

Synthesis of Aliphatic Polyesters by a Chain-Extending Reaction with Octamethylcyclotetrasilazane and Hexaphenylcyclotrisilazane as Chain Extenders

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ABSTRACT: Aliphatic HO-terminated polyesters such as poly(diethylene glycol adipate) (PDEGA), poly(ethylene adipate) (PEA), and poly(butylene succinate) (PBS) with molecular weight from 1247 to 1948 were synthesized through condensation polymerization from adipic acid or butanedioic acid with excess diethylene glycol, ethylene glycol, or butylene glycol. From the HO-terminated polyesters, polyesters with high molecular weight were synthesized by a chain-extending reaction with octamethylcyclotetrasilazane (OMCT) or hexaphenylcyclotrisilazane (HPCT) as chain-extenders. Gel permeation chromatography (GPC) characterization shows that the M_n of chain-extended PDEGA is from 12,644 to 32,870, M_w is from 22,786 to 70,048; M_n of chain-extended PEA is 11,368, M_w is 19,877; and the M_n of chain-extended PBS is from 9823 to 39,873, M_w is from 18,823 to 137,192. The chain-extended polyesters were also

characterized by $^1\text{H-NMR}$ spectrum, IR spectra, and DSC spectra. The multiple peaks at 7.37 and 7.67 ppm in the $^1\text{H-NMR}$ spectrum of chain-extended PDEGA and peaks at 3051.1 and 1593.4 cm^{-1} in the IR spectrum of the chain-extended PBS show the evidence of the $-\text{SiPh}_2-$ structure in the polyesters obtained from the chain-extending reaction. DSC study shows that the bulky $-\text{SiPh}_2-$ units introduced by the chain-extending reaction lower the regularity of the polyester chains, so the melting point of the chain-extended PBS and PEA decreases compared to that of the original HO-terminated PBS and PEA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3333–3337, 2004

Key words: biodegradable polyesters; polycondensation; heteroatom-containing polymer

INTRODUCTION

Condensation polymerization is a common method to synthesize polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), unsaturated polyester resin, alkyd resin, and polyesters with low molecular weight used in polyurethane. However, through common condensation polymerization, it is difficult to get aliphatic polyesters having high enough molecular weight to use as biodegradable plastics, due to the side reactions such as thermal degradation, thermal oxidation decomposition, and so on occurring in the condensation polymerization process. In recent years, aliphatic polyesters with high molecular weight were synthesized through chain-extending reaction from HO- or HOOC-terminated polyesters with diisocyanate,¹ tetracarboxylic dianhydride,² and diglycidyl³ as extenders. In this article, we used octamethylcyclotetrasilazane (OMCT) and hexa-

phenylcyclotrisilazane (HPCT) as chain extenders and synthesized poly(diethylene glycol adipate) (PDEGA), poly(ethylene adipate) (PEA), and poly(butylene succinate) (PBS) through a chain-extending reaction from HO-terminated polyesters with low molecular weight. The chain-extended polyesters obtained were characterized by gel permeation chromatography (GPC), IR spectrum, $^1\text{H-NMR}$ spectrum, and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Adipic acid (Beijing Chemical Plant, Beijing, China) and succinic acid (Guangdong Shantou Beining Chemical Plant, Shantou, China), obtained as common chemical reagents, were purified two times by crystallization before use. Ethylene glycol (Beijing Chemical Plant), diethylene glycol (Tianjin Beichen Huayve Chemical Reagent Plant, Tianjin, China), and 1,4-butanediol (First Shanghai Reagent Plant, Shanghai, China) were redistilled under reduced pressure. Dibutyltin oxide (Bu_2SnO , 99%) was purchased from Acros Co. and used directly. Octamethylcyclotetrasilazane, boiling point (bp) 220°C, and hexaphenylcyclotrisilazane, melting point (mp) 213°C, were prepared by aminolysis of Me_2SiCl_2 (Fourth Beijing Chemical

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TABLE I
Properties of the HO-Terminated Polyesters

HO-terminated polyesters	Acid value	Hydroxyl number	Molecular weight ^a (M_n)	M_n (GPC)	M_w (GPC)	M_w/M_n (GPC)
PDEGA-1	0.53	56.2	1948	3703	7063	1.91
PDEGA-2	0.83	82.4	1348	2429	4238	2.20
PEA	1.25	67.8	1626	3175	5646	1.78
PBS	0.50	89.8	1247	—	—	—

^a Molecular weight calculated from the hydroxyl number.

