

Preparation and Characterization of Poly(silyl ester)s Containing 2,2-Bis(*p*-dimethylsiloxy-phenyl)propane Units in the Polymer Backbones

Nianfeng Han, Zonglin Liu, Liqiang Jin, Yun Yue

School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, People's Republic of China

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ABSTRACT: The two poly(silyl ester)s containing 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbones have been prepared via polycondensation reaction of di-*tert*-butyl adipate and di-*tert*-butyl fumarate with 2,2-bis(*p*-chloro dimethylsiloxy-phenyl)propane to give *tert*-butyl chloride as the condensate. The polymerizations were performed under nitrogen at 110°C for 24 h without addition of solvents and catalysts to obtain the poly(silyl ester)s with weight average molecular weights typically ranging from 5000 to 10,000 g/mol. Characterization of the poly(silyl ester)s included ¹H NMR and ¹³C NMR spectroscopies, infrared spectroscopy, ultraviolet spectroscopy, differential

scanning calorimetry, thermogravimetric analysis (TGA), gel permeation chromatography, and Ubbelohde viscometer. The glass transition temperatures (T_g) of the obtained polymers were above zero because of the introducing 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbones. The TGA/DTG results showed that the obtained poly(silyl ester)s were stable up to 180°C and the residual weight percent at 800°C were 18 and 9%, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1937–1942, 2006

Key words: poly(silyl ester); bisphenol A; 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units; polycondensation

INTRODUCTION

Poly(silyl ester)s are being investigated as a new degradable material with the potential for an extremely broad range of degradation behavior through variation in the silicon side chain substituents, the backbone composition adjacent to the silicon atoms, or the backbone composition adjacent to the carbonyl moieties.^{1–4} Karen Wooley and coworkers have reported several routes to synthesize poly(silyl ester)s including transsilylation reaction,^{5–8} hydrosilylation reaction,^{9,10} and crossdehydrocoupling polymerizations.^{11,12} In a previous study,¹³ we reported a route to synthesize poly(silyl ester)s via the polycondensation reaction of di-*tert*-butyl ester of dicarboxylic acid with dichlorosilane by eliminating *tert*-butyl chloride as a driving force.

In the design of degradable materials, the physical and mechanical properties must be considered for performance in serving the expected function. Bisphenol A is an important industrial intermediate, which is among the cheapest and most used intermediates in macromolecular synthesis, especially in the preparation of polycarbonates^{14–16} and epoxy resins.^{17,18} To change the

properties of the poly(silyl ester)s, we firstly introduce bisphenol A moiety into the polymer backbones, where the silicon atoms are connected by phenoxy, causing an increase in the electrophilicity of the silicon. So the poly(silyl ester)s are more susceptible toward nucleophilic attack in comparison to the corresponding poly(silyl ester)s based upon disiloxane monomers, and more importantly, the 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the poly(silyl ester)s increase the T_g by decreasing the flexibility of the polymer. The poly(silyl ester)s with high T_g are expected to possess good mechanical properties and have more potential applications in some advanced technology.

In this work, we firstly prepared 2,2-bis(*p*-chlorodimethylsiloxy-phenyl)propane by the reaction of bisphenol A with dimethyldichlorosilane, and then the new poly(silyl ester)s containing 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbones were synthesized via polycondensation reaction of 2,2-bis(*p*-chlorodimethylsiloxy-phenyl)propane with di-*tert*-butyl adipate and di-*tert*-butyl fumarate respectively. The synthesis routes are as follows.

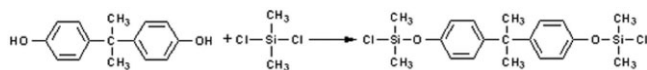
Correspondence to: Z. Liu (Liuzl@sdu.edu.cn).

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EXPERIMENTAL

Equipments

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer with the sol-



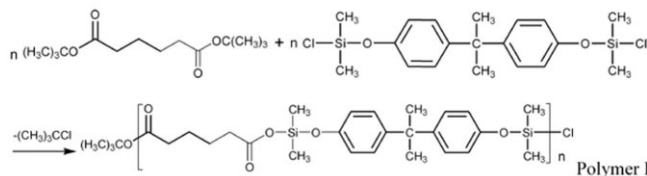
Scheme 1

vent proton and carbon signals as standards, respectively. IR spectra were obtained on a Nicolet FTIR 20SX spectrometer as solid on KBr pellets.

