

Synthesis and Characterization of Hyperbranched Poly(silyl ester)s

Nianfeng Han, Zonglin Liu, Liqiang Jin

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

Received 22 August 2005; accepted 11 January 2006

DOI 10.1002/app.24119

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hyperbranched poly(silyl ester)s were synthesized via the $A_2 + B_4$ route by the polycondensation reaction. The solid poly(silyl ester) was obtained by the reaction of di-*tert*-butyl adipate and 1,3-tetramethyl-1,3-bis- β (methyl-dichlorosilyl)ethyl disiloxane. The oligomers with *tert*-butyl terminal groups were obtained via the $A_2 + B_2$ route by the reaction of 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyl-trisiloxane with excess amount of di-*tert*-butyl adipate. The viscous fluid and soft solid poly(silyl ester)s were obtained by the reaction of the oligomers as big monomers with 1,3-tetramethyl-1,3-bis- β (methyl-dichlorosilyl)ethyl disiloxane. The polymers were characterized by ^1H NMR, IR, and UV spectroscopies, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The

^1H NMR and IR analysis proved the existence of the branched structures in the polymers. The glass transition temperatures (T_g 's) of the viscous fluid and soft solid polymers were below room temperature. The T_g of the solid poly(silyl ester) was not found below room temperature but a temperature for the transition in the liquid crystalline phase was found at 42°C. Thermal decomposition of the soft solid and solid poly(silyl ester)s started at about 130°C and for the others it started at about 200°C. The obtained hyperbranched polymers did not decompose completely at 700°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3430–3436, 2006

Key words: poly(silyl ester); hyperbranched poly(silyl ester)s; polycondensation reaction; synthesis; characterization

INTRODUCTION

Poly(silyl ester)s were recently reported as a new class of degradable polymers.^{1–4} Several synthetic routes have been developed to synthesize poly(silyl ester)s, including transsilylation systems,^{2–7} hydrosilylation, and cross-dehydrocoupling polymerizations.^{7–9} We have synthesized new poly(silyl ester)s by a new route via polycondensation reaction of di-*tert*-butyl ester of dicarboxylic acid with dichlorosilane.¹⁰ This new route bears several benefits, including short time, low temperature, volatile byproduct, no solvents and catalysts.¹⁰ Among the aforementioned approaches, only the cross-dehydrocoupling route has been applied to prepare hyperbranched poly(silyl ester)s by the self-polymerization of AB_2 monomers.⁹ Hyperbranched polymers possess enhanced physical properties, such as high solubility, low viscosity, and low glass transition temperature, in comparison to their linear analogues.^{9,11} Hyperbranched polymers are highly branched structures having a large number of functional end groups, and this functionality can also be manipulated by appropriate and simple techniques.¹¹

The novel physical properties render these polymers as ideal candidates for use in a wide range of applications such as drug carrier, drug release, additives, coatings, macromolecule catalyst, and initiator.^{8,12} So these polymers have gained an increasing interest from both polymer science and technology.^{11,13} Hyperbranched polymers could be synthesized by the $A_2 + B_m$ ($m \geq 3$) route.^{11–14} However, using this route to synthesize hyperbranched poly(silyl ester)s has not been reported in the literature. Aharoni et al. have obtained the high branched polyamide gels by the $A_2 + B_4$ monomers.¹⁵ In this article, the polycondensation reaction by using the $A_2 + B_4$ monomers to synthesize the hyperbranched poly(silyl ester)s is described. First, we obtained the solid poly(silyl ester) by the reaction of the di-*tert*-butyl adipate (monomer 1) and 1,3-tetramethyl-1,3-bis- β (methyl-dichlorosilyl)ethyl disiloxane (monomer 3). Furthermore, we prepared a series of linear oligomers with *tert*-butyl as terminal groups. Then we obtain the hyperbranched poly(silyl ester)s with various state and properties by the reaction of the oligomers with monomer 3, respectively.

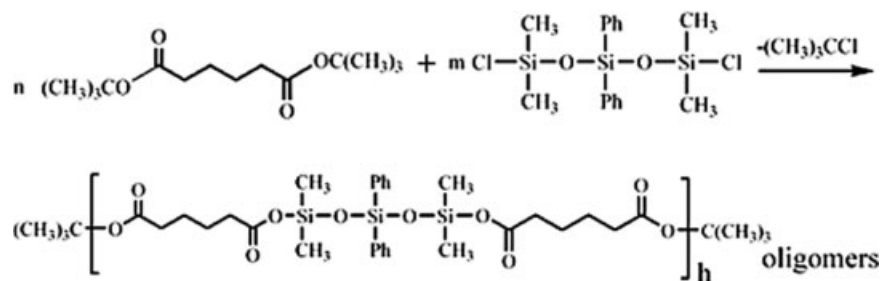
EXPERIMENTAL

Materials

Adipic acid (Chemical Industry Factory of Shandong University, China) was purified by vacuum evaporation. Thionyl chloride (Tianjin Reagent Factory, China)

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

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20274022.



