Chain Extension of Polybutylene Adipate and Polybutylene Succinate with Adipoyl- and Terephthaloyl-Biscaprolactamate

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ABSTRACT: HO-terminated polybutylene adipate (HO-PBA-OH) with molecular weight from 1040 to 3540 and HO-terminated polybutylene succinate (HO-PBS-OH) with intrinsic viscosity of 0.37 dL/g were synthesized through melt condensation polymerization from adipic acid or succinic acid with excess of butanediol. Chain extension of HO-PBA-OH or HO-PBS-OH with adipoyl biscaprolactamate and terephthaloyl biscaprolactamate was carried out at 200–240°C under reduced pressure. At the optimal conditions, chain-extended PBA with M_n up to 50,700, and M_w up to 125,700 was synthesized, and the chain-extended PBS with intrinsic viscosity of 1.25 dL/g was obtained. Meanwhile, *p*-toluenesulfonic acid, $SnCl_4$ and zinc acetylacetonate catalyzed chain-extending reaction of HO-PBA-OH and HO-PBS-OH was also studied. The chain-extended polyesters were characterized by IR spectra, ^{1}H-NMR spectra, and differential scanning calorimetry (DSC). The chain extension proceeds through the elimination of caprolactam rings in the chain-extenders, the adipoyl groups or the terephthaloyl groups couple the hydroxyl-terminated polyesters together and make the molecular weight of PBA or PBS increased, whether the acid catalyst such as *p*-toluenesulfonic acid was present or not. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 590–598, 2007

Key words: chain extension; adipoyl biscaprolactamate; terephthaloyl biscaprolactamate; biodegradable polyesters; polycondensation

INTRODUCTION

Chain extension is one of the important methods to enhance the molecular weight of the polyesters prepared from melt polycondensation. It is commonly swift and efficient. For some kinds of chain-extenders, the chain extension can be completed in several minutes.[1–3] Chain-extended polyesters such as polyethylene terephthalate can be used as bottle materials, which require higher molecular weight than the fiber usage. Chain extension connected with melt polycondensation is also an important method to synthesize aliphatic polyesters with high molecular weight. The common aliphatic polyesters used as biodegradable plastics include polybutylene succinate (PBS), polyethylene succinate, polybutylene adipate (PBA), etc. They are prepared from aliphatic glycols such as ethylene glycol or butanediol with succinic acid or adipic acid. In the chain extension of polyesters, different chain-extenders were used to the polyesters with different terminal groups. Chain-extenders such as bisoxazolines,[4] bisaziridines, and diepoxides[5] were usually used in the chain extension of the HOOC-terminated polyesters; others such as diisocyanate,[6] tetracarboxylic dianhydride,[7] carbonyl biscaprolactam,[8] 1,3-isophthaloyl biscaprolactamate[9] or terephthaloyl biscaprolactamate (TBC),[10–12] and octamethylcyclotetrasilazane or hexaphenylcyclotrisilazane[13] were used in the chain extension of the HO-terminated polyesters. In this article, we synthesized HO-terminated polybutylene adipate (HO-PBA-OH) and HO-terminated polybutylene succinate (HO-PBS-OH) with low molecular weight, and studied the chain extension using adipoyl biscaprolactamate (ABC) and TBC as chain-extenders, to get PBA or PBS with high molecular weight. Meanwhile, the acid or Lewis acid catalyzed chain-extending reaction was also studied. The chain-extended polyesters obtained were characterized by IR spectrum, ^{1}H-NMR spectrum and differential scanning calorimetry (DSC).

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EXPERIMENTAL

Materials

Adipic acid and succinic acid, obtained as common chemical reagents, were purified two times by crystallization with deionized water before used. 1,4-Butanediol was redistilled under reduced pressure. Dibutyltin oxide (Bu_2SnO), 99%, was purchased from ACROS Company and used directly. Other materials such as phosphorous acid, toluene, caprolactam, triethylamine, $SOCl_2$, pyridine, tetrahydrofuran (THF), *p*-toluenesulfonic acid (*p*-TSA), and $SnCl_4$ are all obtained as reagent grade and used directly. Zinc acetylacetonate [$Zn(acac)_2$] was synthesized as described in the Ref. 14.

Synthesis of HO-terminated PBA and HO-terminated PBS

HO-PBA-OH and HO-PBS-OH were prepared by a similar method as described in literature.[13] As an example, HO-terminated PBA was synthesized as follows:

In a 250-mL four-necked flask, 50 g (0.34 mol) adipic acid, 36.7 mL (0.41 mol) butanediol, 0.26 g dibutyltin oxide, and 0.17 g phosphorous acid were added. The mixture was mechanically stirred and heated under N_2 atmosphere to 150–160°C, until 10 mL water formed was collected. The temperature was gradually raised to 200°C. At 200°C, the pressure in the flask was reduced in stages to 1 mmHg over a period of 6 h, the excessive butanediol were distilled off. The acid value of the polyester obtained is 1.59, which was determined by titration with 0.05*N* NaOH. The hydroxyl number is 58.43.

