

## Preparation and characterization of a type of ladder-like poly(phenyl silsesquioxane) based hybrid star-shaped copolymer of $\epsilon$ -caprolactone

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**ABSTRACT:** Combination of the organic–inorganic hybrid such as silsesquioxane with  $\epsilon$ -caprolactone will lead to materials expected to be environmentally friendly and applicable to biomedical usages. A ladder-like poly(phenyl silsesquioxane) based hybrid star-shaped copolymer of  $\epsilon$ -caprolactone was prepared by ring opening polymerization of  $\epsilon$ -caprolactone catalyzed by Sn(Oct)<sub>2</sub> with hydroxyl terminated ladder-like poly(phenyl silsesquioxane) as initiator. The copolymers were characterized by proton nuclear magnetic resonance (<sup>1</sup>H-NMR), silicon nuclear magnetic resonance (<sup>29</sup>Si-NMR), Fourier-transform infrared spectrometer (FT-IR), size exclusion chromatography (SEC), thermo gravimetric analysis (TGA), and differential scanning calorimetry (DSC) in detail. Furthermore, the enzymatic degradation property of the copolymers was also investigated. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42335.

**KEYWORDS:** biodegradable; block copolymers; polysiloxanes

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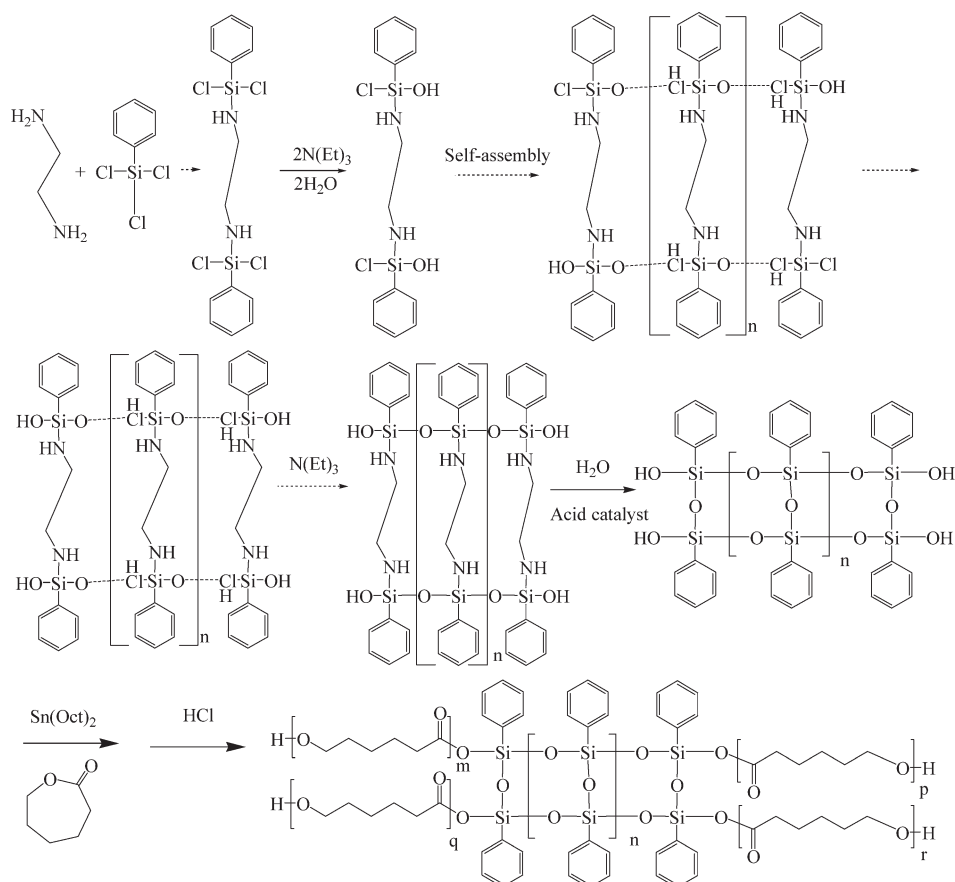
### INTRODUCTION