Scheme 1

was purified by distillation. Tetrahydrofuran (Tianjin Reagent Factory) was distilled in the presence of sodium/benzophenone. *tert*-Butyl alcohol (Tianjin Reagent Factory) was distilled in the presence of sodium. Dimethyldichlorosilane (Shanghai Yuanfan Reagent Company, China) was distilled prior to use. 1,3-divinyl-1,1,3,3-tetramethyl disiloxane (Chenguang Chemical Industry Academe, China) was purified by distillation prior to use. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was from Shanghai Reagent Factory (China).

Measurements

^1H NMR spectrum was recorded on a FX-90 spectrometer (Japan Joel) in deuterium chloroform (CDCl_3), using CHCl_3 as internal reference. IR spectrum was recorded on a Nicolet FT-IR 20SX spectrometer (Nicolet Instruments, Madison, USA) by using films for liquids and KBr pellets for solids. The viscosity values were measured at 25°C with a NDJ-5S digital viscosimeter (Shanghai Jing Mi Science Instrument Company, China). UV spectrum was examined on a UV-4100 spectrometer (Hitachi, Japan) with 20 mg:25 mL product solution in THF. The glass transition temperatures of the polymers were examined by differential scanning calorimetry (DSC) (Rheometric Scientific DSC SP, USA), at a rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was carried out using a TGA/SDTA-851 (Mettler Toledo, Switz.) to investigate the thermal properties of samples. The samples were heated from 35 to 800°C at a rate of $10^\circ\text{C}/\text{min}$ in an inert atmosphere of nitrogen.

Synthesis of di-*tert*-butyl adipate (monomer 1);^{16, 10} 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyl-trisiloxane (monomer 2);^{17, 10} and 1,3-tetramethyl-1,3-bis- β (methyl-dichlorosilyl)ethyl disiloxane (monomer 3)^{18, 19}

Preparation of the Pt catalyst

To the 100 mL conical flask was added 1 g $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 20 mL THF. After being dissolved, the flask was set in desiccator and kept aphotic.

Synthesis of monomer 3

1.86 g (10 mmol) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane was added to a 25 mL round-bottom flask. After the flask was full of nitrogen atmosphere for 30 min, 30 mmol of MeSiHCl_2 (3 mL excess, about 50% freshly distilled), 5 mL THF, and 5 drop Pt catalyst were added to the flask via syringe. The reaction was typically allowed to stir under nitrogen at room temperature for half an hour then heated to 40°C for 4 h. The THF and excess MeSiHCl_2 were removed under reduced pressure and the monomer 3 was obtained (4.08 g, 9.8 mmol): yield 98%.

^1H NMR (90 MHz, CDCl_3 , ppm, δ): 0.77(s, 6H, SiCH_3Cl_2), 1.45–1.62 (t, 4H, $\text{CH}_2\text{CH}_2\text{SiCH}_3\text{Cl}_2$), 3.15–3.45 (t, 4H, $\text{CH}_2\text{CH}_2\text{SiCH}_3\text{Cl}_2$), 0.09 (s, 12H, $\text{Si}(\text{CH}_3)_2$)

General procedure for the synthesis of oligomers (scheme 1)

3.4400 g (8.5666 mmol) monomer 2 and 2.4344 g (9.4232 mmol, excess 10%) monomer 1 were added to a 25 mL round-bottom flask. The reaction was typically allowed to stir under nitrogen at 100°C for 12 h. The oligomer **a** was obtained. Keeping the weight of the monomer 2 constant, the weight of the monomer 1 was changed. The mole ratio of the monomer 2 to monomer 1 was 1 : 1.2, 1 : 1.3, 1 : 1.5, and 1 : 1.8, respectively. The oligomers **b**, **c**, **d**, and **e** were obtained by the aforementioned reaction process. The viscosities of the oligomers are given in Table I.

Polymerization of the monomer 3 and the monomer 1 (scheme 2)

2.9319 g (7.3040 mmol) monomer 3 and 3.6375 g (14.0797 mmol) monomer 1 were introduced into 25 mL flask. The reaction was allowed to stir under nitrogen at 100°C for 2 h until the system turned to solid and the reaction was finished.

