

Crosslinking of Poly(silyl ester)s Containing Fumaryloxyl Units in the Main Chain and Characteristics of the Crosslinked Products

Nianfeng Han,^{1,2} Zonglin Liu,² Dejie Zhou,¹ Liqiang Jin,² Congwen Shi²

¹Institute of New Materials, Shandong Jiaotong University, Jinan, Shandong 250023, China

²School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, China

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ABSTRACT: Two unsaturated poly(silyl ester)s that contained innocuous fumaryloxyl units in the main chain were prepared by the polycondensation reaction of 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane or 1,3-dichlorotetramethylidisiloxane with di-*tert*-butyl fumarate under nitrogen at 100°C for 1–3 days. To investigate the crosslinking reaction of the unsaturated poly(silyl ester)s, the two unsaturated poly(silyl ester)s were crosslinked in the presence of 2,2'-azobisisobutyronitrile as a radical initiator. After the crosslinking, the unsaturated poly(silyl ester)s, which were viscous liquids, turned into solid products. The characterization of the two poly(silyl ester)s and the crosslinked products included infrared spectroscopy, ¹H-NMR spectroscopy, differential scanning

calorimetry, and thermogravimetric analysis. Comparisons were made between the linear poly(silyl ester)s and the crosslinked poly(silyl ester)s. After the crosslinking, the important resonance signal for ethenylene (C=C) disappeared, and this showed that the crosslinking reaction was carried out progressively. The glass-transition temperatures of the crosslinked poly(silyl ester)s were higher than those of the uncrosslinked poly(silyl ester)s, and the thermal stability of the crosslinked poly(silyl ester)s was better than that of uncrosslinked poly(silyl ester)s. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1221–1225, 2007

Key words: poly(silyl ester); fumaryloxyl units; crosslinking

INTRODUCTION

Poly(silyl ester)s, as new degradable materials, have attracted considerable interest.^{1–4} Wooley and co-workers^{5–12} initiated the study of poly(silyl ester)s. We have prepared a series of linear poly(silyl ester)s and hyperbranched poly(silyl ester)s by a new route via the condensation of di-*tert*-butyl ester of dicarboxylic acid with chlorosilane. Two unsaturated poly(silyl ester)s containing C=C in the polymer backbones have been obtained by this new route.¹³ The crosslinking reaction of linear unsaturated poly(silyl ester)s has not been described in the literature. To further explore the properties of this new family of degradable polymers and to extend the stability, we now report the synthesis and characterization of self-crosslinked poly(silyl ester)s. Just like the crosslinked unsaturated polyesters, the crosslinked poly(silyl ester)s can bear some degree of chemical crosslinking, and so the mechanical strength of the poly(silyl ester)s can be improved. Otherwise, the crosslinked poly(silyl ester)s still possess silyl ester bonds, so they are still degrad-

able. The degradation results for the self-crosslinked poly(silyl ester)s should be similar to those of the uncrosslinked poly(silyl ester)s, innocuous fumaric acid and poly(siloxane)s, and therefore could serve as solid, degradable materials for medical and environmental purposes.¹³

In this work, the viscous liquid poly(1,1,5,5-tetramethyl-3,3-diphenyltrisiloxylfumarate) (I) and poly(tetramethylidisilyloxyl fumarate) (II) were crosslinked with 2,2'-azobisisobutyronitrile (AIBN) as the initiator and tetrahydrofuran (THF) as the solvent (Schemes 1 and 2). After the crosslinking reaction, the solid crosslinked polymers were obtained. The properties of the crosslinked products changed accordingly in comparison with the uncrosslinked polymers. The obtained results are described and discussed.

