

Synthesis of Poly(butylene succinate-co-butylene terephthalate) (PBST) Copolyesters with High Molecular Weights via Direct Esterification and Polycondensation

Shengli Luo,¹ Faxue Li,¹ Jianyong Yu,² Amin Cao³

¹Key Laboratory of Textile Science and Technology, Ministry of Education, Donghua University, Shanghai 201620, People's Republic of China

²Modern Textile Institute, Donghua University, Shanghai 200051, People's Republic of China

³Laboratory for Polymer Materials, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Received 2 April 2009; accepted 17 August 2009

DOI 10.1002/app.31346

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, biodegradable poly(butylene succinate-co-butylene terephthalate) (PBST) copolyesters with high molecular weights were synthesized by direct esterification and polycondensation route. The reaction conditions and catalytic systems were investigated in detail. Through balancing the reaction efficiency and the costs of reactants, the proper molar ratio of diol to diacid was determined. Titanium tetraisopropoxide (TTiPO) was found to be an effective catalyst both in esterification and polycondensation reaction, and its content was optimized based on the esterification ratio and amount of formed by-products. The complex reaction was determined to be the dominant catalytic reaction mechanism. By importing the additives of metal oxides coupled with TTiPO, the weight-average molecular

weights of PBST increased sharply from 8.51×10^4 to 14.38×10^4 , manifesting the additives promoted the polymerization reaction greatly. The enhancement of carbonyl polarization and provision of suitable reaction space arose from the metal oxides were the reasons for promoting the polymerization reaction. With respect to thermal properties, the same melting point and heat of fusion were found, while thermal stability increased with the import of additives. The result was prone to be interpreted by the higher molecular weights of PBST in the presence of additives. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2203–2211, 2010

Key words: PBST copolyesters; direct esterification; feed ratio; TTiPO, additives, reaction mechanism

INTRODUCTION

Recently, a wide variety of biodegradable polymers has attracted much attention owing to the increasing environmental concerns about waste pollution. Aliphatic polyesters, one of the most promising structural materials for biodegradable or compostable fibers, nonwovens, films, sheets, bottles, and injection-molded products, have already been found to be the most attractive biodegradable polymers.^{1–4} However, the high production costs and inherent unfavorable thermal and mechanical properties restrained the various applications as ever expected, although these aliphatic polyesters have already been available on the market for more than 10 years. Therefore, the attempt

to improve physical properties of the biodegradable aliphatic polyesters has been a challenging task.

So far, aromatic polyesters have been known to possess excellent thermal and mechanical properties compared to the aliphatic polyesters. Introducing aromatic units into the main chains of aliphatic polyesters may be an effective strategy to prepare new aliphatic-aromatic copolyesters, capable of its combination of desirable biodegradability and good mechanical properties. For instance, an aliphatic-aromatic BTA-based copolyester, was commercialized under the trademarks of Ecoflex[®] and Easter-bio[®] by BASF and Eastman Chemical, respectively.⁵ As another important aliphatic-aromatic copolyester, poly(butylene succinate-co-butylene terephthalate) (PBST) has attracted much more attention.^{6,7} It can reduce the oil consumption because the raw materials of 1,4-butanediol (BD) and succinic acid (SA) can be obtained by the method of bio-ferment.^{8–10} Nevertheless, the above PBST generally had low molecular weights for film application. In our previous work,^{11–14} the PBST with high molecular weights were synthesized via transesterification route, and

Correspondence to: F. Li (fxlee@dhu.edu.cn) or J. Yu (yujy@dhu.edu.cn).

Contract grant sponsor: Natural Science Foundation of Shanghai Municipality; contract grant number: contract grant number: 09ZR1401700.

their chemical and sequential fine structures, thermal properties, crystallization behaviors and enzymatic degradation were studied intensively. The experimental results showed that the PBST with 70 mol % of butylene terephthalate (BT) units possessed excellent thermal and mechanical properties as well as good biodegradability, and the PBST filament had elastic property based on its rubbery-like stress-strain curve. Thus, the research objective in this article was focused on PBST with 70 mol % of BT units by adjusting the feed ratio of SA to terephthalic acid (TPA).

Generally, the aliphatic-aromatic copolyesters were synthesized through the strategy of transesterification and polycondensation. The high costs of raw materials (dimethyl esters) and complex separation of by-products [e.g., methanol and tetrahydrofuran (THF)] confined their bulk production. Thus, it was being substituted for the route of direct esterification and polycondensation due to lower costs of raw materials (diacid). Furthermore, the latter is commercially feasible because THF by-product is easier to separate from water (direct esterification route) than from methanol (transesterification route). Therefore, the route of direct esterification and polycondensation was selected to prepare the biodegradable PBST with high molecular weights for fiber application.