^1H NMR, δ (ppm): 0.07(6H, s, $(\text{OSi}(\text{CH}_3)_2\text{O})$), 0.31(3H, s, $\text{CH}_2\text{SiCH}_3(\text{OCO})_2$), 0.38(3H, s, $\text{CH}_2\text{SiCH}_3\text{ClOCO}$), 0.77(3H, s, $\text{CH}_2\text{SiCH}_3\text{Cl}_2$), 1.4–1.9 (4H, t, $\text{CH}_2\text{CH}_2\text{SiCH}_3$; 4H, t, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 1.5(9H, s, $\text{C}(\text{CH}_3)_3$), 2.1–2.5 (4H,

TABLE I
Viscosities of the Oligomers and the Polymers

	Viscosity(mPa s)
<i>Oligomer code</i>	
a	8,550
b	8,190
c	7,484
d	5,846
e	1,098
<i>Polymer code</i>	
II	12,700
III	15,900
IV	20,400
V	28,400
VI	Soft solid

$\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.5–2.8(2H, t, $\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{OCO})_2$), 2.8–3.0(2H, t, $\text{CH}_2\text{CH}_2\text{SiClCH}_3\text{OCO}$), 3.6–3.8(2H, t, $\text{CH}_2\text{CH}_2\text{SiCl}_2\text{CH}_3$).

IR (cm^{-1}): 1695, 2961, 2917, 2878, 1045, 514.7, 1138, 777, 839.3, 1282.

Polymerization of the monomer 3 and the oligomers (scheme 3)

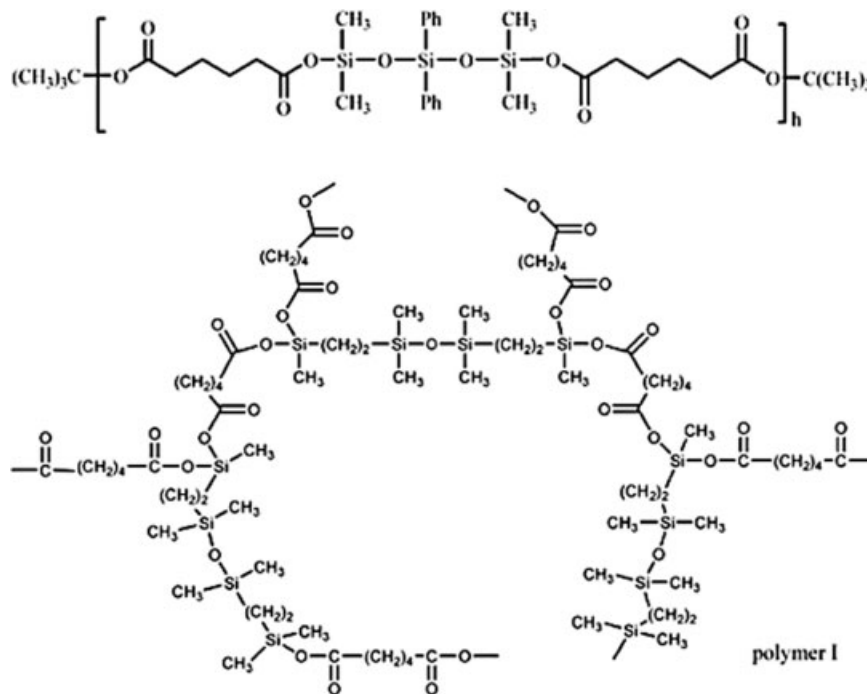
0.1783 g (0.4283 mmol) monomer 3 was introduced into the 25 mL flask containing the oligomer **a**. The mole of the monomer 3 was an half of the excess mole of the di-*tert*-butyl adipate in oligomer **a**. The reaction was typically allowed to stir under nitrogen at 100°C for 12 h. Polymer II was obtained. The monomer 3,

which was an half of the excess mole of the di-*tert*-butyl adipate in oligomer **b**, **c**, **d**, and **e**, respectively, was added to the oligomers **b**, **c**, **d**, and **e**, respectively, according to the aforementioned reaction process. Polymers III, IV, V, and VI were obtained. The viscosities of the polymers are given in Table I.