Preparation of adipoyl chloride and terephthaloyl chloride

Adipoyl chloride and terephthaloyl chloride were freshly synthesized by the reaction of adipic acid or terephthalic acid with thionyl chloride respectively, under the catalysis of pyridine. As an example, adipoyl chloride was synthesized as follows:

In a 250-mL three-necked flask, 15 g (0.10 mol) adipic acid was suspended in 50 mL toluene. At 80°C, 18 mL (0.25 mol) $SOCl_2$ in 15 mL toluene was dropped slowly in 1 h, and 0.5 mL pyridine was added in the flask. The reaction was kept at 80°C for about 10 h until all the solid disappeared. After cooled, the excessive $SOCl_2$ and the solvent were distilled in a rotatory evaporator under reduced vacuum. Adipoyl chloride (15.8 g) was obtained. The yield was 84.0%.

Synthesis of ABC and TBC[15]

ABC was synthesized by the reaction of adipoyl chloride with caprolactam in THF at 0–5°C, using triethylamine to neutralize the HCl formed. The ammonium salt formed was filtered and the solvents in the filtrate were evaporated under reduced pressure. The solid material remained was crystallized with 1 : 1 (v/v) water–ethanol. Its melting point is 72–73°C.

Anal. Calcd. for $C_{18}H_{28}N_2O_4$ (%): C, 64.29; H, 8.33; N, 8.33. Found (%): C, 64.30; H, 8.40; N, 8.43. ^{1}H-NMR spectrum: δ = 3.90(4H, two =*N*—CH$_2$— in the two caprolactam rings); 2.81–2.83(4H, two —C(=O)—CH$_2$— in the caprolactam rings); 2.73-2.74(4H, two —C(=O)—CH$_2$— in the adipoyl group); 1.61–1.75 (16H, two middle —CH$_2$— in the adipoyl group and two middle —CH$_2$—CH$_2$—CH$_2$— in the caprolactam rings). IR spectrum: The characteristic peaks at 1703 and 1677 cm^{-1} correspond to the stretching vibration of two kinds of C=O groups in the amide linkages one corresponds to the carbonyl groups in the caprolactam rings, and the other corresponds to that in the adipoyl structure.

TBC was synthesized by the reaction of terephthaloyl chloride with caprolactam in toluene at 85°C for 2.5 h, using pyridine to neutralize the HCl formed. After cooled, the mixture was poured into ice water and stirred thoroughly. The filtered solid was washed with water and methanol. Solid material was crystallized with butanone. Its melting point is 201–202°C.

Anal. Calcd. for $C_{20}H_{24}N_2O_4$ (%): C, 67.42; H, 6.74; N, 7.87. Found (%): C, 67.45; H, 6.92; N, 7.74. ^{1}H-NMR spectrum: δ = 7.55 (4H, —C$_6$H$_4$—); 3.98 (4H, two =*N*—CH$_2$— in the two caprolactam rings); 2.72 (4H, two —C(=O)—CH$_2$— in the caprolactam rings); 1.87 (12H, two middle —CH$_2$—CH$_2$—CH$_2$— in the caprolactam rings). IR spectrum: The characteristic peaks at 1715 and 1681 cm^{-1} correspond to the stretching vibration of two kinds of C=O groups in the amide linkages one corresponds to the carbonyl groups in the caprolactam rings, and the other corresponds to that in the terephthaloyl group.

Chain extension of HO-terminated PBA or PBS

In a 100-mL three-necked round-bottom flask, 5.0 g HO-terminated PBA or PBS and ABC or TBC with different molar ratios were stirred and heated under nitrogen to 200–240°C. The reaction was maintained for about 30 min under normal pressure and 1 h under reduced pressure, until no further change of the viscosity was observed. The chain-extended polyesters obtained were purified two times through dissolving-precipitation cycles using 20 mL $HCCl_3$ as solvent and 200 mL methanol as nonsolvent, before detected by GPC, ^{1}H-NMR, FTIR, and DSC spectra.

The catalyzed chain extending reaction was carried out similarly as the noncatalyzed one. The catalyst was added after the HO-terminated PBA or PBS and the chain extender were melted and mixed homogeneously. The control of the reaction conditions was similar. The catalyzed chain extended polyesters were also purified through dissolving-precipitation cycles using $HCCl_3$ as solvent and methanol as nonsolvent.

TABLE I
Properties of the HO-PBA-OH and HO-PBS-OH

HO-terminated polyester	Acid value (mg KOH/g)	Hydroxyl number (mg KOH/g)	Molecular weight (g/mol)[a]	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	M_w/M_n (GPC)
PBA-1	1.45	106.02	1,040	2,290	4,010	1.75
PBA-2	1.59	58.43	1,870	3,580	6,990	1.95
PBA-3	0.52	48.27	2,300	5,750	11,400	1.98
PBA-4	0.58	31.11	3,540	6,450	12,800	1.98
PBA-5	3.00	42.35	2,470	4,940	10,900	2.21
PBA-6	1.56	51.90	2,100	3,810	6,980	1.83
HO-PBS-OH	0.57	29.18	3,770	–	–	–

[a] Molecular weight calculated from the hydroxyl number.