TABLE II
Chain-Extending Reaction of HO-Terminated PDEGA with OMCT^a

HO-terminated polyesters	Polyester/—SiMe ₂ —NH— (Molar ratio) ^b	M_n (GPC)	M_w (GPC)	M_w/M_n (GPC)
PDEGA-1	1 : 1.0	12679	22786	1.80
	1 : 1.2	28514	79538	2.79
	1 : 1.4	12644	22909	1.81
	1 : 1.6	28754	71174	2.48
PDEGA-2	1 : 1.4	32870	70048	2.13

^a Reaction temperature: 100°C.

^b Polyester/—SiMe₂—NH—molar ratio means the molar ratio of HO-terminated polyester to —SiMe₂—NH—in OMCT.

Plant, Beijing, China) and Ph₂SiCl₂ (Jilin Chemical Industrial Corp., Jilin, China), respectively.⁴

Synthesis of the HO-terminated polyesters

HO-terminated PDEGA was prepared in a 250-mL four-necked flask to which were added 43.8 g (0.30 mol) adipic acid, 33.3 mL (0.35 mol) diethylene glycol, 0.22 g dibutyltin oxide, and 0.08 g phosphorous acid. The mixture was mechanically stirred and heated under N₂ atmosphere to 150°C. During the reaction, the water formed was collected. The temperature was gradually raised to 190°C for 5 h, until 8 mL water formed was collected. At 190°C, the pressure in the flask was reduced in stages to 3 mmHg over a period of 3 h, and the excess glycol was distilled off. The acid value of the polyester obtained is 0.8, and the hydroxyl number is 52.4.

HO-terminated PEA and PBS were synthesized in a similar way as described above.

Chain-extending reaction of HO-terminated polyesters

Ten grams of HO-terminated polyester and OMCT or HPCT with a molar ratio (HO-terminated polyester/—SiR₂—NH—, R is Me or Ph) from 1 : 1.0 to 1 : 1.8 were stirred and heated under nitrogen to 100–140°C. The reaction was maintained for about 10 h until no ammonia was detected. The chain-extended polyester obtained was purified two times through dissolving-precipitation cycles before being detected by GPC, ¹H-NMR, FTIR, and DSC spectra.

Measurements

The M_n , M_w , and molecular weight distribution of the polyesters were measured by GPC on a Waters 150C spectrometer at 35°C by using THF as eluant and polystyrene as standards. ¹H-NMR spectrum was recorded on Varian Unity 200 spectrometer. FTIR spectra were recorded on a Nicolet 60SXB FTIR spectrometer. The DSC spectra were recorded on PE PYRIS I thermal analyzer.

TABLE III
Chain-Extending Reaction of HO-Terminated PDEGA and PEA with HPCT

HO-terminated polyesters	Polyester/—SiPh ₂ —NH— (molar ratio) ^a	M_n	M_w	M_w/M_n
PDEGA-1	1 : 1.0	14,738	25391	1.72
	1 : 1.2	24,293	41436	1.71
	1 : 1.4	30,728	62092	2.02
	1 : 1.6	11,368	19877	1.75
PEA	1 : 1.6	11,368	19877	1.75

^a Polyester/—SiPh₂—NH—molar ratio means the molar ratio of HO-terminated polyester to —SiPh₂—NH—in HPCT.

TABLE IV
Chain-Extending Reaction of HO-Terminated PBS with HPCT

HO-terminated polyester	Polyester/—SiPh ₂ —NH— (molar ratio) ^a	M _n (GPC)	M _w (GPC)	M _w /M _n (GPC)
PBS	1 : 1.0	9823	18,823	1.92
	1 : 1.2	22,536	64,910	2.88
	1 : 1.4	28,525	120,375	4.22
	1 : 1.6	35,804	134,237	3.75
	1 : 1.8	39,873	137,192	3.44

^a Polyester/—SiPh₂—NH—molar ratio means the molar ratio of HO-terminated polyester to—SiPh₂—NH—in HPCT.