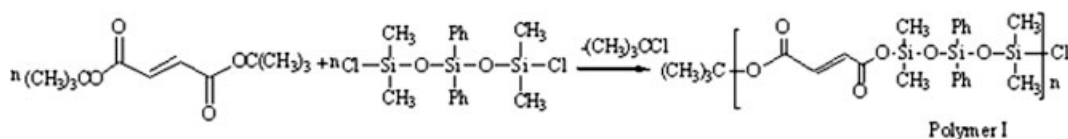
EXPERIMENTAL

Equipment

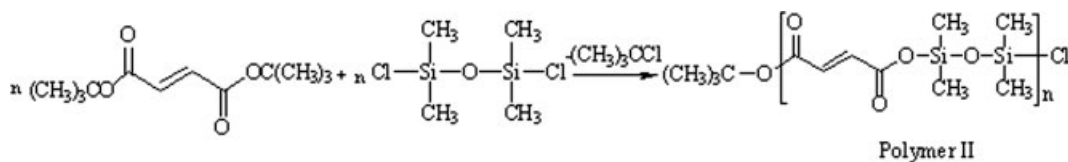
¹H-NMR spectra were recorded on a Bruker Avance (400 MHz, Bruker Co., Switzerland) spectrometer in deuteriochloroform (CDCl₃). Infrared (IR) spectra were obtained with a Nicolet 20SX (Nicolet Instruments, Madison, USA) Fourier transform infrared (FTIR) spectrometer as solids on KBr pellets. Thermogravimetric analyses (TGAs) were carried out with a

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

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Scheme 1



Scheme 2

TGA/SDTA-851 (Mettler–Toledo, Switzerland) to investigate the thermal properties of the 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 (T_g 's) of the polymers were examined with differential scanning calorimetry (DSC; DSC 822^e, Mettler–Toledo) at a rate of 10°C/min.

Materials

Fumaric acid was obtained from Tianjin Fuchen Reagent Factory (Tianjin, China) and purified by vacuum evaporation before use. Dimethyldichlorosilane was purchased from Shanghai Yuanfan Reagent Co. (Shanghai, China) and distilled before use. Thionyl chloride was purchased from Tianjin Reagent Factory (Tianjin, China) and was purified by distillation before use. THF was purchased from Tianjin Reagent Factory and distilled in the presence of sodium/benzophenone. *tert*-Butyl alcohol was obtained from Tianjin Reagent Factory and distilled in the presence of sodium. Di-*tert*-butyl fumarate, 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane, and 1,3-dichlorotetramethyldisiloxane were prepared according to literature procedures.^{14–16}

Synthesis of the polymers

Polymers **I** and **II** were prepared according to the literature procedures.¹³ The molecular weights data and molecular weight distributions for **I** and **II** are shown in Table I.

TABLE I
Molecular Weights and Molecular Weight Distributions for Polymers **I** and **II**

Polymer	M_w	PDI	DP_w
I	3612	1.2	8
II	2207	1.1	9

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

Crosslinking of polymer I

Polymer **I** (3.5713 g), 0.07143 g of AIBN, and 10 mL of THF were successively introduced into a 25-mL, round-bottom 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 70°C for 12 h. The solvent was removed under reduced pressure, and crosslinked polymer **I** was obtained.

IR (KBr, cm^{-1}): 3071, 2963, 1707, 1643, 1429, 1311, 1125, 1070, 810, 700. ¹H-NMR (CDCl_3 , ppm, δ): 7.36 (m, 6H, aromatic), 7.64 (m, 4H, aromatic), 0.23 [s, 12H, Si(CH₃)₂], 1.55 (m, 2H, CH).

Crosslinking of polymer II

Polymer **II** (2.1382 g), 0.04276 g of AIBN, and 10 mL of THF were successively introduced into a 25-mL, round-bottom 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 70°C for 12 h. The solvent was removed under reduced pressure, and crosslinked polymer **II** was obtained.

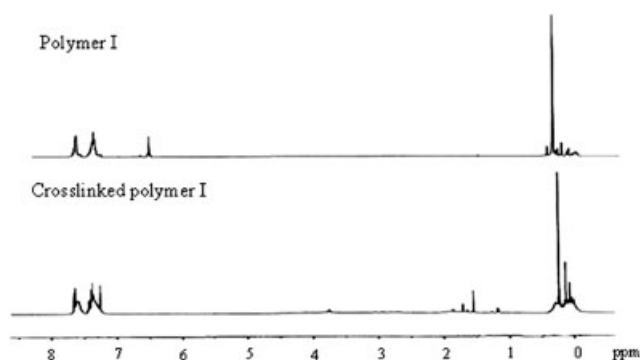


Figure 1 ¹H-NMR spectra of polymer **I** and crosslinked polymer **I**.