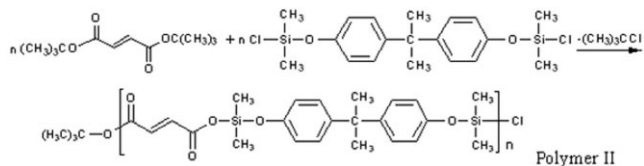
Thermogravimetric analyses (TGA) were carried out using a TGA/SDTA-851 (METTLER TOLEDO, Switzerland) to investigate the thermal properties of samples. The samples were heated from 35 to 800°C at a rate of 10°C/min in an inert atmosphere of nitrogen. The glass transition temperatures of the polymers (T_g) were examined by differential scanning calorimetry (DSC) (DSC 822^e METTLER TOLEDO), at a rate of 10°C/min. The gel permeation chromatography (GPC) analysis of poly(silyl ester)s was performed by using a system consisting of a Waters 515 pump, two Waters styragel columns (HT3, HT4), and a Waters 2414 refractive index detector (Waters Chromatography Division/Millipore, Milford, MA) and shipped in tetrahydrofuran (THF). The system was calibrated using narrow molecular weight polystyrene standards. Ultraviolet (UV) spectra were examined on a Perkin-Elmer UV Spectrophotometer (Lambda 35) with 20 mg, 10 mL product solution in THF. The intrinsic viscosity values of the polymers were measured with an Ubbelohde viscometer in THF at (30.00 ± 0.05)°C.

Materials

Adipic acid and fumaric acid were obtained from Tianjin Fuchen Reagent Factory (Tianjin, China), and purified by vacuum evaporation prior to use. Bisphenol A was purchased from Shanghai Reagent Company (Shanghai, China) and recrystallized twice from toluene. Dimethyldichlorosilane was purchased from Shanghai Yuanfan Reagent Company (Shanghai, China) and distilled prior to use. Thionyl chloride was purchased from Tianjin Reagent Factory (Tianjin, China) and was purified by distillation prior to use. THF was purchased from Tianjin Reagent Factory (Tianjin, China), and distilled in the presence of sodium/benzophenone. *tert*-butyl alcohol was obtained from Tianjin Reagent Factory (Tianjin, China) and distilled in the presence of sodium.



Scheme 2



Scheme 3

Synthesis of the monomers

Di-*tert*-butyl adipate¹⁹

A mixture of 9.52 g (65.2 mmol) adipic acid and 20 mL (275 mmol) thionyl chloride was heated at gentle reflux for 2.5 h followed by distillation to generate adipoyl chloride. The adipic chloride was added dropwise to a stirring mixture of *N,N*-dimethyl aniline (26 mL) and *tert*-butyl alcohol (20 mL) in anhydrous ether. This mixture was stirred vigorously for an additional 20 h at room temperature, and then it was put into the saturated brine. The product was isolated by extraction with ether followed by distillation under reduced pressures [bp, 140–145°C (10 mmHg)], affording 13.3 g of di-*tert*-butyl adipate as a low-melting solid (mp, 29–31°C) with 80% yield.

¹H NMR (CDCl₃, δ ppm): 1.38 (s, 18H, (CH₃)₃), 2.16 (t, 4H, CH₂C=O), 1.4–1.6 (m, 4H, CH₂CH₂C=O).

Di-*tert*-butyl fumarate²⁰

Di-*tert*-butyl fumarate was synthesized by mixing 36 g fumaryl chloride and 4.2 g sodium *tert*-butoxide in freshly dried 200 mL *tert*-butyl alcohol followed by vigorously stirring for 20 h at room temperature. The solution was poured into water and then extracted with ether. The resulting extract was dried with anhydrous magnesium sulfate and evaporated. The pure product was obtained by sublimation, affording 11.1 g of di-*tert*-butyl fumarate (mp, 67–68°C) with 21% yield.

¹H NMR (CDCl₃, δ ppm): 6.66 (s, 2H, CH=CH), 1.5 (s, 18H, CH₃).