Aliphatic polyesters such as poly( $\epsilon$ -caprolactone) (PCL) are of great interest due to their biodegradability, biocompatibility, and permeability for environmentally packing materials<sup>1–3</sup> such as implantable polymeric scaffold materials for tissue engineering<sup>4,5</sup> and internal bone xation.<sup>6</sup> The branched structure of the star polymers resulted in lowering solution and melt viscosities compared with those of their linear counterparts of the same molecular weight.<sup>7</sup> The star-shaped macromolecular topologies are attracting considerable attention for the potential applications in the biomedical fields.<sup>7–11</sup> Zhu and coworkers<sup>12</sup> reported the preparation the drug-conjugated amphiphilic miktoarm star copolymers composed of 14 PCL arms and seven PEG arms with b-cyclodextrin as core. Mesut Gorur *et al.*<sup>13</sup> prepared a novel hexa-armed pyrene end-capped phosphazene-cored star polymer of CL via “click chemistry”. Moreover, Birol Iskin<sup>14</sup> synthesized a type of ABC type miktoarm star copolymer with polystyrene, poly( $\epsilon$ -caprolactone) (PCL), and polyethylene glycol (PEG) arms using controlled polymerization techniques in combination with thiol-ene and copper catalyzed azide-alkyne “click” reactions. To improve the thermomechanical characteristics of polymer material, Mireia Morell *et al.*<sup>15</sup> synthesized a new multi-arm star polymer based on hyperbranched poly(styrene) core and PCL Arms. James<sup>4</sup> investigated the acrylated star-poly(CL-co-D,L-lactide) and acrylated star-poly(CL-co-trimethylene carbonate),

the result of which demonstrated that the mechanical properties for a load-bearing soft tissue scaffold were improved obviously.

All these studies mentioned above have dealt with the synthesis of star copolymers of PCL with organic core. Using organic-inorganic nanoparticles such as polyhedral oligomeric silsesquioxanes (a kind of cage like polysiloxanes named POSS with formula of R<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>) to modify aliphatic polyesters are one of the most effective strategies in improving thermal and mechanical properties.<sup>16–19</sup> It is worth pointing out that a star-shaped PCL with POSS core was prepared via ring-opening polymerization of CL using octa(3-chloropropyl) POSS [(ClCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>] as an initiator catalyzed by Stannous (II) octanoate [Sn(Oct)<sub>2</sub>].<sup>20</sup> Zheng and coworkers<sup>21</sup> also have interestingly reported the synthesis of octaarmed star PCL with a POSS core. Almost at the same time, a series of silsesquioxane-based hybrid star PCL with different arm length were synthesized from ring-opening polymerization of CL initiated by silsesquioxane-based polyol.<sup>22</sup> Also interestingly, a polyphenylsilsesquioxane-b-polycaprolactone (PPSQ-b-PCL) copolymer was synthesized from condensation polymerization of  $\alpha,\omega$ -hydroxyl PCL prepolymer and polyphenylsilsesquioxane (PPSQ).<sup>23</sup>

The combination of the silsesquioxane with polymerized CL leads to the new hybrid materials and is expected to be environmentally friendly and applicable to biomedical usages such as



**Figure 1.** Synthetic route to LPPSQ based hybrid star-shaped copolymer of CL.

drug delivery and tissue engineering. The presence of siloxane component may link with a low crystallinity and improvement of mechanistic strength and thermal stability. However, the previous reported organic-inorganic star-shaped PCLs were all using POSS as inorganic cores. Recently, as a kind of structurally well-defined polysilsesquioxanes, ladder-like *polysilsesquioxanes* (LPSQs) have drawn much attention due to their outstanding performances such as excellent solubility, high thermal stability, low dielectric constant, good mechanical properties, and chemical resistance.<sup>24,25</sup> To the best of our knowledge, the copolymer with both LPSQ and CL units is never reported before. Those results above prompted us to use this strategy in the preparation of an ABC miktoarm star polymer. In this work, we present a type of ladder-like poly(phenyl silsesquioxane) (LPPSQ) based hybrid star-shaped copolymer of CL via ring opening polymerization of CL catalyzed by  $\text{Sn}(\text{Oct})_2$  with hydroxyl terminated LPPSQ as initiator according to Figure 1. The copolymers were characterized by  $^1\text{H-NMR}$ ,  $^{29}\text{Si-NMR}$ , FT-IR, SEC, TGA, and DSC in detail. Furthermore, the enzymatic degradation property of the copolymer was also investigated.

## EXPERIMENTAL

### Materials

$\text{PhSiCl}_3$  (99.9%) was from Xin'an Chemicals Co. Toluene and 1,4-dioxane were distilled over sodium benzophenone ketyl before used. CL (Acros product, AR.), 1,2-ethylenediamine (Acros product, AR.), and triethylamine (TEA, AR.) were dried over

$\text{CaH}_2$  and distilled before used. Porcine pancreatic lipase (PPL) and polyvinyl alcohol (PVA, AR. 98% (mol/mol) degree of hydrolysis) were purchased from Aladdin Industrial Corporation. Stannous octoate ( $\text{Sn}(\text{Oct})_2$ , 97%) and other reagents were from Shanghai Lingfeng Chemical Reagent Co. and used as received.