Nevertheless, it should be pointed out that some challenging tasks still existed in preparing the PBST based on the direct esterification route, such as a long reaction time, high depletion of diol caused by side reactions, low molecular weight of prepared products. In the present work, these problems were effectively solved and the PBST with high molecular weights were prepared via direct esterification route. Accordingly, the reaction conditions, catalytic systems were investigated, and the catalytic reaction mechanism was also explored in this article.

EXPERIMENTAL

Materials

Raw materials of 1,4-butanediol (1,4-BD), TPA, and SA were purchased from Linfeng Chemical Reagent Co., Shanghai, China. Titanium tetraisopropoxide (TTiPO) of AR grade was obtained from Jingrui Chemical Reagent Co., China. The additive of stannic oxide (A) and germanium dioxide (B), were purchased from Shanghai Chemical Reagent Co., China. All the chemicals were commercially received and used without further purification.

Synthesis of PBST

Apparatus for the synthesis of PBST

The synthesis of PBST was carried out in a 1-L stainless steel reactor with a nitrogen gas inlet, an outlet

attached to a condenser, a mechanical stirrer at a maximum stirring rate of 80 rpm and a vacuum line. The reactor was heated using conducting oil and its temperature was controlled by a proportion integration differentiation temperature controller. The pressure of reaction system was displayed by a pressure transmission case.

Procedure

The reactor was charged with 0.70 mol TPA, 0.30 mol SA and designated amount of 1,4-BD with gentle stirring under nitrogen atmosphere. The feed molar ratio of 1,4-BD to the total amount of diacids was preset to 1.3, 1.4, 1.5, 1.7, 2.0, respectively. After the raw materials were mixed well, the predetermined amount of TTiPO and/or additive with its molar ratio to TTiPO equal to 0.5 were added to the reactor. Afterward, the reactor was heated to 210°C gradually and the esterification reaction occurred at a certain pressure with a stirring rate of 80 rpm for 2 h. Subsequently, the polycondensation was carried out under the gradually reduced pressure with a final degree of vacuum less than 50 Pa. Meanwhile, the inner temperature of the reactor was raised up to 250°C. The polycondensation was finally terminated when the real-time torque of the mechanical stirrer approached a maximum value. The as-prepared products were dissolved in chloroform, and then precipitated from cold methanol for purification. White solid products (purified PBST copolyesters) were obtained after drying to constant weight in vacuum oven.

Characterization

¹H-NMR characterization

Measurements of ¹H-NMR spectra were conducted under ambient temperature in CDCl₃ solution on a Varian VXR 300 FT-NMR spectrometer operating at a resonance frequency of 300.1 MHz for the proton nuclei, and tetramethylsilane was employed as internal chemical shift reference.

Gas chromatography

The amount of THF by-product in the esterification reaction was determined by 6890N capillary gas chromatography instrument (Agilent Technologies). The carrier gas was nitrogen gas and the detector was FID. The injector temperature was 280°C, while the detector temperature was set to 300°C. The column temperature was increased from the initial 50°C to 230°C at a heating rate of 10°C/min, and then was kept for 10 min. The composition of esterification by-products was determined based on the available external standard. The esterification ratio is determined by the ratio of the water amount in by-products to that in theory.

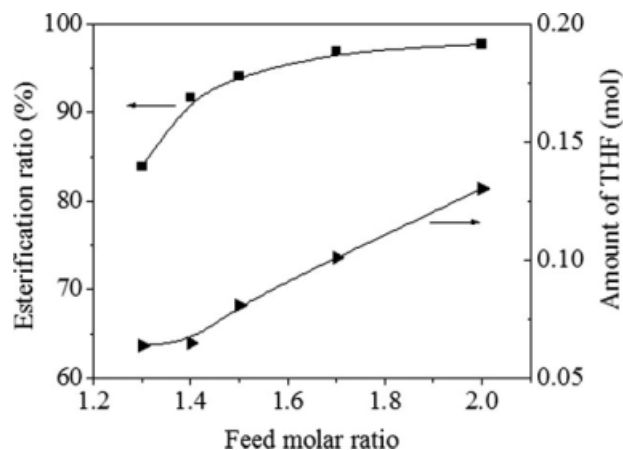


Figure 1 The changes of esterification ratio and amount of formed THF versus feed molar ratio of diol to diacid.