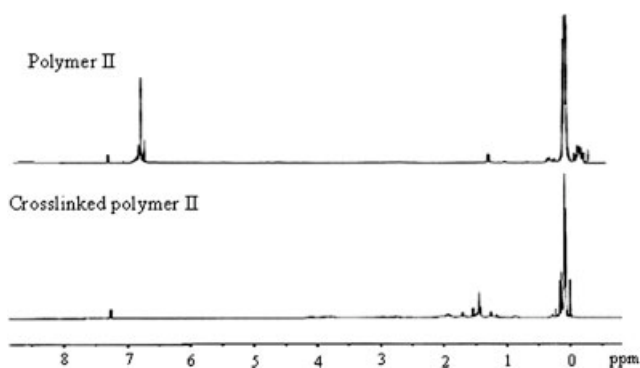


Figure 2 $^1\text{H-NMR}$ spectra of polymer II and crosslinked polymer II.

IR (KBr, cm^{-1}): 2963, 1782, 1723, 1410, 1369, 1261, 1051, 807. $^1\text{H-NMR}$ (CDCl_3 , ppm, δ): 1.44 (m, 2H, CH), 0.12 [s, 12H, $\text{Si}(\text{CH}_3)_2$].

RESULTS AND DISCUSSION

$^1\text{H-NMR}$ and FTIR spectroscopy analysis

The chemical structures of the unsaturated poly(silyl ester)s and the crosslinked polymers were characterized with $^1\text{H-NMR}$ and FTIR spectra. The $^1\text{H-NMR}$ spectra of polymer I and crosslinked polymer I are shown in Figure 1. The $^1\text{H-NMR}$ spectra of polymer II and crosslinked polymer II are shown in Figure 2.

In Figures 1 and 2, the peaks of the ethylene $\text{C}=\text{C}$ protons of polymers I and II are at 6.65 and 6.66 ppm, respectively. In Figure 1, for crosslinked polymer I, the disappearance of the peak of the ethylene $\text{C}=\text{C}$ proton at 6.65 ppm and the appearance of the new ($\text{C}-\text{C}$) proton peak at 1.55 ppm indicate that the crosslinking reaction of polymer I was completed. In

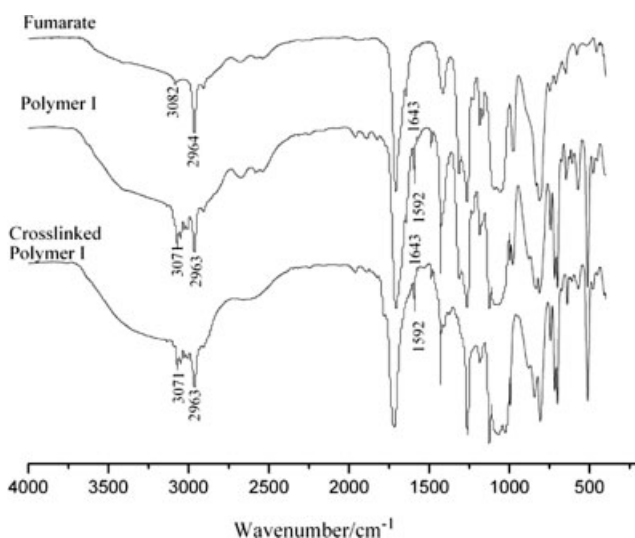


Figure 3 IR spectra of fumarate, polymer I, and crosslinked polymer I.

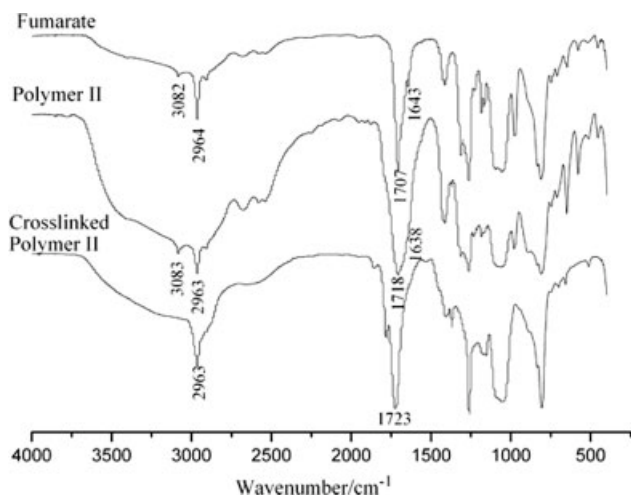


Figure 4 IR spectra of fumarate, polymer II, and crosslinked polymer II.

