Poly(silyl ester)s: A New Route of Synthesis via the Condensation of Di-*tert*-butyl Ester of Dicarboxylic Acid with Dichlorosilane

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ABSTRACT: Poly(silyl ester)s were synthesized by a new route via the condensation of di-*tert*-butyl ester of dicarboxylic acid with dichlorosilane by the elimination of *tert*-butyl chloride as a driving force. Three new poly(silyl ester)s with molecular weights typically ranging from 2000 to 5000 amu were produced by the condensation of di-*tert*-butyl adipate with 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyl trisiloxane and di-*tert*-butyl fumarate with 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyl trisiloxane or 1,3-dichlorotetramethyl disiloxane. Each polymer was characterized with infrared, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, and thermogravimetric analysis. This new approach showed several advantages. First, it did not require a catalyst or solvent. Second, the *tert*-butyl chloride byproduct was volatile and was easily eliminated. Third, there was no reaction between the growing poly(silyl ester)s and the condensation byproduct, *tert*-butyl chloride. Fourth, the monomers could be readily purified. Finally, the polymerization could be performed at relatively low temperatures and in a short time. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1378–1384, 2006

Key words: poly(silylester); polycondensation reaction; di-*tert*-butyl ester of dicarboxylic acid; degradable

INTRODUCTION

Poly(silyl ester)s have recently been reported as a new type of degradable material with rapid and tunable degradative properties.[1–4] The degradative properties depend on the substituents attached to the silicon atoms and carbonyl groups of the silyl ester linkages as well as the physical properties of the polymeric material, such as the hydrophobicity, solubility, and crystallinity.[4–7] Nucleophilic attack on acyloxysilane groups can occur at both the silicon atom and the carbonyl carbon.[5,6] With increasing steric bulk or increasing electron-donating capabilities of the substituents attached to the silicon atom, the nucleophilic attack at the carbonyl carbon increases.[3] Otherwise, an increasing amount of attack occurs at the silicon atom. In most cases, the times required for the complete breakdown of poly(silyl ester)s to monomeric components are on the order of seconds to weeks, so poly(silyl ester)s are of potential interest as, for example, matrices in drug release, temporary coatings, and temporary adhesives.[4,8] Several routes have been reported for synthesizing poly(silyl ester)s, including the transsilylation of AA/BB monomer systems,[2,9,10] the transsilylation of AB monomer systems,[8] the hydrosilylation of AB monomer system,[8,11] and the cross-dehydrocoupling polymerizations of AB and AB$_n$ monomer systems (Scheme 1).[8] In this study, we synthesized poly(silyl ester)s via the condensation of di-*tert*-butyl ester of dicarboxylic acid with dichlorosilane by eliminating *tert*-butyl chloride as a driving force. The polymerization with the new approach was carried out at 100°C for only 1–3 days and had no need for a catalyst or solvent.

EXPERIMENTAL

Instruments

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Unity Plus (400 MHZ CDCl$_3$) spectrometer with the solvent proton and carbon signals as standards, respectively. Infrared (IR) spectra were obtained on a Mattson Polaris spectrometer as thin films on NaCl disks. The gel permeation chromatography (GPC) analysis of poly(silyl ester)s was performed with a system consisting of a Waters 515 pump, two Waters Styragel columns (HT3 and HT4), and a Waters 2410 refractive-index detector (Waters Chromatography Division, Millipore, Milford, MA) and was shipped in tetrahydrofuran (THF). The system was calibrated with narrow-molecular-weight polystyrene standards. Thermogravimetric analyses