Meanwhile, the residue of the catalyst was removed by this way.

Measurements

In a 100-mL ground glass flask, 2.0 g HO-PBA-OH or HO-PBS-OH was refluxed with 10.00 mL 12.3 wt % phthalic anhydride-pyridine solution for 1.5 h. After cooling, 10 mL deionized water was added to hydrolyze the excessive phthalic anhydride. The mixture solution was titrated with 0.5*N* NaOH solution, and the hydroxyl number (Q_v, mgKOH/g) of the HO-terminated polyester was calculated by the following formula:

$$Q_v = \frac{56.1c(V_0 - V_s)}{m}$$

in which V_0 and V_s (mL) represent the NaOH solution volume consumed in the titration of the blank assay and the sample respectively; c (mol/L) is the concentration of the NaOH solution; m (g) is the weight of the sample; 56.1 is the molecular weight of KOH in g/mol.

The M_n, M_w and molecular weight distribution of HO-terminated PBA and the chain-extended PBA were measured on Waters GPC515-2410 system equipped with three Styragel columns (HT3-HT5-HT6E) and a refractive index detector at 25°C. THF was used as eluent with a flow rate of 1mL/min and polystyrene was used as standards. As HO-terminated PBS and the chain-extended PBS are insoluble in THF, their intrinsic viscosity were determined at 30°C by Ubbelohde viscometer using chloroform as solvent. ^{1}H-NMR spectrum was recorded on Bruker AC-600 spectrometer using DCC_{l3} as solvent of the polyesters. FTIR spectra were recorded on NICOLET 60SXB FTIR spectrometer. The DSC spectra were recorded on PE PYRIS I thermal analyzer with heating rate at 10°C/min.

RESULTS AND DISCUSSION

Synthesis of HO-terminated PBA and HO-terminated PBS

HO-terminated PBA and HO-terminated PBS were prepared by a similar method as described in literature.[13] Table I showed the properties of HO-PBA-OH and HO-PBS-OH synthesized. The molecular weight of the HO-PBA-OH calculated from the hydroxyl number is in the range from 1040 to 3540. As HO-PBS-OH is insoluble in THF, its intrinsic viscosity was determined by viscometric method and the [η] is 0.37 dL/g. Meanwhile, M_n, M_w, and M_w/M_n detected by GPC method were also compiled in Table I to compare conveniently with that of the chain-extended polyesters. The difference of the molecular weight detected by GPC from that calculated by the hydroxyl number is due to different methods of the measurements. Molecular weight calculated from the hydroxyl number is the absolute molecular weight. But M_n and M_w detected by GPC are relative molecular weight. The calibration curve of log M versus elution volume (V_e) used here was obtained using polystyrene (PS) as standard. Szesztay et al.[16] had reported the log $M - V_e$ calibration curve using PBA and polyhexylene adipate (PHA) oligomers as standards. The log $M - V_e$ calibration curve with PBA and PHA oligomers as standards was located much lower than that with polystyrene as standard. It means that if the GPC molecular weights of PBA are detected with PS as standard, the M_n and M_w obtained will be much higher than its real molecular weight or the absolute molecular weight. So the M_n and M_w of HO-terminated PBA detected by GPC in Table I is much higher than the molecular weight calculated from the hydroxyl number. Different solvation effect of PBA from that of PS in THF may be the reason. PBA has a lot of polar ester groups in its main chains and its molecular chain is much flexible than PS. Meanwhile, the terminal HO— groups of HO-PBA-OH may also take part in the solvation through hydrogen bonding with the etheric oxygen of THF. This effect results in that

TABLE II
The Influence of the Reaction Temperature and the ABC/HO-PBA-OH Molar Ratios on the Chain Extension[a]

HO-PBA-OH	ABC/ HO-PBA-OH (molar ratio)	Reaction temperature (°C)	The chain-extended PBA M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	M_w/M_n (GPC)
PBA-2	0.8	240	10,200	25,200	2.47
	1.0	240	26,600	54,400	2.05
	1.1	240	19,600	48,400	2.47
	1.2	240	20,300	42,200	2.08
PBA-3	1.1	200	9,210	25,900	2.81
	1.1	220	18,900	40,600	2.15
	1.1	240	24,000	55,300	2.30

[a] Reaction time is 1.5 h.

the HO-PBA-OH has more stretched molecular state and bigger molecular size in THF than PS with the same molecular weight. So HO-PBA-OH having the same molecular weight shows lower elution volume, and higher GPC molecular weight than PS with PS as standard. Similar result of polycaprolactone was also reported in the literature.[17] The molecular weights calculated from the hydroxyl number were used to calculate the molar ratios of the chain extenders to the HO-terminated polyesters.