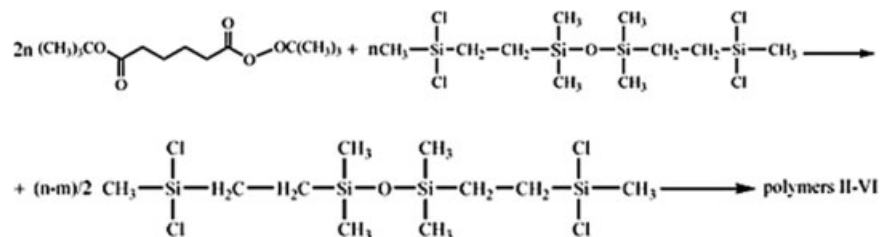
RESULTS AND DISCUSSION

About oligomers

We have obtained linear poly(silyl ester)s via polycondensation reaction of di-*tert*-butyl ester of dicarboxylic acid with dichlorosilane.¹⁰ The reaction was irreversible because *tert*-butyl chloride was eliminated as the driving force. Generally, the irreversible polycondensation reaction proceeds completely according to the polycondensation reaction theory,¹⁹ and so the polymerization degree of the oligomers obtained can be expressed by $\text{DP} = 1/q$ (DP denote the degree of polymerization, q denotes an excess fraction of either monomer). In this reaction the di-*tert*-butyl adipate was excess and so the obtained oligomers should be the *tert*-butyl as the terminal groups. This was consistent with the experimental result that the terminal groups are the *tert*-butyl groups in the ^1H NMR spectra of oligomer **a** (Fig. 2). So the oligomers as A_2 big monomers can be used to synthesize the hyperbranched poly(silyl ester) by the $A_2 + B_4$ route with monomer 3. Polymerization routes are shown in Schemes 1, 2, and 3.



Scheme 2



Scheme 3

Chemical structure identification of the polymers

^1H NMR analysis

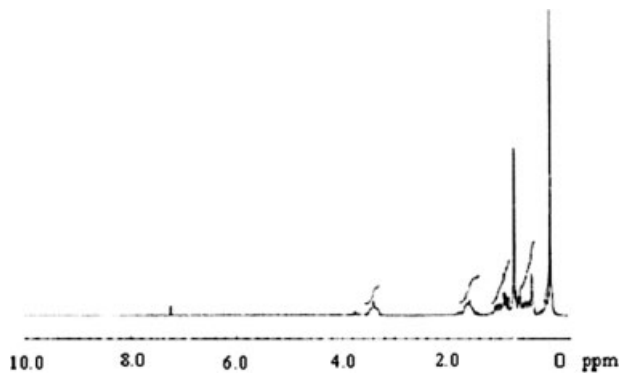
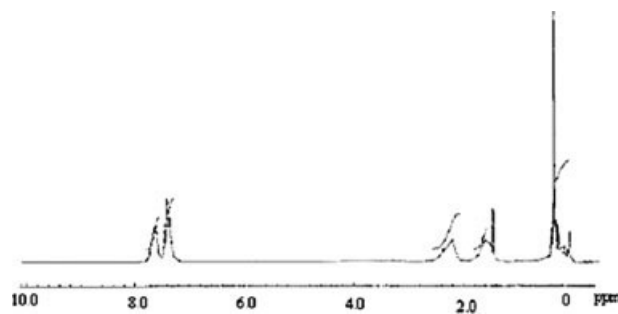
To identify the polymerization, the ^1H NMR spectra of the monomer 3 and the oligomer **a** are also shown in Figures 1 and 2, respectively. To compare with the linear poly(silyl ester), we obtained the linear poly(silyl ester) **L** by the reaction of equimolar amounts of monomer 1 and monomer 2 at 100°C for 10 h. The ^1H NMR spectra of the polymers **L**, **I**, and **II** are shown in Figures 3, 4, and 5, respectively.

In Figure 1, the disappearance of vinyl peak in the range 5.72–6.12 ppm and the appearance of a new silyl methyl peak at 0.77 ppm show that the hydrosilycation reaction was completed and monomer 3 was pure. In Figure 2, the peak of terminal silyl methyl proton at 0.51 ppm in monomer 2 disappeared and the peak of *tert*-butyl proton reduced but did not disappear completely. These results indicate that the terminal groups of oligomer **a** were *tert*-butyl groups. The ^1H NMR spectrum of polymer **L** shows the *tert*-butyl signal at 1.5 ppm and the silyl methyl signal at 0.51 ppm disappeared completely and new resonance signal appeared at 0.32 ppm for silyl methyl signal, which indicate the polymerization reaction can be proceeded completely under the aforementioned experiment conditions. The ^1H NMR spectrum of polymer **I** in Figure 4 shows that the peak of *tert*-butyl proton at 1.5 ppm and the peak of silyl methyl proton at 0.77 ppm decreased obviously and new silyl methyl proton