AA/BB transsilylation

AB hydrosilylation

AB transsilylation

Cross-Dehydrocoupling

Scheme 1
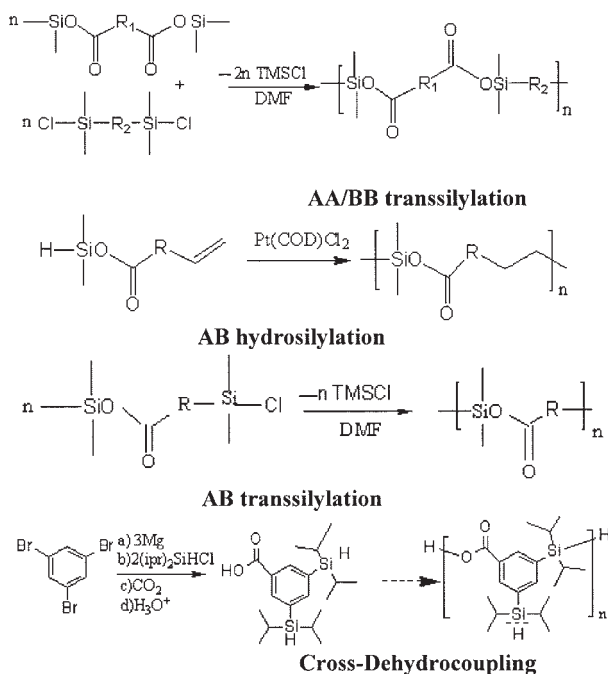
(TGAs) were carried out with a Rheometric Scientific (Piscataway, NJ) TGA 1500 to investigate the thermal properties of the samples. The samples were heated from 35 to 500°C at a rate of 10°C/min under an inert atmosphere of nitrogen. The glass transition temperatures of the polymers (Tg) were examined by differential scanning calorimetry (DSC) (DSC 822e Mettler Toledo), at a rate of 10°C min − 1.

Reagents and materials

Adipic acid and fumaric acid were obtained from the Chemical Industry Factory of Shandong University (Shandong, China) and were purified by vacuum evaporation before use. Thionyl chloride was purchased from the Tianjin Reagent Factory and was purified by distillation before use. THF was purchased from the Tianjin Reagent Factory (Tianjin, China) and distilled in the presence of sodium/benzophenone. *tert*-Butyl alcohol was obtained from the Tianjin Reagent Factory (Tianjin, China) and distilled in the presence of sodium. Dimethyl dichlorosilane was purchased from Shanghai Yuanfan Reagent Co. (Shanghai, China) and distilled before use.

Synthesis of the monomers

Synthesis of di-*tert*-butyl adipate (1)[12]

A mixture of adipic acid and thionyl chloride (1 : 4 mol/mol) was heated at gentle reflux for 2.5 h, and this was followed by distillation to generate bis(adipic acid chloride). The bis(adipic acid chloride) was added dropwise to a stirring mixture of *N,N*-dimethylaniline and *tert*-butyl alcohol in anhydrous ether. This mixture was stirred vigorously for an additional 20 h at room temperature, and then it was diluted with 10% (w/v) aqueous sodium chloride. The product was isolated by extraction with ether, and this was followed by evaporative distillation [bp = 140–145°C (10 mm)], which afforded **1** as a low-melting solid with a melting point of 29–31°C in an 80% yield.

^{1}H-NMR (CDCl$_3$, ppm, δ): 1.38 [s, 18H, (CH$_3$)$_3$], 2.16 (t, 4H, CH$_2$C=O), 1.4–1.6 (complex m, 4H). ^{13}C-NMR (CDCl$_3$, ppm, δ): 23.94 (COCH$_2$CH$_2$), 34.67 (COCH$_2$CH$_2$), 27.54 [C(CH$_3$)$_3$], 79.49 [C(CH$_3$)$_3$], 172.25 (carbonyl).

Synthesis of di-*tert*-butyl fumarate (2)[13]

2 was synthesized via the mixing of fumaryl chloride and sodium *tert*-butoxide in freshly dried *tert*-butyl alcohol followed by vigorous 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 (mp = 67–68°C) in a 21% yield.

^{1}H-NMR (CDCl$_3$, ppm, δ): 6.66 (s, 2H, CH=CH), 1.5 (s, 18H, CH$_3$). ^{13}C-NMR (CDCl$_3$, ppm, δ): 27.49 [C(CH$_3$)$_3$], 81.15 [C(CH$_3$)$_3$], 134.07 (CH=CH), 163.93 (carbonyl).

Synthesis of 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyl trisiloxane (3)[14]

Solid diphenylsilanediol (18 g, 0.083 mol) was added in portions to a mixture of 20 mL (0.167 mol) of dimethyl dichlorosilane, 23 mL (0.167 mol) of triethylamine, and 200 mL of benzene with stirring under nitrogen at 0–10°C. The mixture was stirred overnight and allowed to warm to room temperature. The precipitate was washed with benzene, and the benzene was removed from the filtrate under reduced pressure. Distillation was then performed under reduced pressures, and 12.67 g (38%) of the product [bp = 170–180°C (10 mm)] was collected.