Chain extension of HO-PBA-OH and HO-PBS-OH with ABC and TBC

Chain extension of HO-PBA-OH or HO-PBS-OH was carried out in bulk state using ABC or TBC as chain-extenders. Table II showed the influence of the reaction temperature on the chain extension of HO-PBA-OH with ABC. From Table II, it was found that as the reaction temperature was changed from 200 to 240°C, the M_n and the M_w of the chain-extended PBA increase. Reaction at 240°C is more favorable to the chain extension of HO-PBA-OH with ABC. Table II also showed the influence of ABC/HO-PBA-OH molar ratios on the chain extension. As the molar ratio of ABC to HO-PBA-OH deviates from 1.0, such as 0.8, 1.1, and 1.2, the M_n and the M_w of the chain-extended PBA decrease. The optimal molar ratio of ABC to HO-PBA-OH is 1.0 for this chain extension.

Table III showed the influence of different HO-PBA-OH on the chain extension. It was found that HO-PBA-OH like PBA-2, PBA-3, and PBA-4 with higher molecular weight has better chain-extending results than the PBA-1. Chain-extended PBA with M_n up to 32,800 and M_w up to 65,200 was obtained when PBA-3 was used as starting material.

Table IV showed the chain extension of HO-PBA-OH with TBC as chain-extender. It was found that the chain extension of HO-PBA-OH with TBC has better results than that with ABC. In a wider range of TBC/HO-PBA-OH molar ratios from 0.8 to 1.2, the chain-extended PBA with M_n over 30,400 and M_w over 63,600 was obtained. The optimal chain-extending temperature with TBC is 220°C, lower than that with ABC. When the TBC/HO-PBA-OH molar ratio is 1.0, the chain extension shows the best result and the chain-extended PBA with M_n of 50,700 and M_w of 109,700 was obtained.

In the literature, Loontjens and coworkers[18,19] had studied the catalyzed reaction of carbonyl biscaprolactam with alcohols such as 1-octanol, 2-octanol, etc. using NaOR, $Zr(OR)_4$ and $MgCl_2$ as catalysts, and found that the reaction proceeded through ring opening of caprolactam rings in carbonyl biscaprolactam. In this article, we studied the catalyzed chain extension of HO-PBA-OH with ABC using acid or Lewis acid catalysts such as *p*-toluenesulfonic acid, $SnCl_4$ as well as $Zn(acac)_2$. Table V showed the results of the catalyzed chain extension. From the phenomenon of the viscosity increasing of the polyesters during the chain extension, it was found that the catalyzed chain extension progressed more rapidly than the noncatalyzed one. Maybe the complexation or protonation of the carbonyl group of the adipoyl structure in ABC with the Lewis acid or *p*-TSA promoted the chain extension. Table V also showed the lower optimal reaction temperature in the catalyzed reaction than that in the noncatalyzed one. *p*-TSA is the best catalyst. Chain-extended PBA with M_n up to 30,600 and M_w up to 74,000 was obtained when 0.20 wt % of *p*-

TABLE III
Influence of Different HO-PBA-OH Prepolymers on the Chain Extension[a]

HO-PBA-OH	The chain extended PBA M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	M_w/M_n (GPC)
PBA-1	17,500	44,800	2.56
PBA-2	26,600	54,400	2.05
PBA-3	32,800	65,200	1.99
PBA-4	24,800	58,200	2.35

[a] ABC/HO-PBA-OH molar ratio: 1.0; Reaction temperature: 240°C; Reaction time: 1.5 h.

TABLE IV
Chain Extension of HO-PBA-OH with TBC[a]

		The chain extended PBA		
TBC/HO-PBA-OH (molar ratio)	Reaction temperature (°C)	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	M_w/M_n (GPC)
1.1	200	25,000	61,700	2.47
0.8	220	30,400	63,600	2.09
1.0	220	50,700	109,700	2.16
1.1	220	38,600	88,200	2.28
1.2	220	31,000	65,400	2.11
1.1	240	20,200	86,000	4.26

[a] HO-PBA-OH: PBA-4; Reaction time: 1.5 h.

TSA was added and the reaction temperature was at 220°C.

Two chain extended PBA samples obtained with ABC and TBC respectively, were used to determine the reaction fraction of the chain extenders in the chain extension. The chain-extended polyesters obtained were dissolved with 20 mL $HCCl_3$ and precipitated with 200 mL methanol. The precipitate was filtered with G5 sintered glass funnel and the clear filtrate obtained was rotatorily evaporated under reduced pressure. For chain extension of 5.0 g PBA-6 or PBA-5 with the molar ratio of ABC or TBC to HO-PBA-OH at 1.0 and 0.20 wt % of *p*-TSA present, after the dissolving-precipitation and the rotary evaporation of the filtrate, about 0.2–0.3 g solid residues was obtained. Figure 1 showed the FTIR spectra of the residues obtained. Figure 1(a) was the IR spectrum of the residue after the treatment of the chain extended PBA with ABC as chain extender. It was found that no characteristic peaks of ABC were showed at 1703 and 1677 cm^{-1}. Similarly in Figure 1(b), no characteristic peaks of TBC were showed at 1715 and 1681 cm^{-1}, even though a weak shoulder peak corresponding to the caprolactam formed in the chain extension emerged at 1664.0 cm^{-1}. In Figure 1(a, b), the stretching vibration of the carbonyl group in the ester linkage of PBA oligomers was the strongest. The residues were mainly the PBA oligomers. So we think the reaction fraction of the chain extenders in the chain extension is nearly 100%.