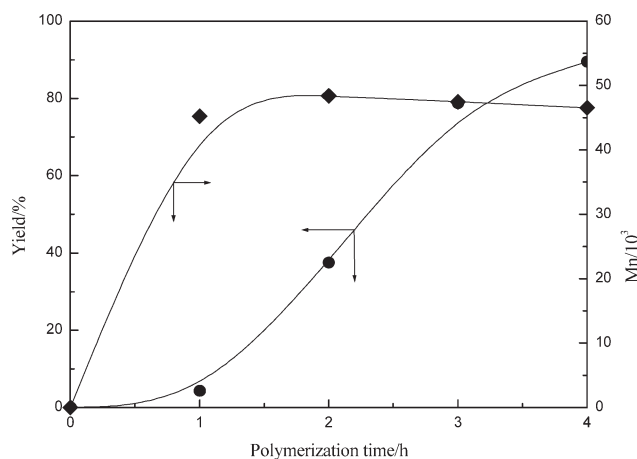
### Synthesis of LPPSQ

A mixture of 1,2-ethylenediamine (20.08 mL, 0.03 mol), TEA (8.36 mL, 0.06 mol), and toluene (100 mL) was dropped into a three-neck flask containing  $\text{PhSiCl}_3$  (9.62 mL, 0.06 mol) and toluene (150 mL) under an atmosphere of dry Argon and stirred quickly over 6 h at  $-10^\circ\text{C}$ . Then the solution was placed at room temperature for 2 h followed by adding a mixture of TEA (9.36 mL, 0.06 mol), deionized water (1.08 mL, 0.06 mol),

**Table 1.** LPPSQ Based Hybrid Star-Shaped Copolymers of CL Prepared at Various Polymerization Temperatures

Entry	Temp./ $^\circ\text{C}$	The conversion		
		of CL/%	$\text{Mn}/\text{kg}\cdot\text{mol}^{-1}$	$\text{Mw}/\text{Mn}$
1	80	2.8	45.3	2.09
2	100	46.4	46.5	1.99
3	120	89.5	55.9	1.82
4	140	81.3	46.6	2.02

Conditions:  $[\text{CL}] = 9.368 \text{ mol/L}$ ,  $n_{\text{CL}}/n_{\text{OH}} = 80$ . Polymerizations were carried out for 4 h.



**Figure 2.** Effect of polymerization time on the LPPSQ based hybrid star-shaped copolymers of CL.

toluene (50 mL), and dioxane (100 mL) for 6 h. Subsequently, the measured pH value of the reaction system was adjusted to 8~9 with TEA. The reaction mixture was filtered using a Buchner funnel to remove solid byproducts after reacted for 4 h at 40°C with vigorous stirring. The filtrate was washed with deionized water until the measured pH value to 7. Later, a white solid was precipitated after the filtrate was mixed with an equal mass of *n*-hexane. Subsequently, the precipitate was collected by a Buchner funnel and dried at 60°C about 24 h under vacuum. The product obtained was dissolved into 100 mL toluene. Then H<sub>2</sub>SO<sub>4</sub> was added and stirred for 4 h at 45°C. After removing precipitation by a Buchner funnel, the filtrate was evaporated and a white powder product of LPPSQ was produced with a yield of 86.8%. FTIR (KBr, cm<sup>-1</sup>): 3697–3568 (s, –SiOH), 3368 (s, NH), 1421 (s, –Si–N), 3000–3080 (m, Ph–H), 1590, 1431 (m, Si–Ph), 990–1190 (s, Si–O–Si). Mn: 4.96 × 10<sup>4</sup>, M<sub>w</sub>/M<sub>n</sub>=1.66.