BHST oligomers were generated. Subsequently, the condensation reaction of BHET and BHST arose under certain conditions with the releasing of by-product. With the occurrence of polycondensation, the final product of high molecular weights PBST copolyesters was obtained.

Influence of feed ratio of diol to diacid on the synthesis

As a result of the release of H^+ ions from the raw material TPA, H^+ ions not only catalyze the esterification reaction, but also catalyze some side reactions.¹⁵ The side reactions generally cause the formation of THF as follows: $HOC_4H_8OH \rightarrow C_4H_8O + H_2O$; $HOC_4H_8OOC C_6H_6- \rightarrow C_4H_8O + HOOC C_6H_6-$; $HOC_4H_8OOCCH_2CH_2- \rightarrow C_4H_8O + HOOCCH_2CH_2-$. Therefore, the effective control on the formation of THF is crucial to the esterification reaction, which directly determines the molecular weight of the prepared products.

The feed ratio of diol to diacid is an important parameter in esterification process. If the feed ratio is too low, the esterification ratio tends to lessen and results in the low molecular weights of the prepared polymers. However, too much excessive diol may give rise to the overmuch occurrence of side reactions and the waste of diol. Therefore, the feed ratio of diol to diacid should be determined appropriately. Figure 1 depicts the effects of the feed ratio of diol to diacid on the amount of formed THF and the esterification ratio in the esterification process under 1/3000 molar ratio of TTIPO to diacid. It was clearly seen that, due to the increased concentration of reactants, the esterification ratio increased from 84 to 98% with the increasing feed ratio. Furthermore, the amount of formed THF also increased with the increasing feed ratio. This can be interpreted that the

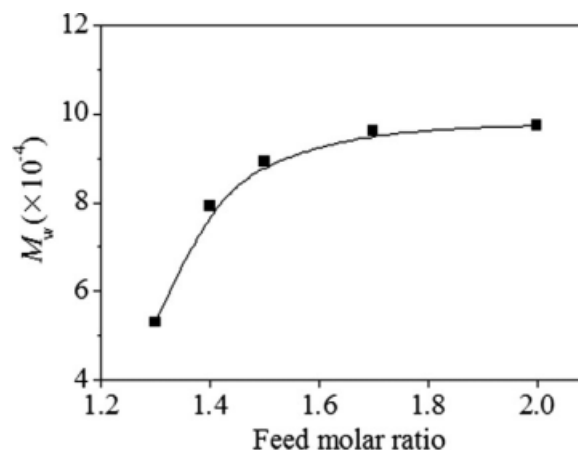


Figure 2 The change of weight-average molecular weights of PBST copolyesters versus feed ratio of diol to diacid.

more dehydration reaction of 1,4-BD occurs with the increase of its amount.

Figure 2 displays the change of the molecular weights of PBST with the increase of feed ratio. It could be found that the molecular weights of PBST increased sharply as the molar ratio increased from 1.3 to 1.5. The increasing amount of diol accelerated the esterification reaction and raised the esterification ratio, which helped to increase the molecular weights of the prepared products. However, as the feed ratio exceeded 1.5, slight increase in the molecular weights of PBST was found. Therefore, the proper feed ratio of diol to diacid was determined to be 1.5 through balancing the reaction efficiency and the costs of reactants.

Influence of catalyst on the synthesis

As to the synthesis of polyesters, TTIPO was found to be an effective catalyst both in esterification and polycondensation process.¹⁶⁻¹⁹ Figure 3 shows the

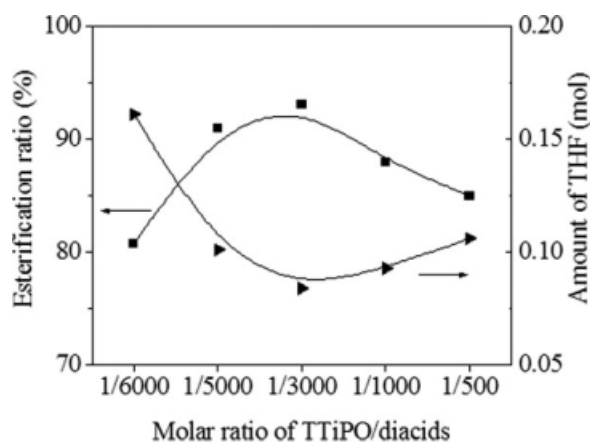


Figure 3 The changes of esterification ratio and amount of formed THF versus the content of TTIPO catalyst.