Figure 2, for crosslinked polymer II, we can also find that the peak of the ethylene ($\text{C}=\text{C}$) proton at 6.66 ppm disappears, and a new proton peak at 1.44 ppm for $\text{C}-\text{C}$ appears. The disappearance of the peak of the ethylene ($\text{C}=\text{C}$) proton in the $^1\text{H-NMR}$ spectra of the crosslinked poly(silyl ester)s proved that the crosslinking reaction was really carried out. The peaks for $\text{Si}(\text{CH}_3)_2$ are at 0.38 and 0.33 ppm for polymers I and II, respectively. After the crosslinking, the proton peaks for $\text{Si}(\text{CH}_3)_2$ are at 0.23 and 0.12 ppm in the corresponding crosslinked products.

To further identify the crosslinking of the polymers, we show the FTIR spectra for di-*tert*-butyl fumarate, polymer I, and crosslinked polymer I in Figure 3 and for di-*tert*-butyl fumarate, polymer II, and crosslinked polymer II in Figure 4. In Figure 3, the characteristic bands for di-*tert*-butyl fumarate and polymer I can be observed at 1643 cm^{-1} for ethylene ($\text{C}=\text{C}$). In the IR spectrum of crosslinked polymer I, the peaks at 1643 cm^{-1} disappear. Figure 4 shows the characteristic

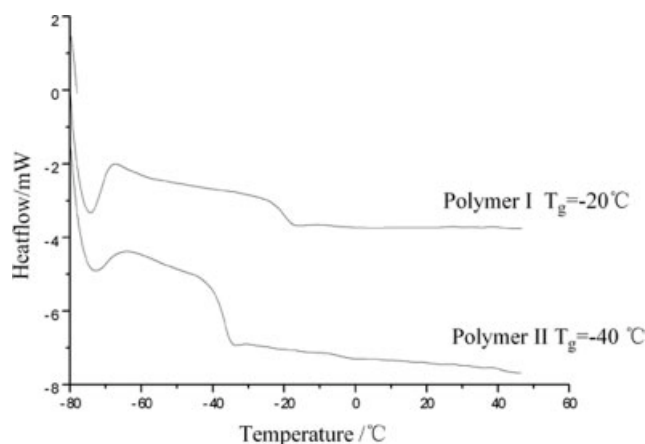


Figure 5 DSC curves of polymers I and II.

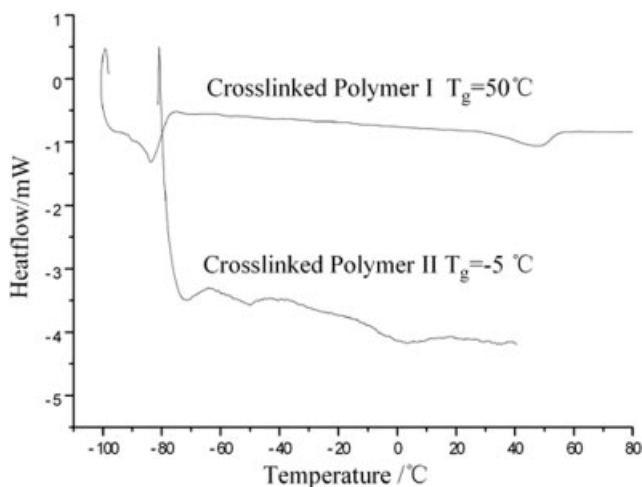


Figure 6 DSC curves of crosslinked polymers I and II.

bands of polymer II at 1638 and 3083 cm^{-1} for ethenylene (C=C) and C—H of ethenylene, respectively. In the IR spectrum of crosslinked polymer II, the peaks at 1638 and 3083 cm^{-1} disappear. The disappearance of ethenylene (C=C) and C—H of ethenylene indicates that the crosslinking reaction was carried out really and progressively.

DSC analysis

The DSC curves of polymer I, polymer II, and the crosslinked products are shown in Figures 5 and 6, respectively. Each of the uncrosslinked poly(silyl ester)s was a viscous fluid and exhibited a T_g well below zero. After crosslinking, the polymers solidified, and the T_g 's increased. Because of the formation of the crosslinking structure in the polymers, the T_g 's of the crosslinked products increased distinctly in comparison with those of the uncrosslinked poly(silyl ester)s.