RESULTS AND DISCUSSION

Synthesis of HO-terminated polyesters

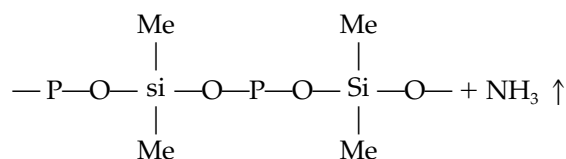
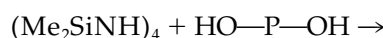
HO-terminated polyesters were synthesized by condensation polymerization of adipic acid or succinic acid with excess of glycols such as diethylene glycol, ethylene glycol, or 1,4-butanediol by using dibutyltin oxide as catalyst. To prevent the polyesters from thermal oxidation, the polymerization was carried out under nitrogen. Meanwhile, about 0.1% H₃PO₃ was added to purge trace of the oxygen in the system. Table I shows the properties of the HO-terminated polyesters such as PDEGA, PEA, and PBS synthesized by this method. It was found that the molecular weight of the HO-terminated polyesters calculated from the hydroxyl number is in the range from 1247 to 1948. 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 obtained in the chain-extending reaction.

Chain-extending reaction of HO-terminated polyesters

Chain-extending reaction of HO-terminated polyesters such as PDEGA, PEA, and PBS was carried out in bulk state by using octamethylcyclotetrasilazane or hexaphenylcyclotrisilazane as chain extending agents. Table II shows the results of chain-extending reaction of HO-terminated PDEGA with OMCT at different

molar ratios (HO-terminated polyester/—SiMe₂—NH—) from 1 : 1.0 to 1 : 1.6. It was found that the M_n and M_w of the chain-extended polyester are highly increased compared to that of the original HO-terminated PDEGA. The M_n of the extended PDEGA is from 12,644 to 32,870; the M_w is from 22,786 to 79,538, and the M_w/M_n is from 1.80 to 2.79.

The extending reaction was described as follows:



where HO—P—OH is the HO-terminated polyester.

From Table II, it was also found that excess OMCT from HO-terminated polyester/—SiMe₂—NH— molar ratio of 1 : 1.2 to 1 : 6 is favorable to get PDEGA with high molecular weight, perhaps because of the consumption of some extender to trace water or other HO-containing impurity in the system.

Table III shows the results of the chain-extending reaction of PDEGA by using HPCT as chain-extending agent. It was found that PDEGA with high molecular weight was obtained; meanwhile, excess —SiPh₂—NH— is also favorable to get high molecular weight. As the substituting groups on the Si atoms are phe-

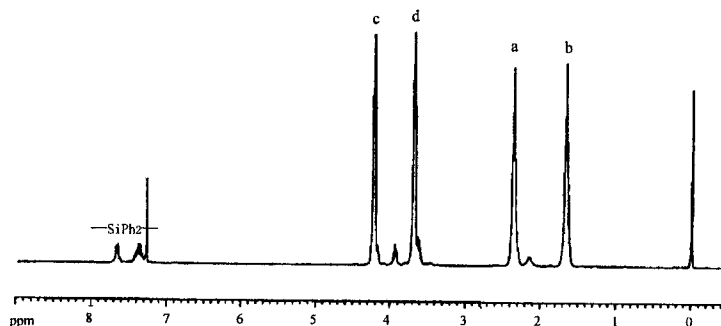


Figure 1 ¹H-NMR spectrum of chain-extended PDEGA by HPCT (M_n, 14,738; M_w, 25,391; HO-terminated PDEGA to —SiPh₂—NH— molar ratio is 1 : 1.0).