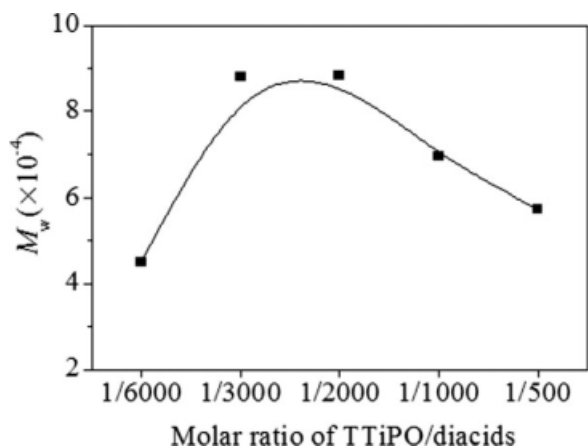


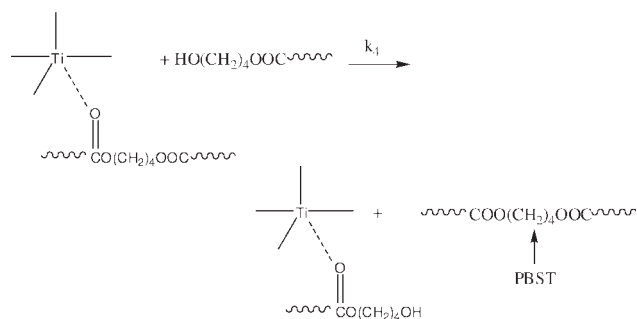
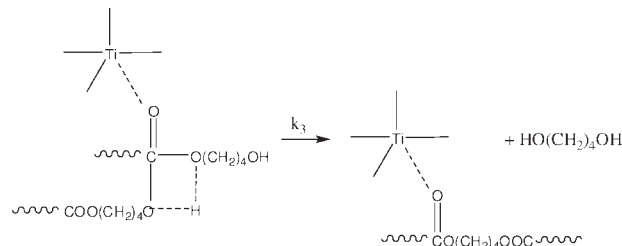
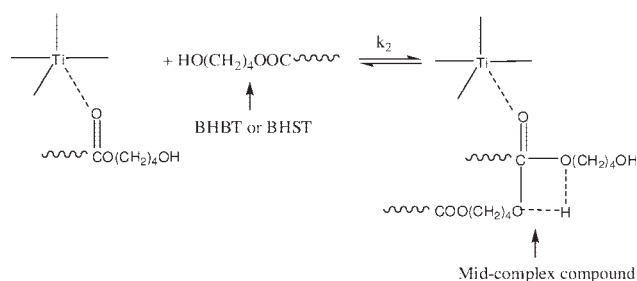
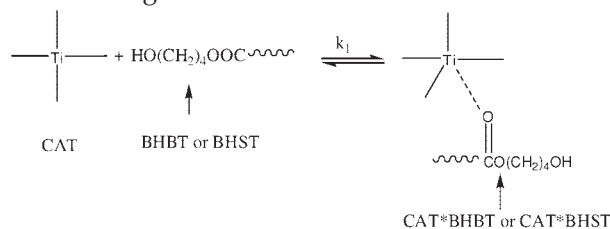
Figure 4 The change of weight-average molecular weights of PBST versus the content of TTiPO catalyst.

dependence of TTiPO content on the amount of formed THF and esterification ratio as the feed molar ratio is 1.5. The esterification ratio was found to initially increase with increasing the catalyst content, and then shift to decrease. When the TTiPO content reached 1/3000 mol to the amount of diacid, the maximum esterification ratio of 93% was obtained. This meant that the low content of catalyst tended to render the reaction rate slow and the reaction time long. In this case, a large amount of THF was formed by the side reactions on the 1,4-BD, which was also displayed in the figure, hence it was necessary to increase the TTiPO content in the synthesis of PBST. Nonetheless, more THF was generated as the TTiPO content exceeded the critical value of 1/3000. The reason may be that excessive catalyst induced its self-association which partially inhibited the catalytic activity.²⁰

To verify the effects of TTiPO content on the polycondensation, the variation of molecular weights of the prepared products at various catalyst contents was presented in Figure 4. Obviously, the molecular weights exhibited a noticeable increase as the TTiPO content varied from 1/6000 to 1/3000, thereafter a decrease in the molecular weights was found. This variation agreed well with that of the esterification ratio depicted in Figure 3, confirming that esterification reaction was the key step to determine the molecular weights of the prepared products.²¹

The polycondensation reaction mechanism of PBST was similar to that of poly(butylene terephthalate) (PBT) reported by Pilati et al.²² It was generally described in terms of coordination of the transition metal to the carbonyl group, or alternatively of basis catalysis. That is to say, the complex reaction was determined to be dominant in the polycondensation reaction. The following scheme represents the reaction route for preparing PBST. The catalyst TTiPO reacted progressively with the BHBT or BHST

oligomers formed by esterification reaction of diol to diacid to generate the unstable mid-complex compounds of CAT*BHBT or CAT*BHST. Subsequently, the mid-complex compounds were decomposed to produce stable PBST adducts and 1,4-BD by-product discharged by the vacuum system. The reaction occurred repeatedly to prepare PBST with high molecular weights.