^{1}H-NMR (CDCl$_3$, ppm, δ): 0.51 (s, 12H, 4CH$_3$), 7.40–7.46 (m, 6H, ph-H), 7.62–7.72 (M, 4H, ph-H).

Synthesis of 1,3-dichlorotetramethyl disiloxane (4)[15]

Ethyl alcohol (30.6 g, 0.67 mol) was added to 258 g (2.0 mol, 100% excess) of dichlorodimethylsilane in 30 min, and the mixture was purged with dry nitrogen for 30 min. About 1 g of ferric chloride was added, and the mixture was slowly heated to reflux (67–83°C). The mixture was filtered, and the filtrate was distilled. **4** was obtained in a 50% yield (bp = 134–138°C).
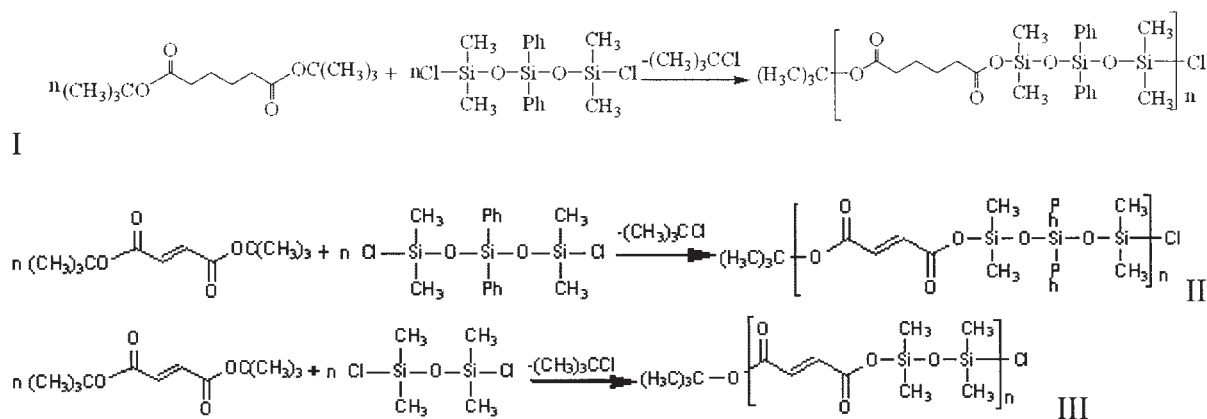
Scheme 2

Synthesis of the polymers

General procedure for the synthesis of poly(silyl ester)s

The appropriate dichlorosilane was distilled into a 25-mL, round-bottom flask. The appropriate di-*tert*-butyl ester of dicarboxylic acid was added to the flask for the preparation of poly(1,1,5, 5-tetramethyl-3,3-diphenyl trisiloxyl adipate) (**I**), poly(1,1,5,5-tetramethyl-3,3-diphenyl trisiloxyl fumarate) (**II**), and poly-(tetramethyldisilyloxyl fumarate) (**III**). The reaction was typically allowed to stir under nitrogen at 100°C for 1–3 days. During the polymerization, the *tert*-butyl chloride was removed by evaporation. Because of the hydrolytic sensitivities of the polymers, no further purification techniques were performed.

Synthesis of I

This was prepared through the reaction of **1** (2.4566 g, 9.5088 mmol) with **3** (3.8184 g, 9.5089 mmol) with heating at 100°C for 10 h.

IR (cm^{-1}): 3069, 3015, 2960, 1696, 1260, 1462, 1406, 1123, 1022, 806, 698. ^{1}H-NMR (CDCl$_3$, ppm, δ): 1.48 (m, 4H, COCH$_2$CH_2), 2.17 (m, 4H, COCH_2CH$_2$), 7.36 (m, 6H, aromatic), 7.64 (m, 4H, aromatic) 0.32 [s, 12H, Si(CH$_3$)$_2$]. ^{13}C-NMR (CDCl$_3$, ppm, δ): 23.70 (COCH$_2$CH$_2$), 34.88 (COCH$_2$CH$_2$), 127.35 (aromatic), 129.77 (aromatic), 133.77 (aromatic), 134.31 (aromatic), 172.47 (carbonyl), −0.52 [Si(CH$_3$)$_2$].