Table VI showed the comparison between the blank reaction and the chain extension of HO-PBA-OH using ABC as chain extender with or without *p*-TSA catalysis. It was found that when ABC was absent, PBA with high molecular weight was not obtained. Under the same chain extending conditions without ABC, the M_n and M_w of PBA were only increased to some extent from the original PBA-6. The increase was just resulted from the reaction and the ester formation between the terminal HO— groups and the residual —COOH groups of the HO-PBA-OH. *p*-TSA also had some catalyzing effect in the blank reaction because of its high acidity. So, whether the *p*-TSA catalyst was present or not, the chain extending effect of ABC is obvious.

Table VII showed the chain extension of HO-PBS-OH using ABC or TBC as chain-extender with and without the presence of *p*-TSA. The intrinsic viscosity of starting material HO-PBS-OH is 0.37 dL/g. After the chain extension, [η] of PBS increased remarkably and the chain-extended PBS with [η] of 0.83–1.25 dL/g was obtained. From Table VII, it was also showed that in the same chain extension time, the [η] of PBS obtained in the *p*-TSA catalyzed chain extension is lower than that in the noncatalyzed one, with either ABC or TBC as chain extender. The reason might be

TABLE V
Catalyzed Chain Extension of HO-PBA-OH with ABC[a]

		The chain extended PBA		
Reaction temperature (°C)	Catalyst	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	M_w/M_n (GPC)
180	CH_3—Φ—SO_3H	17,200	62,000	3.60
200	CH_3—Φ—SO_3H	26,800	88,600	3.31
220	–	23,800	50,400	2.12
	CH_3—Φ—SO_3H	30,600	74,000	2.42
	$SnCl_4$	25,900	70,900	2.74
	$Zn(acac)_2$	26,400	61,900	2.34
240	CH_3—Φ—SO_3H	14,800	61,500	4.16

[a] ABC/PBA-5 molar ratio: 1.0; Catalyst: 0.20 wt %; Reaction time: 1.5 h.