2,2-Bis(*p*-chlorodimethylsiloxy-phenyl)propane

Bisphenol A (7.55 g, 33 mmol) was added to a 100-mL four-necked round-bottomed flask. The flask was equipped with a mechanical stirrer, a reflux condenser equipped with a drying tube of calcium chloride, a constant pressure dropping funnel, and a nitrogen inlet tube. After the flask was full of nitrogen atmosphere for 30 min, 7.97 mL (66 mmol) dimethyldichlorosilane was dropped into the flask from the constant pressure dropping funnel and 20 mL THF was added into the flask. The reaction was typically allowed to stir under nitrogen and gently refluxed for 4 h. The

solvent was removed under reduced pressure and the product was obtained.

^1H NMR (CDCl_3 , δ ppm): 6.78–6.91 (m, 4H, aromatic protons), 7.04–7.17 (m, 4H, aromatic protons), 1.64 (s, 6H, $\text{C}(\text{CH}_3)_2$), 0.61 (s, 12H, $\text{Si}(\text{CH}_3)_2$).

Synthesis of the poly(silyl ester)s

Poly[2,2-bis(*p*-dimethylsiloxy-phenyl)propane adipate] (I)

2,2-Bis(*p*-chlorodimethylsiloxy-phenyl)propane (4.02 g, 9.72 mmol) and di-*tert*-butyl adipate (2.51 g, 9.72 mmol) were successively introduced into a 25-mL round-bottomed flask. The flask was equipped with an electromagnetic stirrer, a reflux condenser equipped with a drying tube of calcium chloride, a nitrogen inlet tube, and a thermometer. The reaction was typically allowed to stir under nitrogen at 110°C for 24 h. During the polymerization, the *tert*-butyl chloride was removed by evaporation.

^1H NMR (deuteroacetone, δ ppm): 6.77–6.83 (m, 4H, aromatic protons), 7.08–7.10 (m, 4H, aromatic protons), 1.58 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.62–1.66 (t, 4H, COCH_2CH_2), 2.29–2.34 (t, 4H, COCH_2CH_2), 0.33 (s, 12H, $\text{Si}(\text{CH}_3)_2$), 2.05 (s, solvent); ^{13}C NMR (deuteroacetone, δ ppm): 118.7 (aromatic), 127.17 (aromatic), 143.87 (aromatic), 151.46 (aromatic), 173.34 ($\text{C}=\text{O}$), 23.76 (COCH_2CH_2), 32.54 (COCH_2CH_2), 29.09 $\text{C}(\text{CH}_3)_2$, 41.06 $\text{C}(\text{CH}_3)_2$, -3.38 ($\text{Si}(\text{CH}_3)_2$), 28.7 (solvent); IR, KBr (cm^{-1}): 3034, 2964, 2872, 1693, 1462, 1407, 1361, 1268, 1082, 1014, 929, 555.

Poly[2,2-bis(*p*-dimethylsiloxy-phenyl)propane fumarate] (II)

2,2-Bis(*p*-chlorodimethylsiloxy-phenyl)propane (2.18 g, 5.27 mmol) and di-*tert*-butyl fumarate (1.20 g, 5.27 mmol) were successively introduced into a 25-mL round-bottomed flask. The flask was equipped with an electromagnetic stirrer, a reflux condenser equipped with a drying tube of calcium chloride, a nitrogen inlet tube, and a thermometer. The reaction was typically allowed to stir under nitrogen at 110°C

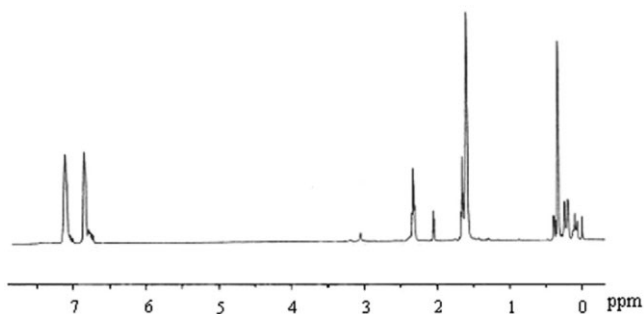


Figure 1 ^1H NMR spectrum of polymer I.