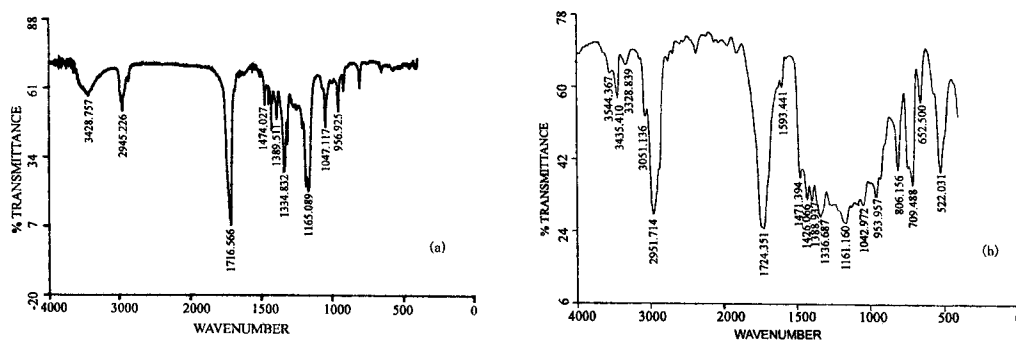


Figure 2 FTIR spectra of the HO-terminated PBS (a) and the chain-extended PBS (b) (M_n , 28,525; M_w , 120,375; HO-terminated PBS to $-\text{SiPh}_2-\text{NH}$ molar ratio is 1 : 1.4).

nyls, HPCT is less reactive than OMCT perhaps because of the d-p π character of the Ph—Si linkage and the location hindrance of Ph groups to Si—N linkage; the chain-extending reaction of HPCT was carried out at 120–140°C.

As the molar ratio of HO-terminated PDEGA to $-\text{SiPh}_2-\text{NH}-$ unit in HPCT decreased from 1 : 1.0 to 1 : 1.4, the M_n increased from 14,738 to 30,728; the M_w increased from 25,391 to 62,092, and the M_w/M_n increased from 1.71 to 2.02. By this chain-extending reaction, PEA with M_n up to 11,368 and M_w up to 19,877 can also be synthesized.

Table IV shows the chain-extending reaction of HO-terminated PBS with chain-extending agent HPCT. It was found that the excess of $-\text{SiPh}_2-\text{NH}-$ is also favorable to get high molecular weight of PBS. As the molar ratio of HO-terminated PBS to $-\text{SiPh}_2-\text{NH}-$ decreased from 1 : 1.0 to 1 : 1.8, the M_n increases from 9823 to 39,873, M_w increases from 18,823 to 137,192.

M_w/M_n up to 4.22 reveals the less uniformity of the extending reaction due to the high viscosity in the last period in bulk reaction state.

Characterization of the chain-extended polyesters

The chain-extended polyesters were also characterized by $^1\text{H-NMR}$ spectrum, IR spectra, and DSC spectra. Figure 1 shows the $^1\text{H-NMR}$ spectrum of the chain-extended PDEGA. In Figure 1, peaks at 1.68 and 2.38 ppm correspond to the hydrogens of b— CH_2 and a— CH_2 — in the adipoyl structure; peaks at 3.70 and 4.24 ppm correspond to the hydrogens of d— CH_2 — and c— CH_2 — in the ethylene units. The multiple peaks at 7.37 and 7.67 ppm correspond to the phenyl groups in the $-\text{SiPh}_2-$ units introduced by the chain-extending reaction. $^1\text{H-NMR}$ spectrum shows evidence of the presence of $-\text{SiPh}_2-$ structure in the chain-extended PDEGA.

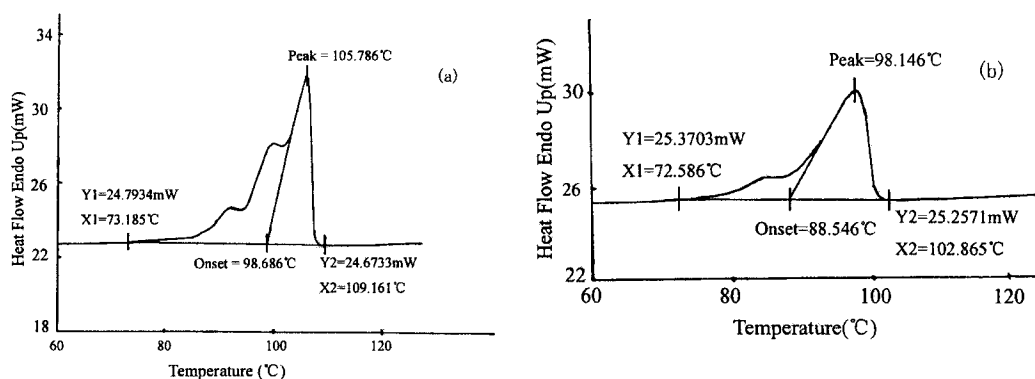
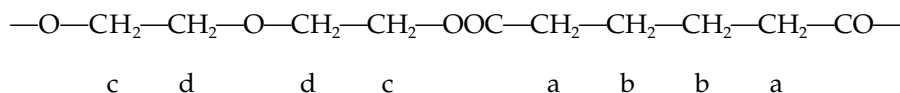


Figure 3 DSC spectra of HO-terminated PBS (a) and chain-extended PBS (b) (M_n , 28,525; M_w , 120,375; HO-terminated PBS to $-\text{SiPh}_2-\text{NH}$ molar ratio is 1 : 1.4).