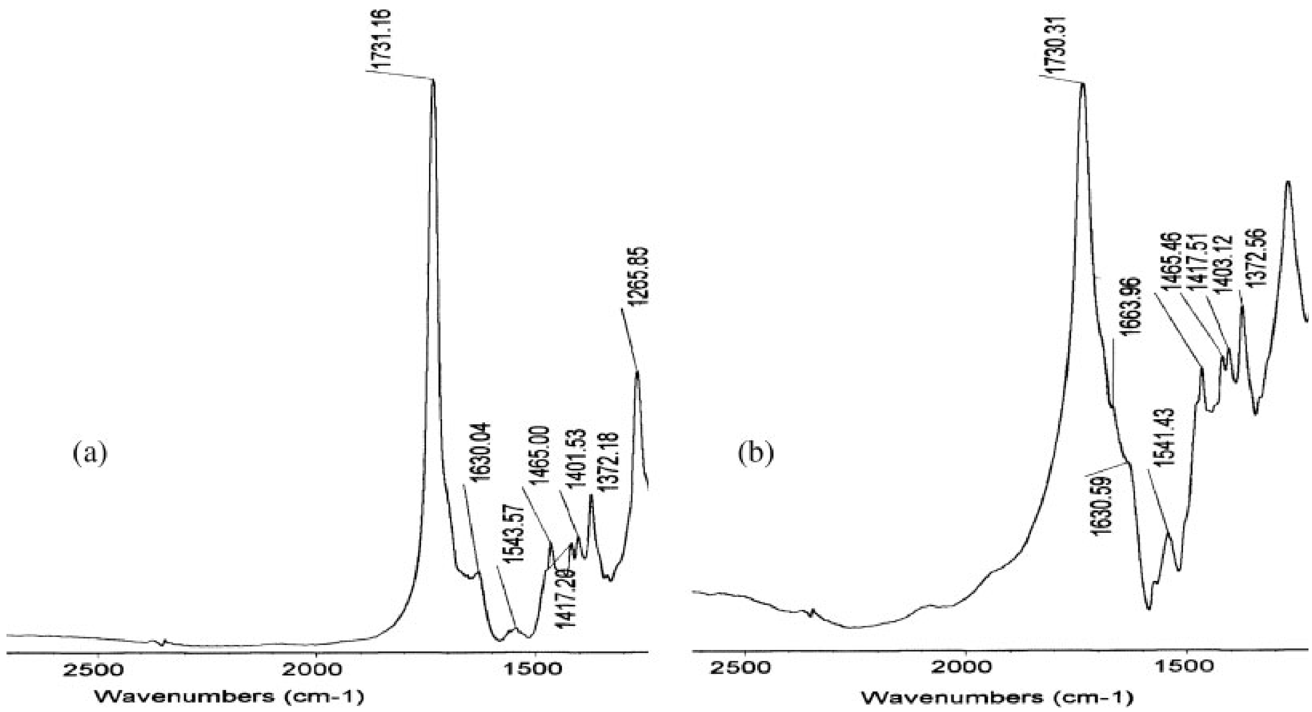


Figure 1 IR spectra of the residues of the filtrates from the dissolving-precipitation of the chain extended PBA and the filtration. [The chain extended PBA used in (a) was prepared at: ABC/PBA-6 molar ratio: 1.0; Catalyst: 0.20 wt %; Reaction temperature: 220°C; Reaction time: 1.5 h. Its M_n is 30,300, and M_w is 125,700. The chain extended PBA used in (b) was prepared at: TBC/PBA-5 molar ratio: 1.0; Catalyst: 0.20 wt %; Reaction temperature: 220°C; Reaction time: 1.5 h. Its M_n is 30,500, and M_w is 63,400.]

that *p*-TSA caused some side reactions such as thermal decomposition and so on. The side reactions are now under investigation. From Table VII and the phenomenon of the viscosity increasing of the chain extension, it was found that the chain extension with TBC as chain extender is faster than that with ABC. Loontjens et al.[9] had studied the reaction of 2-hydroxyethylbenzoate (HEB, a model compound of polyethylene terephthalate) with 1,3-isophthaloyl biscaprolactamate (IBC) and 5-nitro-isophthaloyl biscaprolactamate (5-nitro-IBC) at 120–150°C. They found that the reaction with 5-nitro-IBC having electron-withdrawing substituent had higher activation energy, and proceeded faster than that with IBC at higher temperature. In the chain extension of HO-terminated polyesters with ABC and TBC, the —$(CH_2)_4$— in ABC is an electron-donating group and the —C_6H_4— in TBC is an electron-withdrawing group. So, when the chain extension of HO-PBS-OH was carried out at 220°C, TBC has higher reactivity than ABC. The chain extension with TBC is faster than that with ABC.

Loontjens et al.[9] also studied the reaction process of HEB with IBC, and found that the HEB units were connected by the 1,3-isophthaloyl structure in IBC, meanwhile the caprolactam groups in chain extender were eliminated. To probe the chain extension way of HO-PBA-OH or HO-PBS-OH with ABC or TBC in the temperature range from 200 to 240°C, with or without the presence of *p*-TSA, we characterized the chain-extended PBA with ^{1}H-NMR and IR spectra. Figure 2

TABLE VI
Comparison Between the Blank Reaction and the Chain Extension of HO-PBA-OH Under the Chain Extension Conditions[a]

		The chain extended PBA		
ABC/PBA-6 (molar ratio)	CH_3—Φ—SO_3H (%)	M_n (GPC) (g/mol)	M_w (GPC) (g/mol)	M_w/M_n (GPC)
–	–	5,970	10,500	1.76
–	0.20	6,730	13,200	1.96
1.0	–	29,300	54,300	1.85
1.0	0.20	30,300	125,700	4.15

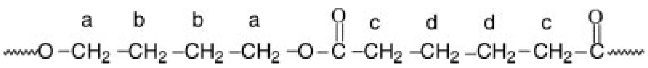
[a] PBA-6: 5.0 g; Reaction temperature: 220°C; Reaction time: 1.5 h.

TABLE VII
Chain Extension of HO-PBS-OH with ABC and TBC[a]

Chain-extender	$CH_3-\Phi-SO_3H$ (wt %)	Reaction time (min)	[η] (dL/g)
ABC	–	90	1.25
ABC	0.13	90	1.18
TBC	–	40	1.07
TBC	0.13	40	0.83

[a] Chain extender/HO-PBS-OH molar ratio: 1.0; Reaction temperature: 220°C.

showed the ^{1}H-NMR and IR spectrum of the chain-extended PBA obtained in the absence of any catalyst with ABC as chain-extender. In Figure 2(a), the peaks at 4.07 and 1.68 ppm were assigned to a- and b-CH_2— hydrogens of the butylene units; the peaks at 2.31 and 1.64 ppm were assigned to the c- and d-CH_2— hydrogens of the adipoyl structure. This ^{1}H-NMR spectrum is almost the same as that of PBA in the literature.[20] The area ratio of the a-, b-, c- and d-CH_2— in Figure 2(a) is exactly 1 : 1 : 1 : 1. The peak at 7.24 ppm was resulted from the $HCCl_3$ impurity in the $CDCl_3$ solvent. No peaks correspondent to the amide groups or caprolactam groups that resulted from the chain-extenders and possibly remained in the final polyester as constitutional units in main chains or as terminal groups were found in the ^{1}H-NMR spectrum.