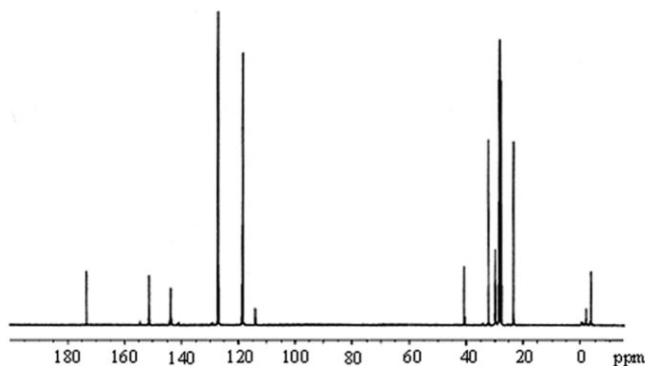


Figure 2 ^{13}C NMR spectrum of polymer I.

for 24 h. During the polymerization, the *tert*-butyl chloride was removed by evaporation.

^1H NMR (deuteroacetone, δ ppm): 6.70 (s, 2H, $\text{CH}=\text{CH}$), 7.03–7.12 (m, 4H, aromatic protons), 6.83–6.84 (m, 4H, aromatic protons), 1.58 (s, 6H, $\text{C}(\text{CH}_3)_2$), 0.34 (s, 12H, $\text{Si}(\text{CH}_3)_2$), 2.05 (s, solvent); ^{13}C NMR (deuteroacetone, δ ppm): 114.1 (aromatic), 127.0 (aromatic), 143.8 (aromatic), 154.5 (aromatic), 133.27 ($\text{CH}=\text{CH}$), 164.67 ($\text{C}=\text{O}$), 30.07 ($\text{C}(\text{CH}_3)_2$), 41.06 ($\text{C}(\text{CH}_3)_2$), -3.43 ($\text{Si}(\text{CH}_3)_2$), 28.7 (solvent); IR, KBr (cm^{-1}): 3083, 3034, 2966, 2871, 1702, 1606, 1508, 1261, 1082, 1014, 931, 838–805.

RESULTS AND DISCUSSION

Poly(silyl ester)s with 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbone have been synthesized via polycondensation reaction of di-*tert*-butyl adipate or di-*tert*-butyl fumarate with 2,2-bis(*p*-chlorodimethyl siloxy-phenyl)propane, respectively. the reaction mixtures were heated at $\sim 110^\circ\text{C}$ under a nitrogen atmosphere for 24 h without the addition of solvent and catalyst. the polymerizations were proved by ^1H nmr spectrum. the conversion of the chlorosilane monomers to silyl esters could be observed by upfield shifts in the resonances for the silyl methyl proton peak according to the ^1H nmr spectrum. because of the moisture sensitivity of poly(silyl ester)s, the crude polymers were characterized without purification.^{1,2,5,8,9,11}

Structural characterization

The chemical structure of the poly(silyl ester)s were confirmed by ^1H NMR, ^{13}C NMR, FTIR, and UV analysis.

In the ^1H NMR spectrum of 2,2-bis(*p*-chlorodimethylsiloxy-phenyl)propane, the disappearance of the peak of hydroxyl proton at 9.16 ppm indicated that the reaction of bisphenol A and dimethylchlorosilane was completed. Figures 1–4 show the ^1H NMR and ^{13}C

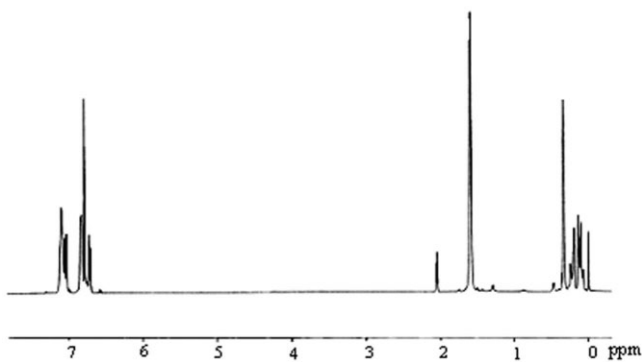


Figure 3 ^1H NMR spectrum of polymer II.

NMR spectra of the polymer I and polymer II, respectively.