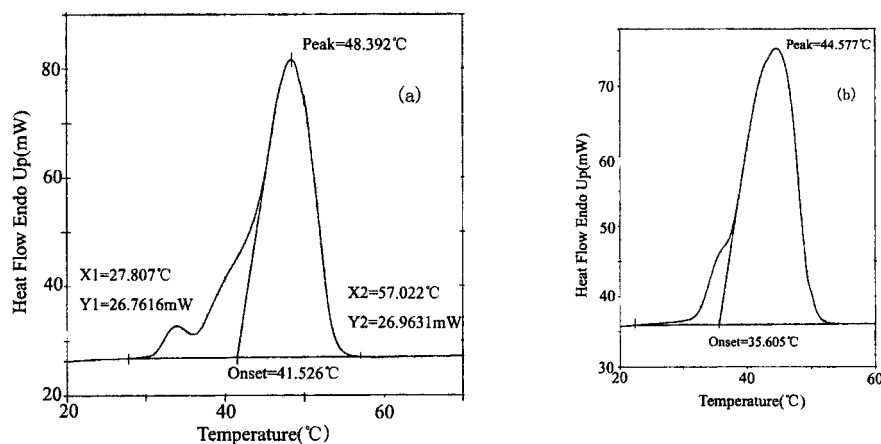


Figure 4 DSC spectra of HO-terminated PEA (a) and chain-extended PEA (b) (M_n , 11,368; M_w , 19,877; HO-terminated PEA to $-\text{SiPh}_2-\text{NH}$ molar ratio is 1 : 1.6).

Figure 2(a) is the FTIR spectrum of the HO-terminated PBS, in which a broad peak corresponding to O—H stretching vibration of the HO-terminal groups appears at 3428.8 cm^{-1} . After the chain-extending reaction [in Fig. 2(b)], this peak became narrow; meanwhile, other peaks such as 3051.1 and 1593.4 cm^{-1} , which correspond to the C—H and C=C stretching vibrations of phenyl groups, respectively, show the evidence of the presence of $-\text{SiPh}_2-$ groups in the chain-extended PBS.

Figure 3(a) shows the DSC spectrum of the original HO-terminated PBS; its melting point is at 105.8°C , lower than the 115°C reported in the literature^{5–7} because of its low molecular weight. Figure 3(b) shows the DSC spectrum of the chain-extended PBS obtained at 1 : 1.4 molar ratio of the HO-terminated polyester to $-\text{SiPh}_2-\text{NH}-$; its melting point is at 98.1°C . As the molar ratio of the HO-terminated polyester to $-\text{SiPh}_2-\text{NH}-$ decreased further to 1 : 1.6, the melting point of the chain-extended PBS is just 93.8°C .

Similarly, even though the melting point of the original HO-terminated PEA is 48.4°C [Fig. 4(a)], that of the chain-extended PEA is just 44.6°C [Fig. 4(b)]. The reason for this phenomenon is that the bulky $-\text{SiPh}_2-$ units introduced by the chain-extending reaction lower the regularity of the polyester chains; so the crystallinity and the melting point of the chain-extended polyesters decrease.

CONCLUSION

Polyesters such as PDEGA, PEA, and PBS with high molecular weight can be synthesized through chain-extending reaction from HO-terminated PDEGA, PEA, and PBS, respectively, by using OMCT or HPCT as chain extender. In the chain-extended polyesters, the $-\text{SiPh}_2-$ units introduced were detected by $^1\text{H-NMR}$ spectrum and IR spectra. DSC study shows that the T_m of PEA and PBS is lower than that of the original HO-terminated PEA and PBS because the bulky $-\text{SiPh}_2-$ units introduced by the chain-extending reaction lower the regularity and crystallinity of the polymer chains.

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