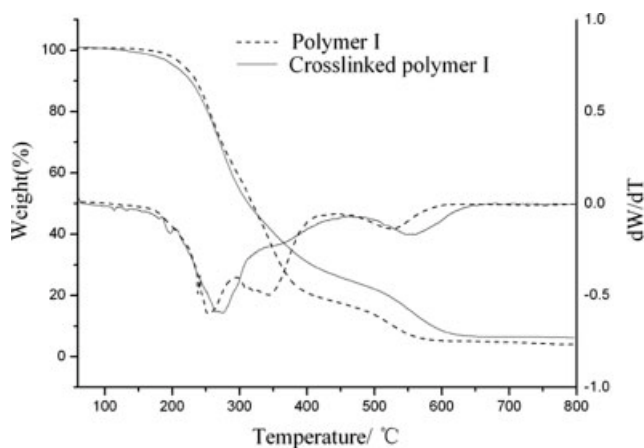


Figure 7 TGA/DTG curves of polymer I and crosslinked polymer I.

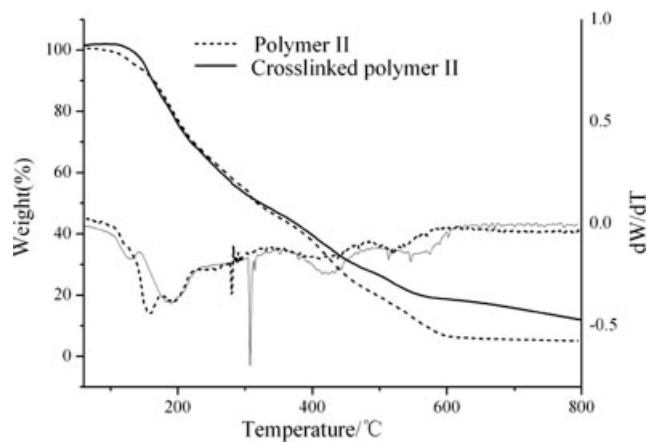


Figure 8 TGA/DTG curves of polymer II and crosslinked polymer II.

TGA

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves of polymer I, polymer II, and the crosslinked polymers are shown in Figures 7 and 8. The obtained data are shown in Table II. T_d and T_{max} denote the 5% degradation temperature and the maximum degradation rate temperature, respectively. In Figure 7, polymer I and crosslinked polymer I show no mass loss up to 180°C. Before 300°C, the TG curves of polymer I and crosslinked polymer I are similar. In the temperature range of 350–600°C, the decomposition rate of polymer I was more rapid than that of crosslinked polymer I. Figure 8 shows that polymer II and crosslinked polymer II began to decompose at about 110°C. The two polymers displayed three-step degradation, and the curves are similar. In the first step, 30% of the mass loss occurred between 150 and 250°C for the small molecules and branched chains. The second and third step occurred from 300 to 600°C, mainly for the crosslinked molecular chains. The thermal stability of the crosslinked polymers was better than that of the uncrosslinked polymers. The data in Table II show that the thermal stability of crosslinked polymer I was better than that of crosslinked polymer II. The T_d values for cross-

TABLE II
TGA Data for the Poly(silyl ester)s and Crosslinked Poly(silyl ester)s

Sample	T_d (°C)	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	Residue	
					500°C	700°C
Polymer I	216	255	345	527	13	4
Crosslinked polymer I	203	274	553	—	22	6
Polymer II	137	189	415	513	16	5
Crosslinked polymer II	150	196	409	543	26	15

linked polymer **I** and crosslinked polymer **II** were 203 and 150°C, respectively. The remaining weight percentages for polymers **I** and **II** and the crosslinked polymers at 700°C are shown in Table II. The degrees of polymer **I** and polymer **II** were 8 and 9, respectively, and the remaining weight percentages for polymers **I** and **II** at 700°C were 4 and 5, respectively. The remaining weight percentages for crosslinked polymers **I** and **II** at 700°C were 6 and 15, respectively. These results show that the final char yields of the polymers were consistent with the Si content and that the final char yields of the crosslinked polymers were higher than those of the corresponding uncrosslinked polymers.

CONCLUSIONS

Viscous and liquid unsaturated poly(silyl ester)s (**I** and **II**) were crosslinked successfully by initiation with AIBN as the initiator to give solid crosslinked poly(silyl ester)s. The disappearance of the characteristic peaks of the ethenylene (C=C) proton in the ¹H-NMR spectra and the ethenylene (C=C) in the IR spectra identified the occurrence of the crosslinking reaction. Because of the formation of the crosslinked structure, the *T_g*'s of the crosslinked poly(silyl ester)s increased distinctly in comparison with those of the uncrosslinked polymers. The thermal stability of the

crosslinked polymers was better than that of the corresponding uncrosslinked polymers, and the thermal stability of crosslinked polymer **I** was better than that of crosslinked polymer **II**.

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