peaks appeared at 0.38 ppm ($-\text{COOSiCH}_3\text{Cl}$) and 0.31 ppm ($-\text{COOSiCH}_3\text{OOC}-$). These indicate that the polymerization had occurred. The peaks at 0.77, 0.38, and 0.31 ppm can be assigned to the silyl methyl protons of chain end, linear, and branching. New methylene (SiCH_2) resonance signals appeared at 2.5–3.0 ppm. These results proved the existence of the branched structures in polymer **I**. Comparing Figure 4 with Figure 5, we can find that new peaks in the range of 7.25–7.42 ppm and in the range of 7.45–7.78 ppm appeared in Figure 5, which is attributed to the existence of phenyl groups at the side chain in polymer **II**. Because of the little amount of the monomer 3, the resonance signal for the methylene at 2.5–4.0 ppm is extremely weak. In conclusion, the ^1H NMR spectra proved the existence of the branched structures.

FTIR analysis

To further identify the structure of the polymers, we show the FTIR spectra for the monomer 1 and polymer **I** in Figure 6. In Figure 6, the carbonyl groups in monomer 1 display bands at 1730 cm^{-1} and the carbonyl groups in polymer **I** display bands at 1695 cm^{-1} , and the latter is broader. The other characteristic bands in polymer **I** are observed at 1045 cm^{-1} for $\text{Si}-\text{O}-\text{Si}$, at 777 cm^{-1} for $\text{Si}-\text{CH}_2$, and at 1282 and 839 cm^{-1} for $\text{Si}-\text{CH}_3$, respectively. These confirmed the formation of the poly(silyl ester). A strong absorption for the $\text{O}-(\text{CH}_3)_3$ stretch at 1151 cm^{-1} is observed in the IR spectroscopy of monomer 1 and the absorption for the $\text{O}-(\text{CH}_3)_3$ stretch is weak in the IR

Figure 1 ^1H NMR spectra of monomer 3.Figure 2 ^1H NMR spectra of oligomer **a**.

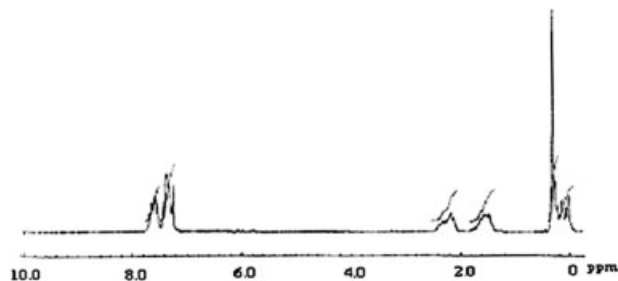


Figure 3 ^1H NMR spectra of the polymer L.

spectroscopy of polymer I. New absorption for the Si—Cl stretch displays bond at 514.7 cm^{-1} in polymer I. These IR data indicate that there are terminal *tert*-butyl and silyl chloride groups in the polymer structure. The branched structures of the polymer I have been supported further by IR spectroscopy.

UV analysis

The UV spectra of some of the obtained polymers are shown in Figure 7 (with the following order from top to bottom: polymer L, II, III, IV, V, and VI). These spectra all show peaks at 253, 258, 264, and 270 nm and the peak heights decreased with decrease of the content of the phenyl groups.²⁰ These are consistent with the expected results.

Properties of the poly(silyl ester)s obtained

Viscosity

The viscosities of the oligomers and the resulting polymers are shown in Table I. The viscosities of the oligomers decreased with increase of the excess percent for monomer 1, which is according with the relationship between the degree of polymerization and the excess fraction ($DP = 1/q$).¹⁹ Polymers II, III, IV, and V were viscous fluid. The viscosities of polymers II–V

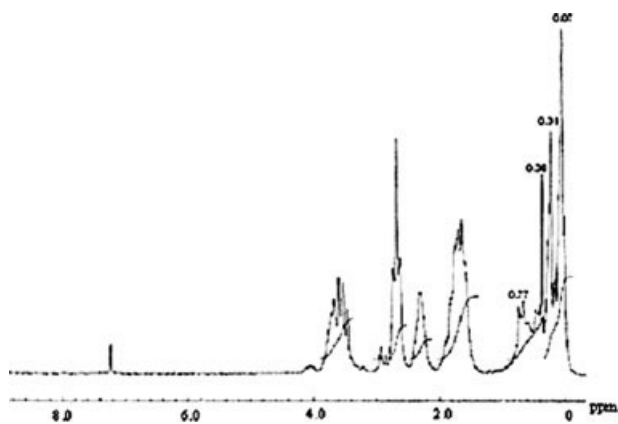


Figure 4 ^1H NMR spectra of the polymer I.