Influence of additive on the synthesis

To endow the as-product higher molecular weights for fiber application, two additives A and B, coupled with the catalyst TTiPO respectively, were chosen for preparing the PBST. Table I summarizes the experimental results of esterification and polycondensation reaction in which the feed ratio is 1.5 and the molar ratio of TTiPO to diacid is 1/3000. Higher esterification ratio and lower amount of THF were attained in the presence of additive A and B.

TABLE I
The Parameters of Polymerization Reaction of PBST Copolyesters Catalyzed with Different Catalysts

Catalyst	Polymerization time ^a (h)	Esterification ratio ^b (%)	Amount of THF ^c (mol)	M_w^d ($\times 10^{-4}$)	M_n^d ($\times 10^{-4}$)	M_w/M_n^d	Yield ^e (%)	Unit ratio ^f BT/BS	Residue ^g (%)		
									Ti	A	B
TiPO	4.2	93.1	0.101	8.51	4.43	1.92	65.3	72.1/27.9	29.9	–	–
TTiPO/A	3.2	99.1	0.069	14.38	5.94	2.42	66.2	71.3/28.7	39.3	20.1	–
TTiPO/B	3.1	98.6	0.074	13.54	5.86	2.31	66.0	71.5/28.5	33.7	–	17.2

^a Polymerization time was the sum of esterification time and polycondensation time.

^b The esterification rate was calculated by the ratio of the water amount in by-products to that in theory.

^c The amount of THF was determined by Gas chromatography.

^d Molecular weights were measured by GPC.

^e The yield was calculated by the ratio of the weight of as-prepared polymer to the total weight of initial feed monomers.

^f Unit ratio was calculated by the ratio of the peak area at chemical shift 8.1 to that at chemical shift 2.6 in the ¹H-NMR spectrum of PBST.

^g Residue was the percentage of catalyst/cocatalyst amount in purified PBST to the initial feeding amount of catalyst/cocatalyst.

Accordingly, the molecular weights of the prepared products were much higher in the complex catalyst than those in pure TTiPO catalyst. Specifically, the weight-average molecular weights of the PBST copolyesters catalyzed by complex catalysts of TTiPO/A and TTiPO/B were 14.38×10^4 and 13.54×10^4 respectively, while that of the products catalyzed only by TTiPO was 8.51×10^4 . Moreover, shorter polymerization time was needed when PBST copolyesters were catalyzed by complex catalysts of TTiPO/A or TTiPO/B than that catalyzed by pure TTiPO as shown in Table I. Therefore, the combination of the additive A and B with TTiPO enhanced the synthesis efficiency greatly.

The residue catalyst, TTiPO, and cocatalyst, A and B, in purified PBST copolyesters were checked by inductively coupled plasma atomic emission instrument. All of them existed in purified PBST copolyesters as shown in Table I, suggesting that partial catalyst and cocatalyst were polymerized in the PBST copolyesters. It can also be seen that the amount of TTiPO in complex catalyst is relatively higher than that of pure TTiPO, meaning that TTiPO is more stable in complex catalyst. Furthermore, the amount of residue A is higher than that of residue B, indicative of more firm combination between catalyst (TTiPO) and cocatalyst (A). However, the failure in the preparation of PBST was found when additive A and B were used to catalyze the polymerization reaction alone, indicating that A and B played a catalytic promoting role.

According to Table I, note that the import of A and B additive increases the esterification ratio, suggesting the additive inhibits the side reactions partially. Furthermore, higher yield obtained in the presence of A or B reconfirmed the restraint of side reactions. Additionally, the higher molecular weights of the prepared products were found in TTiPO/A

complex catalyst than those in TTiPO/B complex catalyst, demonstrating that the former was more effective than the latter in catalyzing the polymerization of PBST copolyesters. The reason may be that A possesses more suitable volume for coordination between the catalyst and the oligomers.