In the ^1H NMR spectrum of the polymer I shown in Figure 1, the peak of silyl methyl proton at 0.61 ppm in 2,2-bis(*p*-chlorodimethylsiloxy-phenyl)propane disappeared and a new silyl methyl proton appeared at 0.33 ppm; the peak of *tert*-butyl proton at 1.38 ppm in di-*tert*-butyl adipate disappeared completely; new peaks appeared at 6.7–6.83 ppm and 7.08–7.10 ppm for the phenylene units and at 1.58 ppm for the methyl groups. These results could identify the formation of the polymer I.¹ In the ^{13}C NMR spectrum of the polymer I (Fig. 2), the peak of *tert*-butyl proton at 27.54 and 79.49 ppm disappeared completely.

In the ^1H NMR spectrum of the polymer II shown in Figure 3, the *tert*-butyl signal at 1.5 ppm in di-*tert*-butyl fumarate disappeared completely; the silyl methyl proton signal at 0.61 ppm in 2,2-bis(*p*-chlorodimethylsiloxy-phenyl)propane obviously reduced and new silyl methyl proton resonance signal appeared at 0.34 ppm for the formation of the silyl ester along the backbone of polymer; new resonance signal appeared at 7.03–7.12 ppm and 6.83–6.84 ppm for the phenylene units and at 1.58 ppm for the methyl groups. Figure 4 shows that the characteristic peaks of the *tert*-butyl groups at 27.49 ppm ($\text{C}(\text{CH}_3)_3$) and 81.15 ppm ($\text{C}(\text{CH}_3)_3$) disappeared completely. This further

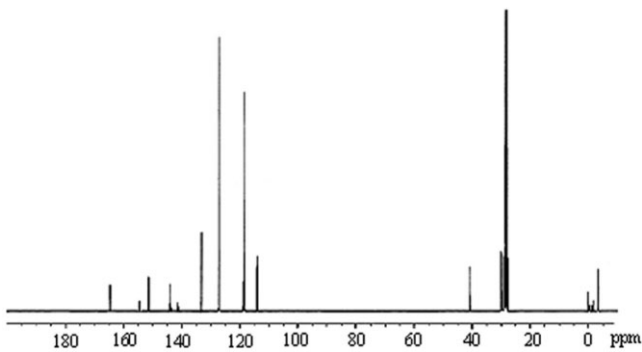


Figure 4 ^{13}C NMR spectrum of polymer II.

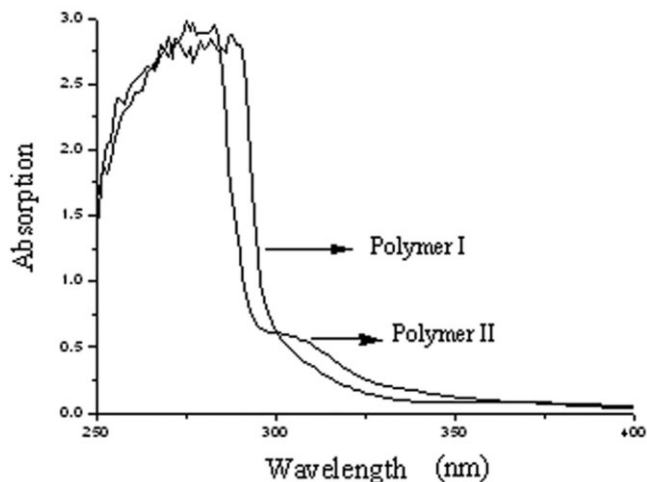


Figure 5 The UV spectra of the poly(silyl ester)s.

identified that the polymerization proceeded completely.

The UV spectra of the polymers show absorption peaks because of the benzene rings (Fig. 5).

GPC and intrinsic viscosity analysis

GPC analysis results showed (Fig. 6) the distribution for the polymer I with a weight average molecular weight (M_w) of 9688 g/mol and a polydispersity index (PDI) of 3.9 and the distribution for the polymer II with M_w of 6912 g/mol and PDI of 3.1 (Table I). Since the polymers were characterized without purification, the molecular weights were calculated from GPC cumulative molecular weight distributions.¹ The intrinsic viscosity of polymer II was lower than that of polymer I, it indicated that the molecular weights of polymer II is lower, which was consistent with the results determined by GPC.