Synthesis of II

This was prepared through the reaction of **2** (2.06 g, 9.0299 mmol) with **3** (3.6260 g, 9.0299 mmol) with heating at 100°C for 36 h.

IR (cm^{-1}): 3049, 3006, 2965, 1704, 1639, 1260, 1401, 1262, 810. ^{1}H-NMR (CDCl$_3$, ppm, δ): 6.65 (s, 2H, 2 =CH), 7.36 (m, 6H, aromatic), 7.64 (m, 4H, aromatic), 0.38 [s, 12H, Si(CH$_3$)$_2$]. ^{13}C-NMR (CDCl$_3$, ppm, δ): 127.5 (aromatic), 130.05 (aromatic), 133.69 (aromatic),

133.79 (aromatic), 134.81 (CH=CH), 163.61 (carbonyl), −0.64 [Si(CH$_3$)$_2$].

Synthesis of III

This was prepared through the reaction of **2** (2.2700 g, 9.9508 mmol) with **4** (2.0256 g, 9.9508 mmol) with heating at 100°C for 65 h.

IR (cm^{-1}): 3049, 3006, 2965, 1591, 1401, 1260, 1091, 803. ^{1}H-NMR (CDCl$_3$, ppm, δ): 6.66 (s, 2H, CH=CH), 0.33 [s, 12H, Si(CH$_3$)$_2$]. ^{13}C-NMR (CDCl$_3$, ppm, δ): 135.11 (CH=CH), 163.68 (carbonyl), −0.976 [Si(CH$_3$)$_2$].

Degradation of polymers I and II

Approximately 20 mg of polymers **I** and **II** was dissolved in 2 mL of THF and water (0.10 mL; 1%), respectively. At 30 min, 1 h, 2 h, and 4 h, 0.1 mL of polymers **I** and **II** solutions was injected into the GPC instrument, and the resulting chromatograms were analyzed (shown later in Figs. 5 and 6). Approximately 10 mg of polymer **II** was placed in individual glass vials. The vials were open to the environment, the temperature of which was about 25°C. At the appropriate times (0 min, 30 min, 1 h, 4 h, and 8 h), polymer **II** was dissolved in THF, and the resulting chromatograms were obtained (shown later in Fig. 7).

RESULTS AND DISCUSSION

Polymerization route

The method used by Wooley and coworkers[2,11] for the synthesis of poly(silyl ester)s is based on the AA/BB monomer systems, involving a transsilylation ester interchange reaction between trimethylsilyl ester and chlorosilane functional groups with the elimination of trimethylsilyl chloride as the driving force. In this study, the organic dicarboxylic acid ester was used as a substitute for the trimethylsilyl ester of dicarboxylic
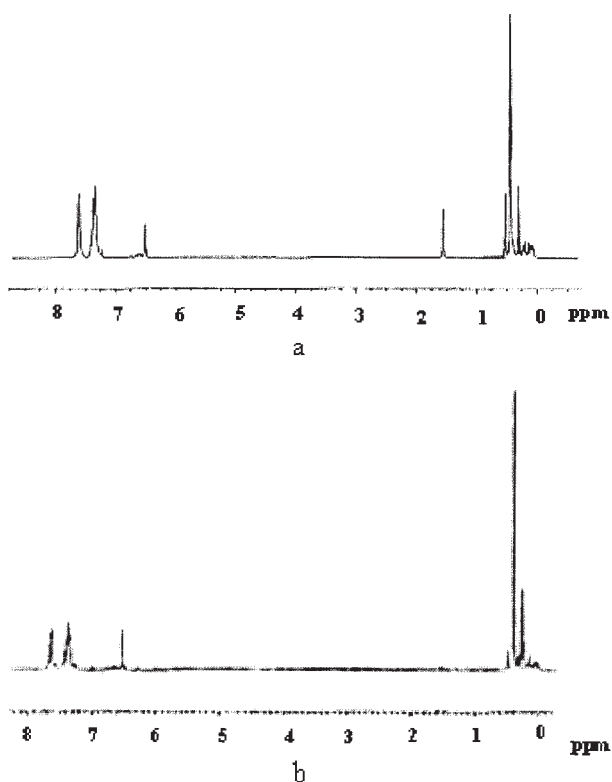
Figure 1 ¹H-NMR (400 MHz, CDCl₃) spectra of polymer **II**: (a) reaction time of 20 h and (b) reaction time of 36 h.