As to the high catalytic efficiency of the complex catalyst, the reasons have not been proved yet. Generally, the cocatalyst added in the complex catalyst tends to increase the catalytic activity surface of catalyst, which can cause the increase of its active sites because the metal oxide A and B can provide suitable reaction space²¹ for the formation of complex compounds shown in Figure 5. It can be seen that the metal ions Mn+ originated from the A or B possess enough volume for coordination between the catalyst and the oligomers. Another probable reason

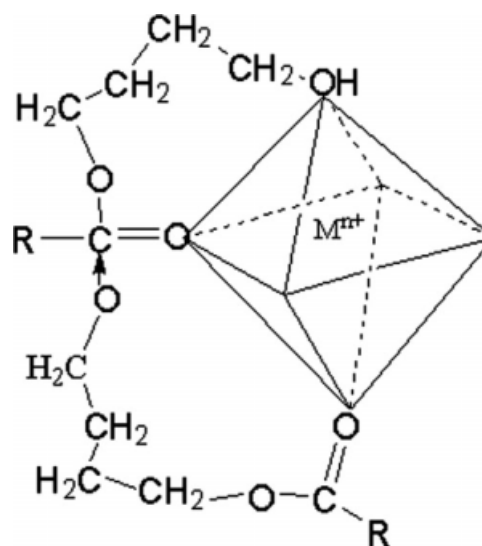


Figure 5 The reaction model of metal oxide catalyzing the polycondensation reaction of PBST.

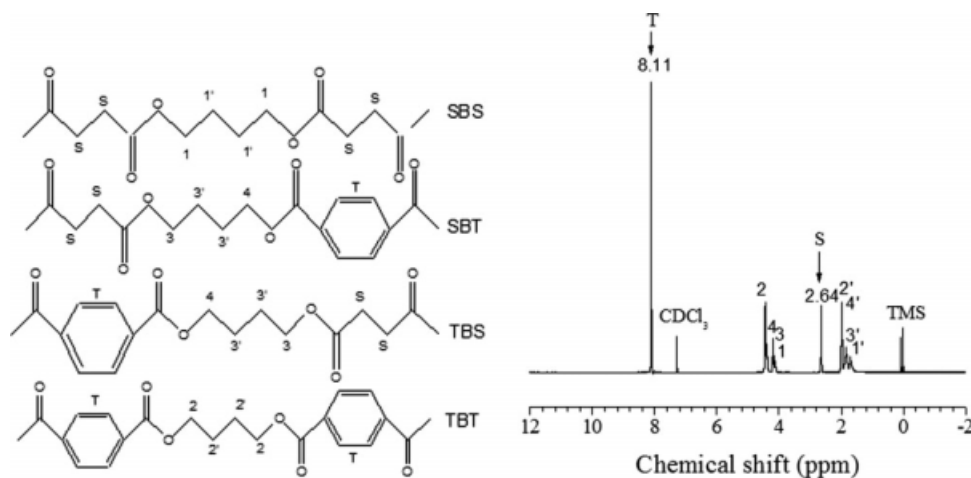


Figure 6 $^1\text{H-NMR}$ spectrum of the prepared PBST.

of the promotion of A and B on the polymerization reaction may be explained as arising mainly from the enhancement of carbonyl polarization.²²

Structure and composition characterization

Figure 6 shows the $^1\text{H-NMR}$ spectrum for the prepared PBST catalyzed by TTiPO/A, and the resonance signals are assigned and seem distinguishable for the diad sequences. The peak value of chemical shift 8.11 ppm was the hydrogen proton of phenyl (terephthalate unit, T), while the peak value at 2.64 ppm corresponded to the hydrogen proton of the methylene of succinate (succinate unit, S). The proton signals were applied to analyze the polymer composition which was calculated by the ratio of the peak area at chemical shift 8.1 to that at chemical shift 2.6. As shown in Table I, the ratio of chain segment composition of BT to BS (BT/BS) was close to

the feed molar ratio of TPA to SA, indicating that the material loss was low during reaction process. Moreover, it was found that both kinds of proton nuclei of butanediol unit (B) were strongly affected by the diad sequential structures, and the proton resonance signals obviously split into four sub-signals. However, during the sequence distribution analysis, only the signals appearing in a range of 4.50–4.00 ppm were used due to their better signal resolution. The integrated resonance intensities for the peaks of 2, 4, 3, and 1 were accordingly assigned to the contributions from corresponding TBT, TBS, SBT, and SBS diad sequences displayed in the left side of the figure.²³

