Adhikari, S.; Chandrapal, C.; Murali, N. *Energy Fuel* **2006**, *20*, 1727.
9. Amass, W.; Amass, A.; Tighe, B. *Polym. Int.* **1998**, *47*, 89.
10. Flieger, M.; Kantorová, M.; Prell, A.; Řezanka, T.; Votruba, J. *Folia Microbiol.* **2003**, *48*, 27.
11. Demirbas, A. *Energy Source Part A* **2007**, *29*, 419.
12. Hiljanen-Vainio, M.; Varpomaa, P.; Seppälä, J.; Törmälä, P. *Macromol. Chem. Phys.* **1996**, *197*, 1503.
13. Rasal, R. M.; Hirt, D. E. *J. Biomed. Mater. Res. A.* **2009**, *88*, 1079.
14. Top Value Added Chemicals from Biomass; Werpy, T.; Petersen, G.; Eds.; United States Department of Energy: Washington, DC, **2004**; Vol. 1, Chapter 9, p 21.
15. Gandini, A.; Silvestre, A. J. D.; Neto, C. P.; Sousa, A. F.; Gomes, M. J. *Polym. Sci. Polym. Chem.* **2009**, *47*, 295.
16. Gomes, M.; Gandini, A.; Silvestre, A. J. D.; Reis, B. J. *Polym. Sci. Polym. Chem.* **2011**, *49*, 3759.
17. Zhu, J. H.; Cai, J. L.; Xie, W. C.; Chen, P. H.; Gazzano, M.; Scandola, M.; Gross, R. A. *Macromolecules* **2013**, *46*, 796.
18. Wu, L. B.; Mincheva, R.; Xu, Y. T.; Raquez, J. M.; Dubois, P. *Biomacromolecules* **2012**, *13*, 2973.
19. Zhou, W. D.; Wang, X.; Yang, B.; Xu, Y.; Zhang, W.; Zhang, Y.; Ji, J. *Polym. Degrad. Stabil.* **2013**, *98*, 2177.

20. Wu, B. S.; Xu, Y. T.; Bu, Z. Y.; Wu, L. B.; Li, B. G.; Dubois, P. *Polymer* **2014**, *55*, 3648.
21. Jacquel, N.; Saint-Loup, R.; Pascault, J. P.; Rousseau, A.; Fenouillot, F. *Polymer* **2015**, *59*, 234.
22. Matos, M.; Sousa, A. F.; Fonseca, A. C.; Freire, C. S. R.; Coelho, J. F. J.; Silvestre, A. J. D. *Macromol. Chem. Phys.* **2014**, *215*, 2175.
23. Wu, H. L.; Wen, B. B.; Zhou, H.; Zhou, J. D.; Yu, Z. L.; Cui, L. Y.; Huang, T.; Cao, F. *Polym. Degrad. Stabil.* **2015**, *121*, 100.
24. Hbaieb, S.; Kammoun, W.; Delaite, C.; Abid, M.; Abid, S.; ElGharbi, R. *J. Macromol. Sci. Pure* **2015**, *52*, 365.
25. *Renewable Polymers: Synthesis, Processing, and Technology*; Mittal, V., Ed.; Wiley: Hoboken, NJ, **2011**.
26. Witt, U.; Müller, R. J.; Deckwer, W. D. *J. Environ. Polym. Degrad.* **1995**, *3*, 215.
27. Müller, R. J.; Witt, U.; Rantze, E.; Deckwer, W. D. *Polym. Degrad. Stabil.* **1998**, *59*, 203.
28. Witt, U.; Yamamoto, M.; Seeliger, U.; Müller, R. J.; Warzelhan, V. *Angew Chem. Int. Ed.* **1999**, *38*, 1438.
29. Siegenthaler, K. O.; Künkel, A.; Skupin, G.; Yamamoto, M. In *Synthetic Biodegradable Polymers*; Rieger, B., Künkel, A., Coates, W. G., Reichardt, R., Dinjus, E., Zevaco, A. T., Eds.; Springer: Berlin, Heidelberg, **2012**; p 91.
30. Honda, N.; Taniguchi, I.; Miyamoto, M.; Kimura, Y. *Macromol. Biosci.* **2003**, *3*, 189.
31. Wu, L. B.; Ding, J. D. *Biomaterials* **2004**, *25*, 5821.
32. Billmeyer, F. W. *J. Polym. Sci.* **1949**, *4*, 83.
33. Rantze, E.; Kleeberg, I.; Witt, U.; Müller, R. J.; Deckwer, W. D. *Macromol. Symp.* **1998**, *130*, 319.
34. Lucas, N.; Bienaime, C.; Belloy, C.; Queneudec, M.; Silvestre, F.; Nava-Saucedo, J. E. *Chemosphere* **2008**, *73*, 429.
35. Nishida, H.; Yamashita, M.; Nagashima, M.; Hattori, N.; Endo, T.; Tokiwa, Y. *Macromolecules* **2000**, *33*, 6595.
36. Codari, F.; Lazzari, S.; Soos, M.; Storti, G.; Morbidelli, M.; Moscatelli, D. *Polym. Degrad. Stabil.* **2012**, *97*, 2460.
37. Chen, X. R.; Chen, W.; Zhu, G. X.; Huang, F. X.; Zhang, J. C. *J. Appl. Polym. Sci.* **2007**, *104*, 2643.
38. Kijchavengkul, T.; Auras, R.; Rubino, M.; Selke, S.; Ngouajio, M.; Fernandez, R. T. *Polym. Degrad. Stabil.* **2010**, *95*, 2641.
39. Li, F. X.; Xu, X. J.; Yu, J. Y.; Cao, A. *Polym. Degrad. Stabil.* **2007**, *92*, 1053.