#### Determination of –Si–OH Content in the LPPSQ

The content of –Si–OH was determined by Karl Fischer–Coulometric titration. About 0.1000 g LPPSQ was dissolved in 5.00 mL toluene in a 250 mL Iodine Flask. Then 25.00 mL toluene solution of tolylene-2,4-diisocyanate (0.5000 mol/L) and 1.00 mL toluene solution of *N,N*-dimethylcyclohexylamine (1.00%) were added into the Iodine Flask. After incubating for 10 min at room temperature, 25.00 mL toluene solution of *N,N*-dimethylcyclohexylamine (1.00%) was added and incubated for 10 min. Subsequently, 20.00 mL isopropyl alcohol and 1~2 drop of bromocresol green were added. Finally, the absorbance of 0.5000 mol/L hydrochloric acid solution was recorded until the mixture turned from green to yellow. All tests were performed in triplicate. The blank test was carried out by the same method. The –Si–OH content (mol/g) in the LPPSQ was calculated using the following equation:

$$\text{The -Si-OH content} = \frac{C_{\text{HCl}} \cdot (V_1 - V_0)}{m \times 1000}$$

where V<sub>0</sub> (mL) was the absorbance of the blank sample, V<sub>1</sub> (mL) was the absorbance in the presence of sample, m (g) was the mass of the sample, and C<sub>HCl</sub> (mol/L) was the concentration of hydrochloric acid solution. The –Si–OH content in the LPPSQ obtained was 4.6443 × 10<sup>-4</sup> mol/g.

#### Typical Reaction for Preparation LPPSQ Based Hybrid Star-Shaped Copolymer of CL

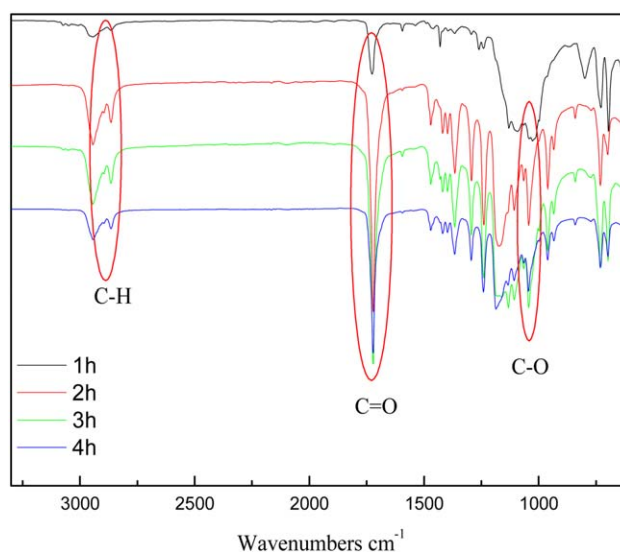
All reactions were performed under an inert atmosphere of nitrogen, using standard Schlenk techniques. A general procedure for the polymerization is as follows: 430 mg LPPSQ (–Si–OH 0.2 mmol) was added into a neat Schlenk ampule, then 81.0 mg Sn(Oct)<sub>2</sub> (0.2 mmol) was introduced by a syringe. The mixture was stirred and aged at 80°C for 0.5 h. Subsequently, 1.707 mL (16 mmol) CL was added and stirred at 120°C for 4 h. Methanol with 5% HCl was used as terminator and precipitator for polymerization. The white copolymer precipitate formed was collected by filtration, washed by methanol for three times to remove residual CL and catalyst. Later the products obtained were dried in vacuum at room temperature overnight.

#### Degradation Property of LPPSQ Based Hybrid Star-Shaped Copolymer of CL

The copolymer micro reactors were prepared by freeze drying of oil emulsion droplets of polymer microspheres in an aqueous of PVA according to the reference.<sup>26,27</sup> Then the degradation property of the copolymer was investigated in an enzyme-containing buffer with pH 7.0 at 37°C, and 180 rpm. The 0.05 g samples of the block copolymer were placed in a vial containing 1 mL of phosphate buffer with 0.1 mg of PPL. The buffer/enzyme system was changed every 24 h to maintain the original level of enzymatic activity. The samples were removed from the incubation medium, washed with distilled water, wiped dry, and then weighed and examined by light microscopy. The weights of the samples were recorded and used to determine the percentage of mass retention. The same was done with the control sample without enzyme.

#### Characterization

<sup>1</sup>H-NMR and <sup>29</sup>Si-NMR spectra were recorded on a Bruker Avance Av400 (400 MHz) spectrometer with a PTFE NMR tube in acetone at room temperature with tetramethylsilane (TMS) as



**Figure 3.** The FT-IR spectra for the products obtained at various polymerization times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table II.** Effect of Various Monomer Concentrations on the LPPSQ Based Hybrid Star-Shaped Copolymers of CL

Entry	[CL]/mol·L <sup>-1</sup>	Mn/kg·mol <sup>-1</sup>	Mw/Mn	The conversion of CL/%
1	9.368	46.5	1.99	89.5
2	4.684	60.0	2.25	82.9
3	3.747	56.7	1.91	81.0
4	3.123	66.2	1.81	83.3