Thermal properties

Figure 7 presents the DSC heating curves of PBST catalyzed in the presence or absence of additive. It was found that the copolyesters showed similar DSC thermograms, indicating there is no distinct enhancement of thermal property by importing the additives. The corresponding DSC parameters were also listed in Table II. The melting points (T_m) and

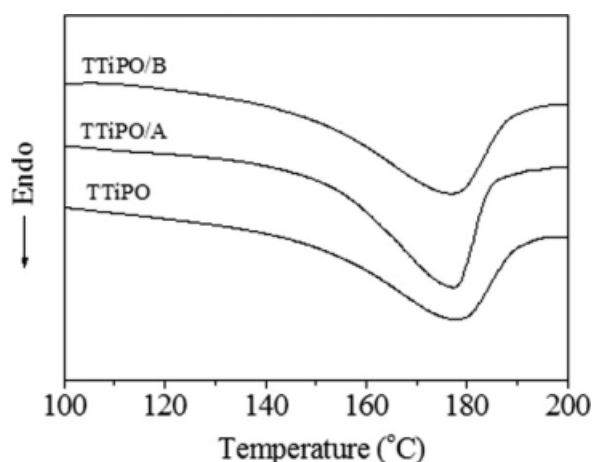


Figure 7 DSC heating curves of PBST catalyzed with different catalysts.

TABLE II
The Parameters of Thermal Properties of PBST Copolyesters Catalyzed with Different Catalysts

Catalyst	T_m^a (°C)	ΔH_m^a (J/g)	T_d^b (°C)	T_{dm}^b (°C)
TiPO	178.4	25.4	374.7	403.9
TTiPO/A	178.2	25.7	379.5	408.6
TTiPO/B	178.4	25.5	378.8	409.8

^a The melting point T_m and heat of fusion ΔH_m were measured by DSC.

^b The thermal degradation temperature (T_d) and temperature at the maximum degradation rate (T_{dm}) were measured by TGA.

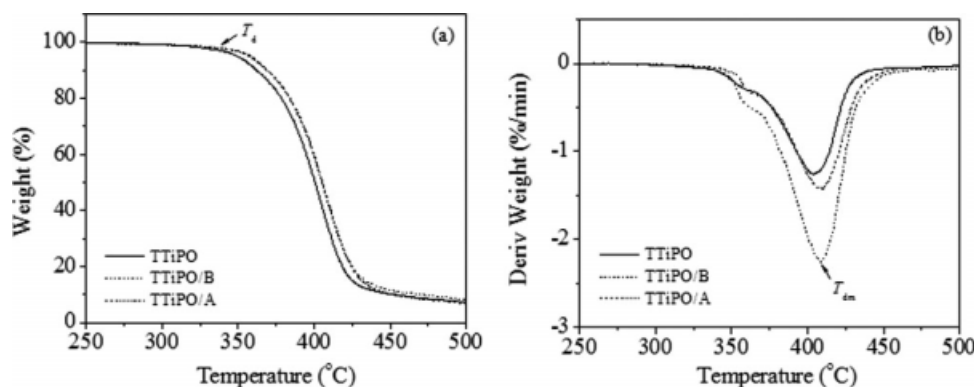


Figure 8 TGA (a) and dTGA (b) traces of the PBST catalyzed with different catalysts.

heat of fusion (ΔH_m) are close to 178°C and 25 J/g respectively, regardless of the import of different additives.

However, the higher thermal degradation temperature (T_d) and temperature at the maximum degradation rate (T_{dm}) were found for the PBST catalyzed in the presence of additive A and B than those in the absence of additive showed in Figure 8, suggesting the import of additive A and B enhanced the thermal stability of PBST to some extent. The result is prone to be accordingly interpreted by the higher molecular weights of PBST in the presence of additive. A similar phenomenon has been found for poly (triethylene terephthalate) (PTT): the T_d and T_{dm} in nitrogen also increased with molecular weight.²⁴ As mentioned in the experiment section, the terminal groups of PBST are hydroxyl, so the shorter the chain, the more the end hydroxyl groups in the material. The thermal stability of end hydroxyl groups in polyesters is relatively poor. It is hydroxyl groups that initiate the thermal degradation of PBST. Thus, the thermal stability enhances with increasing the molecular weight.