acid in the synthesis of poly(silyl ester)s. The three new poly(silyl ester)s were obtained through the reaction between di-*tert*-butyl ester of dicarboxylic acid and dichlorosilane. However, with dimethyl, diethyl, and diisopropyl esters of the dicarboxylic acids substituted for the *tert*-butyl esters, the desired results were not achieved. The new polymerization route is shown in Scheme 2.

Polymerization process

The typical resonance signal of the ¹H-NMR spectrum of monomer **2** is at 1.5 ppm for *tert*-butyl, and that of the ¹H-NMR spectrum of monomer **3** is at 0.51 ppm for silyl methyl. Polymer **II** has been chosen as an example to examine the process of the condensation polymerization for monomers **2** and **3**. Figure 1(a,b) shows the ¹H-NMR spectra of the products obtained with the reaction between monomers **2** and **3** at 20 and 36 h at 100°C, respectively. In Figure 1(a), we can find three important resonance signals: at 0.38 ppm for silyl methyl (in the middle segments of the polymer chain), at 1.5 ppm for *tert*-butyl (at the end of the polymer chain), and at 0.51 ppm for silyl methyl (at the end of the polymer chain); in Figure 1(b), we can also find one important resonance signal at 0.38 ppm for silyl methyl (in the middle of the polymer chain), and we do not find two other clear peaks as shown in Figure

1(a). The peak at 0.38 ppm is the sign of polymer **II**. Under the aforementioned experimental conditions, when the polymerization of monomer **2** with monomer **3** is processed for 36 h, the synthesis of polymer **II** can be completed. The condensation of di-*tert*-butyl ester of dicarboxylic acid with dichlorosilane is carried out progressively.

Characterization of the polymers

Because these three new polymers (**I**–**III**) obtained according to the aforementioned methods are moisture-sensitive, they have been characterized without purification with ¹H-NMR,¹³C-NMR, and IR spectroscopy, GPC, differential scanning calorimetry (DSC), and TGA.

Chemical structure identification of the polymers

As before, Figure 1 has been initially used to demonstrate the identification of polymer **II**. Because of the moisture sensitivity of polymer **II** and the dichlorosilane, a small amount of poly(dimethylsiloxane) can be observed at 0−0.3 ppm. To further identify the structure of the polymers, we show the ¹³C-NMR spectra of monomers **1** and **2** and polymers **I**–**III** in Figure 2. The *tert*-butyl groups are the characteristic groups; they are at δ = 27.54 [C(CH₃)₃] and 79.49 [C(CH₃)₃] for monomer **1** and at δ = 27.49 [C(CH₃)₃] and 81.15 [C(CH₃)₃] for monomer **2**. The resonance signal at 76
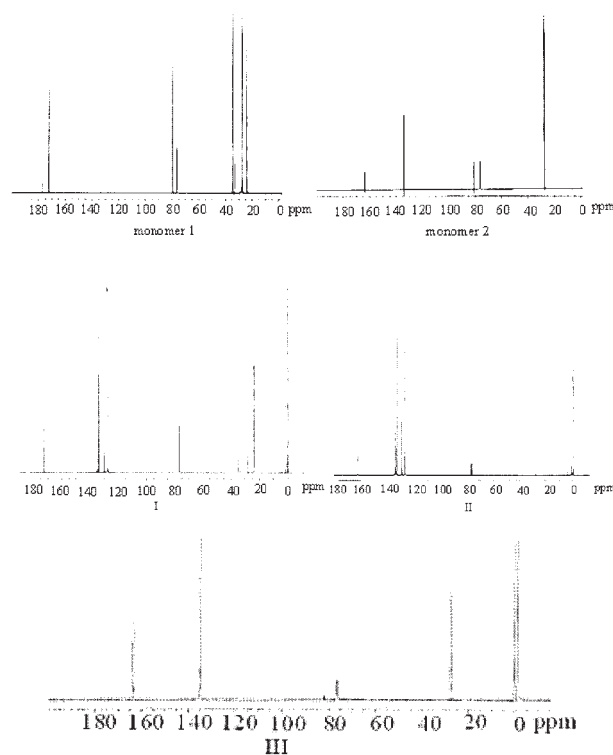
Figure 2 ¹³C-NMR (400 MHz, CDCl₃) spectra of monomers **1** and **2** and polymers **I**–**III**.