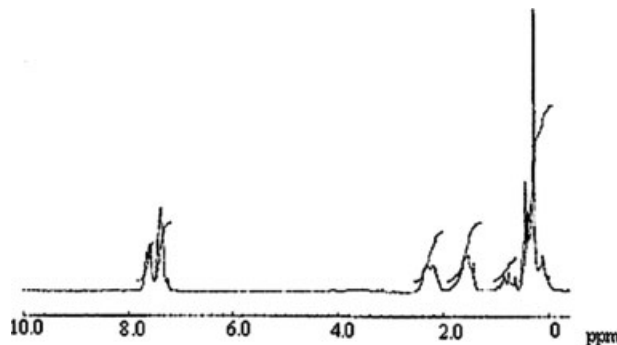


Figure 5 ^1H NMR spectra of the polymer II.

increased with increase in the amount for monomer 3. The aforementioned polymers are all hyperbranched polymers, but during the polymerization the crosslinking reaction should inevitably take place because of the existence of tetra-function monomer, and the degree of crosslinking increased with increase in the ratio of the tetra-function monomer 3. So the viscosities of polymers II–V increased. As a result, when the monomer 3 increased to some extent, the polymers VI and I turned into soft solid and solid, respectively.

Differential scanning calorimetry analysis

DSC curves of polymers I–VI and polymer L are shown in Figure 8. The T_g 's for polymers II–VI were lower than that of the linear polymer L, which indicate that some terminal groups in the hyperbranched polymers can depress the T_g .²¹ The T_g 's for polymers II, III, and IV decreased orderly mainly because of the decrease in the phenyl groups content. Comparing with polymers II, T_g 's for polymers IV and V increased, which is because with increase of the content of monomer 3 the branched and crosslinked structures increased. Because of the polymer I, the T_g is not found

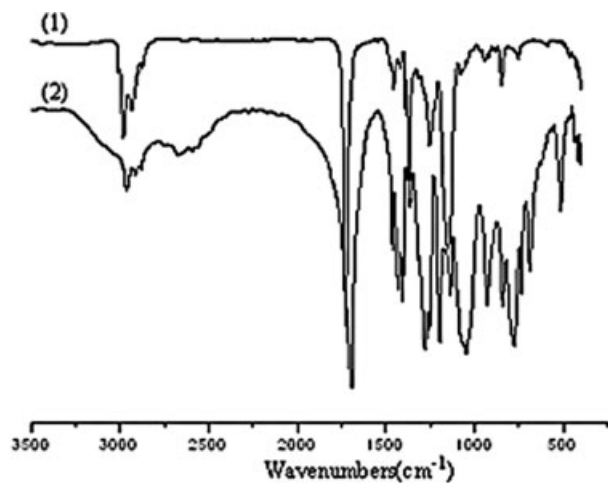


Figure 6 IR spectra of (1) monomer 1 and (2) polymer I.

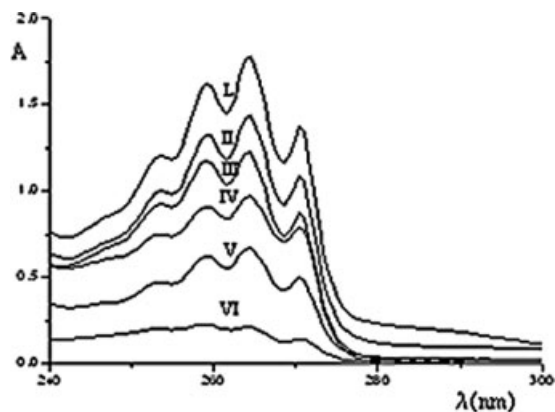


Figure 7 UV spectra of polymer II to polymer VI and polymer L.

and an endothermic peak appears at 42°C. We surmise that the aculeated endothermic peak is related to transition in the liquid crystalline phase.