CONCLUSIONS

Biodegradable PBST with high molecular weights were derived from 1,4-butanediol, succinic and TPAs via the direct esterification and polycondensation route. The proper feed ratio of diol to diacid was determined to be 1.5 based on the balance of the reaction efficiency and the costs of reactants. As catalyst, TTiPO was proved to be efficient and its optimized content was 1/3000 mol to the amount of diacid through analyzing the esterification ratio and the amount of THF by-product. The complex reaction was determined to be the dominant catalytic reaction mechanism. Furthermore, higher esterification ratio and lower amount of THF were attained in the presence of additive A and B, although the failure in the synthesis of

PBST when A and B were used alone. The M_w of PBST characterized by GPC increased from 8.51×10^4 to 14.38×10^4 in the presence of additives. These indicated that A and B promoted the polymerization reaction greatly. The sequence distributions analyzed by means of $^1\text{H-NMR}$ demonstrated that the polycondensations of PBST were in well accordance with the random copolymerization model. Moreover, DSC measurement showed that PBST catalyzed in the presence or absence of additives exhibited similar DSC thermograms, while the higher thermal degradation temperature (T_d) and temperature at the maximum degradation rate (T_{dm}) characterized by TGA were found for the PBST catalyzed in the presence of additives than those in the absence of additives, suggesting the import of additives enhanced the thermal stability of PBST to some extent.

References

- Mochizuki, M.; Mukai, K.; Yamada, K.; Ichise, N.; Murase, S.; Iwaya, Y. *Macromolecules* 1997, 30, 7403.
- Ichikawa, Y.; Kondo, H.; Igarashi, Y.; Noguchi, K.; Okuyama, K.; Washiyama, J. *Polymer* 2000, 41, 4719.
- Montes De Oca, H.; Ward, I. M. *J Polym Sci Part B: Polym Phys* 2007, 45, 892.
- Agarwal, S.; Wendorff, J. H.; Greiner, A. *Polymer* 2008, 49, 5603.
- Muller, R. J.; Kleeberg, I.; Deckwer, W. D. *J Biotech* 2001, 86, 87.
- Nagata, M.; Goto, H.; Sakai, W.; Tsutsumi, N. *Polymer* 2000, 41, 4373.
- Honda, N.; Taniguchi, I.; Miyamoto, M. *Macromol Biosci* 2003, 3, 189.
- Stieglitz, B.; Weimer, P. *J Appl Environ Microbiol* 1985, 49, 593.
- Chatterjee, R.; Millard, C. S.; Clark, D. P.; Donnelly, M. I. *J Appl Environ Microbiol* 2001, 67, 148.
- Donnelly, M. I.; Millard, C. S.; Clark, D. P.; Chen, M. J.; Rathke, J. W. *J Appl Biochem Biotech* 1998, 70, 187.
- Li, F. X.; Hao, Q. F.; Li, Q. B.; Yu, J. Y.; Cao, A. M. *J Polym Sci Part B: Polym Phys* 2006, 44, 1635.
- Li, F. X.; Xu, X. J.; Li, Q. B.; Li, Y.; Zhang, H. Y.; Yu, J. Y.; Cao, A. M. *Polym Degrad Stab* 2006, 91, 1685.

13. Li, F. X.; Xu, X. J.; Yu, J. Y.; Cao, A. M. *Polym Degrad Stab* 2007, 92, 1053.
14. Xu, X. J.; Li, F. X.; Yu, J. Y.; Cao, A. M. *Int J Nonlinear Sci Num Simul* 2008, 9, 31.
15. Kazunori, S.; Kazuhige, M.; Kazuhiro, H.; Atsushi, T.; Teruo, F. *J Polym Sci Part A: Polym Chem* 1998, 36, 3021.
16. Ahn, B. D.; Kim, S. H.; Kim, Y. H.; Yang, J. S. *J Appl Polym Sci* 2001, 82, 2808.
17. Ki, H. C.; Park, O. O. *Polymer* 2001, 42, 1849.
18. Yang, J.; Cao, A. M. *Polym Degrad Stab* 2003, 81, 1.
19. Cao, A. M.; Okamura, T.; Ishiguro, C.; Nakayama, K.; Inoue, Y.; Masuda, T. *Polymer* 2002, 43, 671.
20. Fortunato, B.; Manaresi, P.; Munari, A.; Pilati, F. *Polym Commun* 1986, 27, 29.
21. Tomita, K. *Polym Symp* 1976, 32, 96.
22. Pilati, F.; Manaresi, P.; Fortunato, B.; Munari, A.; Passalacqua, V. *Polymer* 1981, 22, 799.
23. Guo, B. H.; Ding, H. G.; Xu, X. L.; Sun, Y. B. *Chem J Chin Univ* 2003, 24, 2315.
24. Wang, X. S.; Li, X. G.; Yan, D. Y. *Polym Degrad Stab* 2000, 69, 361.