Compound	M_w	PDI	DP_w
I	4585	1.4	10
II	3612	1.2	8
III	2207	1.1	8.9

M_w, weight-average molecular weight; PDI, polydispersity index; DP_w, degree of polymerization.

ppm is for the solvent $CDCl_3$. The *tert*-butyl signals in the polymers disappear in comparison with the *tert*-butyl signals in monomer **1** or **2**, and thus the structures of polymers **I–III** can be identified.

GPC analysis

GPC with online viscometry and polystyrene standards was used for the determination of the molecular weights and molecular weight distributions. The typical molecular weights of the three poly(silyl ester)s range from 2000 to 5000 amu, as determined by GPC (Table I).

Thermal analysis

Glass-transition temperatures (T_g's) of the poly(silyl ester)s were measured by DSC under N_2 (Fig. 3). Each of the poly(silyl ester)s was a viscous fluid and exhibited a T_g well below room temperature. The relative values of the T_g's correlate well with the chemical structures. The T_g values of polymers **I** and **II** are higher than that of polymer **III** because the phenyl groups in polymers **I** and **II** reduce their flexibility and increase their T_g values. Because of the chain rigidity caused by the double bond (C=C) introduced between both carboxy groups in the polymer backbone, the T_g value of polymer **II** is higher than that of polymer **I**.

The thermal stabilities of polymers **I–III** were evaluated by TGA from 35 to 500°C in nitrogen.
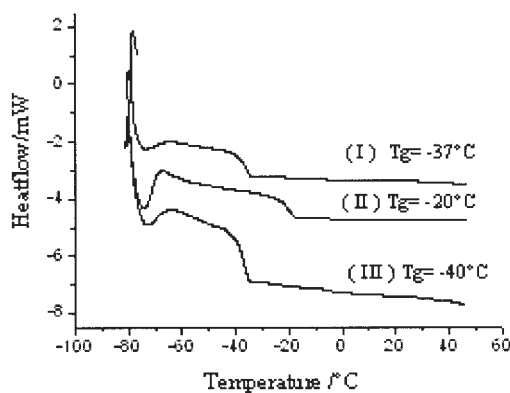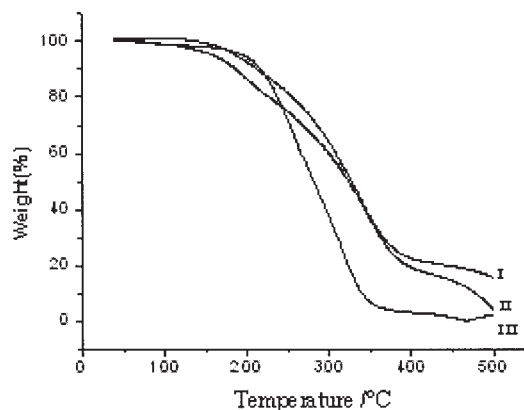
Figure 4 TGA curves of polymers **I–III**.