Thermal stability analysis

Polymers I, III, V, VI, and L as instances are used to demonstrate the thermal stability of the poly(silyl ester)s, with the data obtained being shown in Figures 9 and 10, and Table II. T_d and T_{max} denote the 5% degradation temperature and the maximum degradation rate temperature, respectively. In Figure 9, polymers I and VI began to decompose at about 130°C and the others began to decompose at about 200°C, but the remainder weight percent of polymers I and VI were the most at 700°C. In Figure 10, polymers I and VI displayed three-step degradation while the other polymers L, III, V had two-step degradation. In the temperature range of 150–300°C, the polymer I and polymer VI decomposed rapidly, the others were not obviously decomposed. In the temperature range of 300–450°C, the polymer L decomposed rapidly and

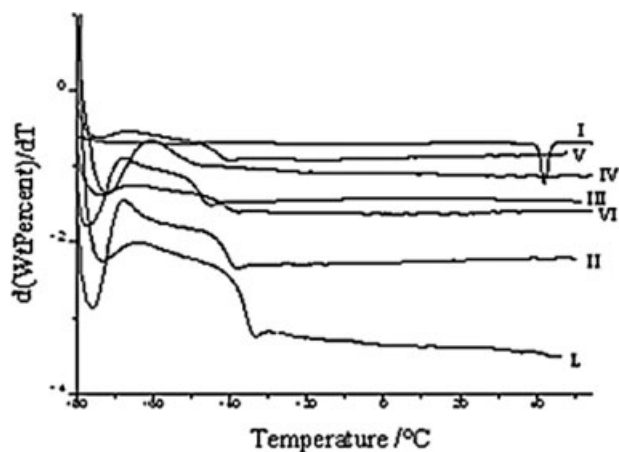


Figure 8 DSC curves of the poly(silyl ester)s.

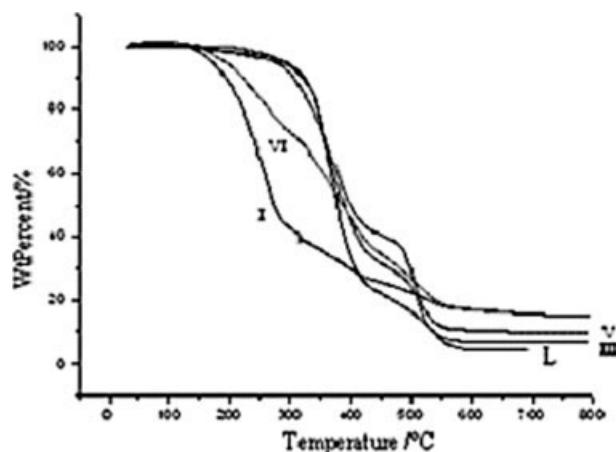


Figure 9 TGA curves of the poly(silyl ester)s.

the order of T_{max} was as follows: $L \leq III \leq V \leq VI \leq I$. In the temperature range of 450–600°C, polymer III and polymer V decomposed rapidly. In the first stage, the existence of a number of the terminal groups decreased the stability of the polymers I and VI.²² With increase of the content of phenyl groups, the stability of polymers increased but the degree of branching and crosslinking reduced. In the second stage, the later was primary, and so the stability of polymers decreased. In the third stage, polymers with the lower degree of the branching or crosslink were more thermolabile. In conclusion, the onset degradation for the polymers is governed by a mass of terminal groups, whereas the degree of the branching or crosslink is the dominant factor for overall thermal stability of the polymers.

Determination of gel fraction

Samples of the prepared hyperbranched poly(silyl ester)s were accurately weighed (W_0) and then extracted

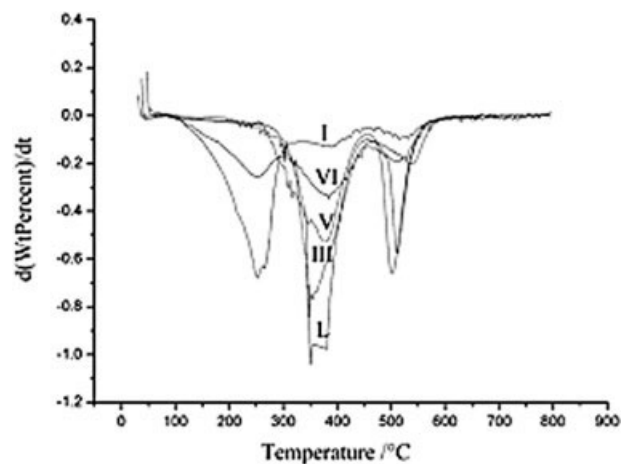


Figure 10 DTG curves of the poly(silyl ester)s.