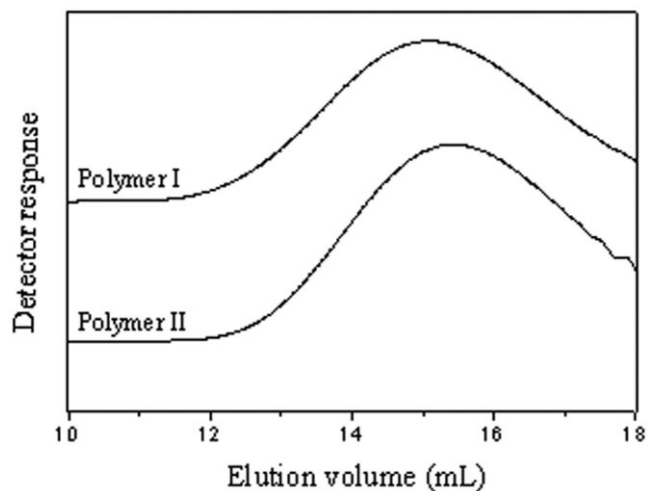


Figure 6 GPC curves of the poly(silyl ester)s.

TABLE I
The Determination Results of GPC and Intrinsic Viscosities

Polymer	M_w (g/mol)	M_n	PDI	DP_w	$[\eta]$ (dL/g)
I	9688	3346	3.9	20.1	0.041
II	6912	2234	3.1	15.6	0.013

M_w is the weight average molecular weight, M_n is the number average molecular weight, PDI is the polydispersity index or the molecular weight distribution, DP is the calculated degree of polymerization, and $[\eta]$ is the intrinsic viscosity in THF at $(30.00 \pm 0.05)^\circ\text{C}$.

DSC analysis

DSC curves of polymer I and polymer II are shown in Figure 7. Each polymer was solid under room temperature and exhibited a T_g well above zero. The T_g of polymer II is higher than that of polymer I and the relative T_g s correlate well with the chemical structures. We obtained the methyl-substituted poly(silyl ester)s based upon disiloxane monomers with the T_g s below zero,⁶ which was consistent with the literature.² The T_g s of the polymers I and II were above zero because of the introduction of 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbones. The 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbones decrease their flexibility and increase the T_g s. Because of the chain rigidity caused by the double bond (C=C) introduced between both carboxyl groups in the polymer backbones, the T_g of the polymer II is higher than that of the polymer I.

TGA analysis

The TG and DTG curves of the polymers at the heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen are shown in Figure 8.

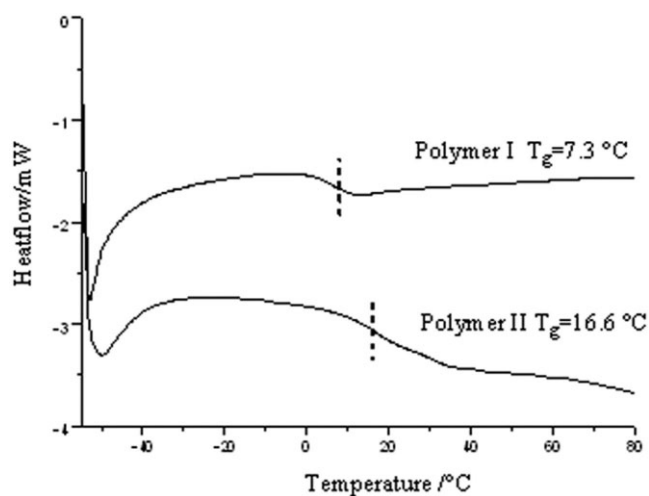


Figure 7 DSC curves of the poly(silyl ester)s.