Figure 4 shows that polymers **I** and **II**, which contain aromatic rings attached to the silicon, are much more stable toward thermal degradation than polymer **III** after 250°C. Polymer **I** is more thermally stable than polymer **II**, which contains double carbon bonds. Differential thermogravimetry (DTG) curves of polymers **I–III** are also shown in Figure 5. There is only one degradation step of polymer **I**, which exhibits a distinct mass loss. Eighty percent of the mass loss occurs between 150 and 430°C, and approximately 20% of the mass remains at 500°C. The maximum decomposition rate temperature of polymer **I** is 335°C. For polymer **II**, which contains a double bond (C=C) in the backbone, there are two distinct mass-loss steps in the DTG curve. In the first step, 23% of the mass loss occurs between 150 and 240°C. In the second step, the mass continues to decrease from 240°C, and only 4% of the original weight remains at 500°C Polymer **III** is the most thermally labile after 250°C and decomposes in two steps. The first step of thermal degradation occurs from 150 to 280°C, with approximately 50% loss. The second step of thermal degradation occurs from 280 to 400°C, and only 2% of the original weight
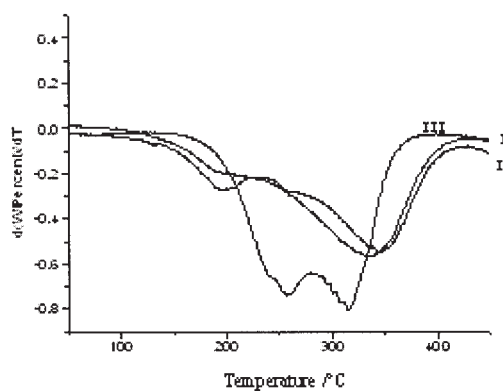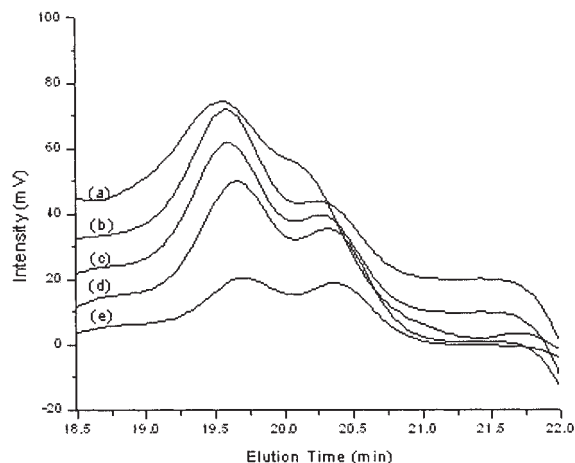
Figure 3 DSC curves of polymers **I–III**.

Figure 5 DTG curves of polymers **I–III**.

Figure 6 GPC chromatograms of polymer **I** as a solution in THF containing 1% H_2O after (a) 0 min, (b) 30 min, (c) 1 h, (d) 2 h, and (e) 4 h.

Figure 8 GPC chromatograms monitoring the degradation of polymer **II** in air at approximately 25°C and 40% humidity after (a) 0 min, (b) 30 min, (c) 1 h, (d) 4 h, and (e) 8 h.

remains at 500°C. The two maximum rates for polymer **III** are at 260 and 320°C, respectively.