TABLE II
TGA Data of the Poly(silyl ester)s

Sample	T_d (°C)	T_{1max} (°C)	T_{2max} (°C)	T_{3max} (°C)	Residue at 500°C (%)	Residue at 700°C (%)
I	171	248	388	522	22	16
III	292	347	510	—	25	6
V	274	377	500	—	30	10
VI	192	250	383	510	27	16
L	289	335	537	—	16	4

with distilled THF using a Soxhlet system for 12 h. After extraction, the samples were dried in a vacuum until a constant weight was reached (W).²³

$$\text{Sol fraction (\%)} = [(W_0 - W)/W_0] \times 100$$

$$\text{Gel fraction (\%)} = 100 - \text{Sol fraction (\%)}$$

The results show that polymers II–V were soluble completely in THF and no gelation occurred, which is in accordance with the literature that the hyperbranched polymers possess high solubility.⁹ Gelation occurred in polymers I and VI and the gel fraction were 50 and 16.7%, respectively. The crosslinking structures in the polymers caused the gelation. The polymerization of the monomer 1 and monomer 3 proceeded for 2 h, and the gel occurred. On the other hand, each of the oligomers and monomer 3 proceeded for 12 h and gelation occurred only in polymer VI. The aforementioned results indicate that the crosslinking reaction occurs easily between the monomer 1 and monomer 3 when compared with the oligomers and monomer 3.

CONCLUSIONS

The hyperbranched poly(silyl ester)s were obtained via the $A_2 + B_4$ route by the reaction of the di-*tert*-butyl adipate or the oligomers with the *tert*-butyl as terminal groups and 1,3-tetramethyl-1,3-bis- β (methyl-dichlorosilyl)ethyl disiloxane. ¹H NMR, IR, and UV

analysis proved the existence of the branched structures in their molecules. The T_g 's of the hyperbranched poly(silyl ester)s are lower than those of the linear poly(silyl ester). The hyperbranched poly(silyl ester)s with abundant terminal groups are the most thermolabile at the onset degradation, whereas the degree of the branching or crosslink is the dominant factors for overall thermal stability. The hyperbranched polymers obtained possess high solubility in THF except that the crosslink occurring caused the gelation. As these hyperbranched polymers contain silyl ester bond groups in their molecules, it is useful as a single type of degradable system that can demonstrate various rates of water degradation. Such an investigation is currently in progress.

References

- Shirai, M.; Miwa, T.; Tsunooka, M. *Chem Mater* 1995, 7, 642.
- Gitto, S. P.; Wooley, K. L. *Macromolecules* 1995, 28, 8887.
- Weinberg, J. M.; Gitto, S. P.; Wooley, K. L. *Macromolecules* 1998, 31, 15.
- Wang, M.; Weinberg, J. M.; Wooley, K. L. *Macromolecules* 1998, 31, 7606.
- Weinberg, J. M.; Wooley, K. L. *Polym Prepr* 1996, 37, 493.
- Wang, M.; Weinberg, J. M.; Wooley, K. L. *J Polym Sci Part A: Polym Chem* 1999, 37, 3606.
- Wang, M.; Wooley, K. L. *Polym Prepr* 2000, 41, 436.
- Wang, M.; Weinberg, J. M.; Wooley, K. L. *Macromolecules* 2000, 33, 734.
- Wang, M.; Gan, D. J.; Wooley, K. L. *Macromolecules* 2001, 34, 3215.
- Liu, Z.; Han, N.; Dong, J. *J Appl Polym Sci*, 2006, 100, 1378.
- Borah, J.; Karak, N. *Polym Int* 2004, 53, 2026.
- Gao, C.; Xu, Y.; Yan, D.; Chen, W. *Biomacromolecules* 2003, 4, 704.
- Scheel, A.; Komber, H.; Voit, B. *Macromol Symp* 2004, 210, 101.
- Yates, C. R.; Hayes, W. *Eur Polym J* 2004, 40, 1257.
- Aharoni, S. M.; Edwards, S. F. *Macromolecules* 1989, 22, 3361.
- James, H. B.; Steven, J. S. *J Org Chem* 1987, 52, 3462.
- Murry, J. G.; Griffith, R. G. *J Org Chem* 1964, 29, 1215.
- Musolf, M. C.; Speier, J. L. *J Org Chem* 1964, 29, 2519.
- Kricheldorf, H. R.; Rost, S. *Macromolecules* 2004, 37, 7955.
- Liu, Z.; Wu, C.; Hu, W. *J Appl Polym Sci* 2001, 82, 1203.
- Kumar, A.; Ramakrishnan, S. *Macromolecules* 1996, 29, 2524.
- Anila, A.; Shi, W. F. *Polym Adv Technol* 2004, 15, 669.
- Nizam El-Din, H. M. M.; El-Naggar, A. M. *J Appl Polym Sci* 2005, 95, 1105.