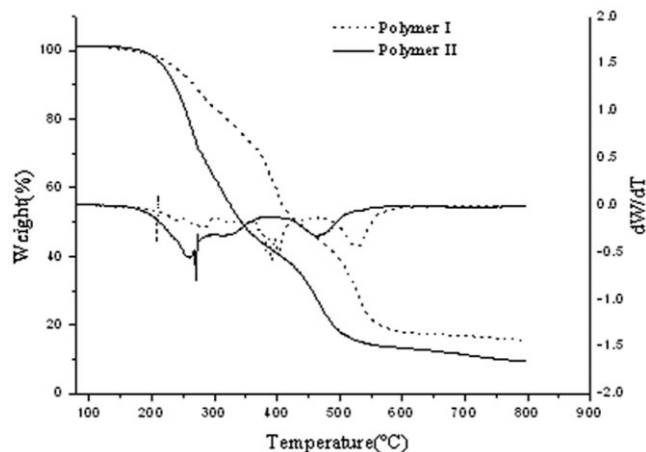


Figure 8 TGA and DTGA curves of the poly(silyl ester)s

Each of the two polymers showed no mass loss up to 180°C .

The polymer I experienced $\sim 39\%$ mass loss by 500°C , 16% of the mass remaining at 800°C . In contrast, polymer II was found to be much more labile toward thermal degradation, exhibiting two distinct mass loss stages in the TGA spectra, $\sim 18\%$ of the mass remaining at 500°C and 9% of the mass remaining at 800°C .

CONCLUSIONS

The two poly(silyl ester)s containing 2,2-bis(*p*-dimethylsiloxy-phenyl)propane units in the polymer backbones were synthesized and characterized. The weight average molecular weights of the two poly(silyl ester)s ranged from 5000 to 10,000 g/mol. The thermal stability of the polymer II was more labile than polymer I. The molecular weight of polymer II is less than that of polymer I, which can effect the thermal analysis and the double bond (C=C) in the backbone also effect the thermal stability of the polymer II. The glass transition temperatures (T_g) were both above zero. Because of the high T_g , the two poly(silyl ester)s are expected to possess good mechanical properties and are highly promising for drug release, temporary coatings, temporary adhesives, or other purposes as solid degradable materials.

References

1. Gitto, S. P.; Wooley, K. L. *Macromolecules* 1995, 28, 8887.
2. Weinberg, J. M.; Gitto, S. P.; Wooley, K. L. *Macromolecules* 1998, 31, 15.
3. Shirai, M.; Miwa, T.; Tsunooka, M. *Chem Mater* 1995, 7, 642.
4. Hudrlik, P. F.; Feasley, R. *Tetrahedron Lett* 1972, 18, 1781.
5. Wang, M.; Weinberg, J. M.; Wooley, K. L. *Macromolecules* 1998, 31, 7606.
6. Weinberg, J. M.; Wooley, K. L. *J. Organomet Chem* 1997, 542, 235.
7. Weinberg, J. M.; Wooley, K. L. *Polym Repr* 1996, 37, 493.

8. Wang, M.; Weinberg, J. M.; Wooley, K. L. *J Polym Sci Part A: Polym Chem* 1999, 37, 3606.
9. Wang, M.; Weinberg, J. M.; Wooley, K. L. *Macromolecules* 2000, 33, 734.
10. Wang, M.; Wooley, K. L. *Polym Prepr* 2000, 41, 436.
11. Wang, M.; Gan, D.; Wooley, K. L. *Macromolecules* 2001, 34, 3215.
12. Li, Y.; Kawakami, Y. *Macromolecules* 1999, 32, 8768.
13. Liu, Z.; Han, N.; Dong, J. *J Appl Polym Sci*, to appear.
14. Gross, S. M.; Roberts, G. W.; Kiserow, D. J.; DeSimone, J. M. *Macromolecules* 2001, 34, 3916.
15. Fustin, C. A.; Bailly, C.; Clarkson, G. J.; Galow, T. H.; Leigh, D. A. *Macromolecules* 2004, 37, 66.
16. Carroccio, S.; Puglisi, C.; Montaudo, G. *Macromolecules* 2002, 35, 4297.
17. Kobayashi, M.; Sanda, F.; Endo, T. *Macromolecules* 2002, 35, 346.
18. Dean, K.; Cook, W. D.; Rey, L.; Galy, J.; Sautereau, H. *Macromolecules* 2001, 34, 6623.
19. James, H. B.; Steven, J. S. *J Org Chem* 1987, 52, 3462.
20. Crivello, J. V.; Shim, S. Y. *J Polym Sci Part A: Polym Chem* 1995, 33, 513.