Degradable analysis

We investigated the hydrolysis behavior of poly(silyl ester)s by GPC analysis. The stability of poly(silyl ester)s toward nucleophilic degradation is affected by many factors, including the steric and electronic effects of the substituting groups on the silicon atoms, the composition of the polymer backbone, and the solvent.[4,6] Molecular weight losses with time for polymers **I** and **II** in THF solutions containing water are shown in Figures 6 and 7, respectively, whereas that for polymer **II** in air is shown in Figure 8. Polymer **II** is more hydrolytically labile than polymer **I**. The ma-
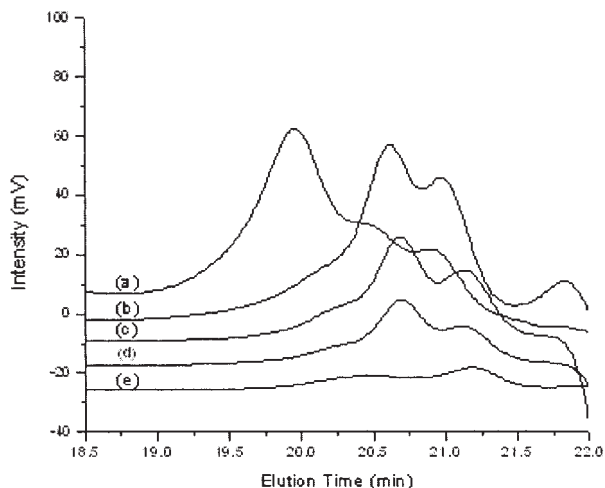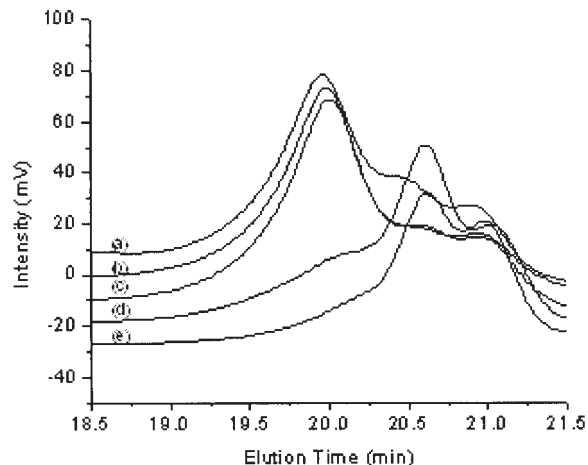
jor difference between the two polymers is the backbone unit attached to the carbonyl carbon atoms (alkyl vs vinyl), in addition to the different chain lengths of their repeating units. The literature shows that changing the chain length of the repeating unit does not affect the polymer stability.[3] Thus, the vinyl backbone of polymer **II** likely increases the electrophilicity of the carbonyl carbon atoms and is responsible for the decreased stability of silyl ester linkages toward nucleophilic attack. The hydrolysis rate of polymer **II** in a THF solution containing water appears to be faster than that in air. The hydrolysis products of polymer **II** contain silanol at both ends, which in turn polymerizes by a self-condensation reaction to form polysiloxane and fumaric acid (Fig. 9). Fumaric acid does not appear in the ^{1}H-NMR measurements because it is insoluble in $CDCl_3$.

CONCLUSIONS

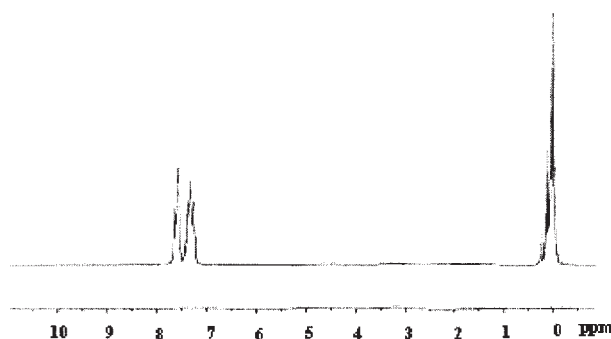Three new poly(silyl ester)s were synthesized via the new reaction route through the condensation of di-

Figure 7 GPC chromatograms of polymer **II** as a solution in THF containing 1% H_2O after (a) 0 min, (b) 30 min, (c) 1 h, (d) 2 h, and (e) 4 h.

Figure 9 H-NMR (400 MHz, $CDCl_3$) spectrum of the hydrolysis of polymer **II**.

tert-butyl ester of dicarboxylic acid and dichlorosilane to give *tert*-butyl chloride as a small-molecule condensate, and they were characterized with ^{1}H-NMR, ^{13}C-NMR, IR, GPC, TGA, and DSC. We tried to use several esters of dicarboxylic acid with the dichlorosilanes to synthesize poly(silyl ester)s, but we found that only di-*tert*-butyl ester of dicarboxylic acid is a good substrate, whereas dimethyl, diethyl, and diisopropyl esters of dicarboxylic acid are not. This can be explained from the viewpoint of organic chemistry.

Polymers **II** and **III**, which contain double bonds (C=C) in the backbone, can be crosslinked, and the resulting crosslinked polymers are still degradable. The potential applications of these poly(silyl ester)s are for matrices in drug release, temporary coatings, and temporary adhesives.[4,11]

The use of *tert*-butyl esters of dicarboxylic acids for the synthesis of poly(silyl ester)s brings several benefits: the monomer di-*tert*-butyl ester of dicarboxylic acid is stable in storage and can be readily purified, the byproduct *tert*-butyl chloride (bp = 50.7°C) is volatile, no reaction occurs between the growing poly(silyl ester) and the condensation byproduct, the polymerization can be performed at relatively low temperatures and without the addition of solvents and catalysts, and the polymerization time is shorter than that of some AA/BB monomer systems of transsilylation esterification. Further investigation is in progress.

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