In Figure 2(b), the broad peak at 3438.2 cm^{-1} was assigned to the stretching vibration of the —OH groups which resulted from the HO-PBA-OH prepolymers and still remained in the final chain-extended polyesters as terminal groups. The peak at 2954.1 cm^{-1}corresponds to the stretching vibration of C—H bonds in the —CH_2— groups. A characteristic peak at 1728.8 cm^{-1} was assigned to the stretching vibration of the C═O groups in the ester linkages of the chain-extended PBA. No evidence of the presence of the amide groups that resulted from the caprolactam rings in ABC by ring opening reaction was found in the IR spectrum.

Figure 3(a,b) showed the ^{1}H-NMR and IR spectrum of the chain-extended PBA obtained with ABC as chain-extender in the presence of *p*-TSA. It was revealed that the chain-extended PBA obtained through the *p*-TSA catalyzed chain extension had almost the same structure as that obtained through the noncatalyzed reaction. Figures 2 and 3 all correspond to the exact PBA structure. So the *p*-TSA catalyzed chain extension as well as the noncatalyzed one has almost the same chain-extending way. Even though the reaction temperature was higher than 200°C, and whether the *p*-TSA catalyst was present or not, the chain extension of HO-PBA-OH or HO-PBS-OH with ABC or TBC proceeds through the elimination of caprolactam rings in the chain-extenders, and the adipoyl groups or terephthaloyl groups couple the hydroxyl-terminated PBA or PBS together. Meanwhile the molecular weight of the polyesters increases obviously. The chain-extending reaction of HO-PBA-OH with ABC was showed as follows (Scheme 1).

DSC study of the HO-PBA-OH and the chain-extended PBA

HO-PBA-OH and the chain-extended PBA were also characterized by DSC spectra. The melting point (T_m) of PBA-2 is at 55.1°C. After the chain-extending reaction with ABC, the T_m of the chain-extended PBA (M_n, 26,600; M_w, 54,400) is at 58.5, 3.4°C higher than that of the original PBA-2. As the chain extension proceeds, the adipoyl groups of the ABC molecules couple the PBA segments of the HO-PBA-OH, with the

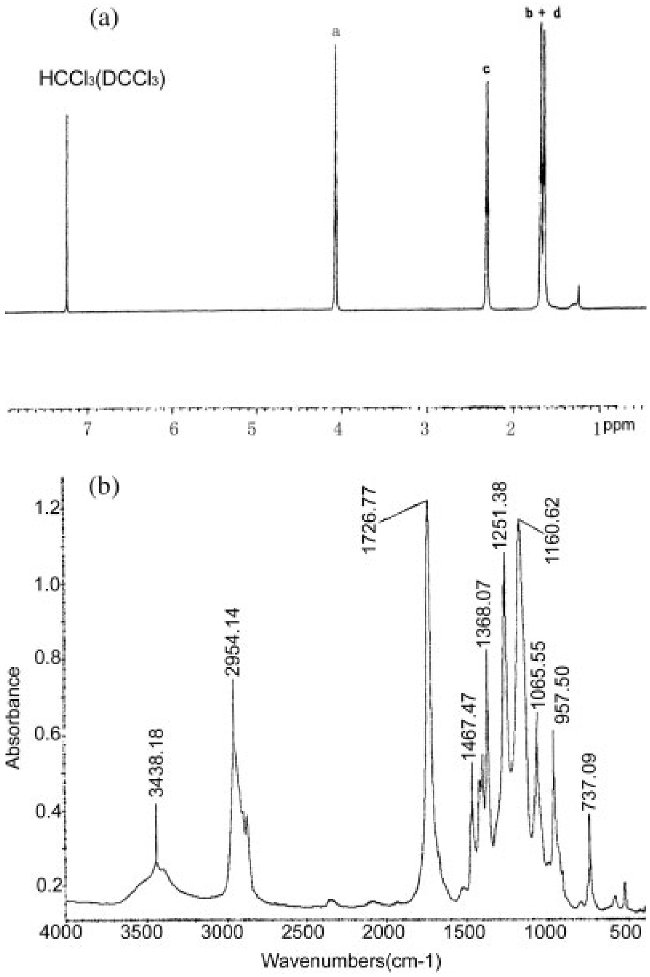


Figure 2 ^{1}H-NMR spectrum (a) and IR spectrum (b) of the chain-extended PBA (M_n, 26,600; M_w, 54,400; prepared at ABC/PBA-2 molar ratio of 1.0).

molecular weight of PBA increased. Meanwhile, the regularity of the PBA is not destroyed, because the adipoyl groups resulted from the ABC molecules are identical to the adipoyl structures in the original HO-PBA-OH. So the T_m of the chain-extended PBA is higher than that of the original HO-PBA-OH. The increase of the T_m after chain extension with ABC is just ascribed to the increase of the molecular weight.

Mita and Suzuki[12] had studied the chain extension of PBS with TBC. The PBS prepolymer used had M_n over 18,000, so after the chain extension, the melting point of the chain-extended PBS is 115°C, almost the same as that of the PBS prepolymer. In this article, we also characterized the chain-extended PBA obtained using TBC as chain-extender with DSC spectra. The T_m of PBA-4 is at 57.9°C. But after the chain-extending reaction with TBC, the T_m of the chain-extended PBA (M_n, 50,700; M_w, 109,700) is at 54.1, 3.8°C lower than that of the original PBA-4. The reason is that the terephthalate ester linkages introduced by TBC are different from the adipate ester linkages already present in the HO-PBA-OH prepolymers, meanwhile the molecular weight of the HO-PBA-OH prepolymers is not high enough. As the chain extension proceeds, the terephthaloyl groups in TBC molecules couple the PBA segments of the HO-PBA-OH with terephthalate

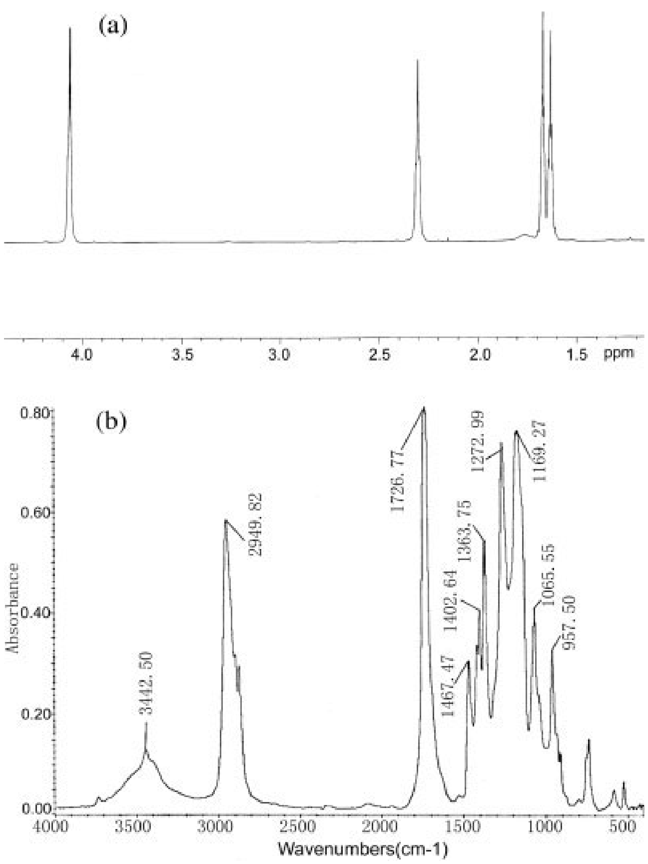
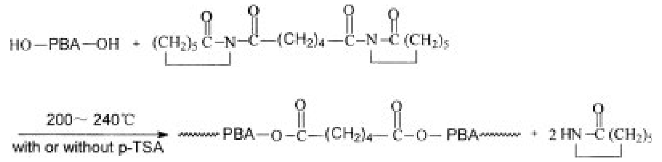


Figure 3 ^{1}H-NMR spectrum (a) and IR spectrum (b) of the chain-extended PBA (M_n, 30,600; M_w, 74,000; prepared at ABC/PBA-5 molar ratio of 1.0 and p-TSA of 0.20 wt %).



Scheme 1 The chain extension of HO-PBA-OH with ABC with or without the p-TSA catalyst.

ester linkages, with the molecular weight of PBA increased. Even though PBA-4 had M_n of 6450, the molecular weight of PBA-4 was perhaps not high enough. When the terephthaloyl groups were introduced as terephthalate ester linkages into the PBA, the regularity of the chain-extended PBA decreased. So the T_m of the chain-extended PBA obtained with TBC as chain-extender is lower than that of the HO-PBA-OH prepolymer.

CONCLUSIONS

Aliphatic polyesters such as PBA and PBS with high molecular weight were successfully synthesized through a chain extension of HO-PBA-OH or HO-PBS-OH with ABC or TBC as chain-extenders. The chain extension was promoted by p-toluenesulfonic acid, $SnCl_4$ and $Zn(acac)_2$. At the optimal conditions, PBA with M_n up to 32,800 and M_n up to 50,700 was synthesized with ABC or TBC as chain-extender respectively. Chain-extended PBS with intrinsic viscosity of 0.87–1.25 dL/g was also obtained. Even though the reaction temperature was higher than 200°C, with or without the presence of p-toluenesulfonic acid, the chain extension proceeds through the elimination of caprolactam rings in the chain-extenders, and the adipoyl or terephthaloyl groups couple the HO-terminated PBA or PBS prepolymers together, making the molecular weight of the polymers increased. The regularity of the obtained PBA is not destroyed through the chain extension with ABC and is lowered through the chain extension with TBC, due to the identity of the adipoyl structure introduced from ABC and the difference of the terephthalate ester linkages introduced from TBC to the adipoyl structures in the original HO-PBA-OH prepolymers. For the chain extension with TBC, the molecular weight of the prepolymers was not high enough is also an important reason. Melting point of the chain-extended PBA obtained with ABC is higher than that of the original HO-PBA-OH. Otherwise, melting point of the chain-extended PBA with TBC as chain-extender is lower than that of the original HO-PBA-OH.

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