Conditions:  $n_{\text{CL}}/n_{\text{OH}}=80$ , Polymerizations were carried out at 120°C for 4 h.

the internal reference. Fourier-transform infrared (FT-IR) spectroscopic analysis was carried out using a Perkin-Elmer FTIR 2000 spectrometer using KBr pellets. The scanning range was from 400 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> and 64 scans were collected for each sample. Size Exclusion Chromatography (SEC) measurements were performed on a Waters 150-C in toluene at 25°C with a flow rate of 1.0 mL/min using commercial polystyrene standards for calibration. XRD (X-ray diffraction) analysis was carried out using a D/Max 2550V/PC X-ray diffractometer with Cu-K $\alpha$  radiation operated at 40 kV and 40 mA in the 2 $\theta$  range of 0 – 80° at a sweep rate of 0.04° s<sup>-1</sup>. DSC curves were recorded using a DSC Q200 apparatus under nitrogen atmosphere with a carrier gas flow rate of 20 mL min<sup>-1</sup>. The samples were heated to 150°C, held for 2 min to erase the thermal history, then cooled to -90°C at a rate of 10°C min<sup>-1</sup>, and finally heated again to 150°C at a heating rate of 10°C min<sup>-1</sup>. TGA was carried out using a TG 209C apparatus (Germany), in which samples were heated from ambient temperature to 400°C at a rate of 10°C min<sup>-1</sup> in a dynamic nitrogen atmosphere. The morphology and behavior of the materials during enzymatic degradation were assessed by light microscopy (Olympus BX51) fitted with a CCD camera (Nikon LV100PDL). Photographs were taken before and after enzymatic degradation.

## RESULTS AND DISCUSSION

### Preparation and Characterization of LPPSQ Based Hybrid Star-Shaped Copolymer of CL

The LPPSQ based hybrid star-shaped copolymers of CL were synthesized at various reaction temperatures. As can be seen from

Table I, when the reaction performed at 80°C, the conversion of the CL was quite low and almost no copolymer obtained. It may be ascribed to the active species of the catalyst formed only at a higher reaction temperature. For the polymerization performed at 100 and 140°C, both the conversions of CL and the molecular weight of products were lower compared to the polymerization carried out at 120°C. Therefore, in this study, we focus on the ring opening polymerization of CL performed at 120°C.

The effect of reaction time on the monomer conversion and molecular weight of the copolymers was explored (Figure 2) and the results exhibited that the conversion of CL increased steadily with the prolongation of the polymerization time. However, a further prolongation of the reaction time will result in a lower molecular weight.

The FT-IR spectra for the copolymers obtained at various polymerization time were depicted in Figure 3. The bands at 2933 cm<sup>-1</sup> and 2860 cm<sup>-1</sup> (C–H stretching of -CH<sub>2</sub>- groups), 1770 cm<sup>-1</sup> (carbonyl group), and 1200 cm<sup>-1</sup> (C–H bending) in the spectra were ascribed to CL unit. It is clearly demonstrated by Figure 3 that the peaks corresponding to the CL increased with the prolongation of the polymerization time. In order to confirm these signals are originated from the PCL copolymerized onto LPPSQ but not from the homo-PCL mixed with LPPSQ, a sample of LPPSQ was prepared by mixing dissolved pulp and homo-PCL by dichloromethane extraction according to reference.<sup>28</sup> The FT-IR spectrum of LPPSQ indicated that homo-PCL could be completely removed, and the signals were solely contributed by the PCL chains in the copolymers.

Table II exhibits the effect of monomer concentration on the polymerization. It can be seen that the conversion of CL was increasing steadily with the increasing of the monomer concentration.

As can be seen from Table III,  $n_{\text{CL}}/n_{\text{OH}}$  has a significant effect on the LPPSQ based hybrid star-shaped copolymers of CL. It obviously can be seen that the molecular weight and  $n_{\text{CL}}/n_{\text{PhSiO}_{1.5}}$  increased with the increasing of  $n_{\text{CL}}/n_{\text{OH}}$ , which implies that with the increasing of  $n_{\text{CL}}/n_{\text{OH}}$ , the block chain of CL unit in the copolymers becomes longer and longer. The result in Table III also indicated that the conversion of CL is the highest when  $n_{\text{CL}}/n_{\text{OH}}=80$ .

As pointed out by SEC curves in Figure 4, the products obtained were all high molecular weight polymers with a single

**Table III.** Effect of  $n_{\text{CL}}/n_{\text{OH}}$  on the LPPSQ Based Hybrid Star-Shaped Copolymers of CL

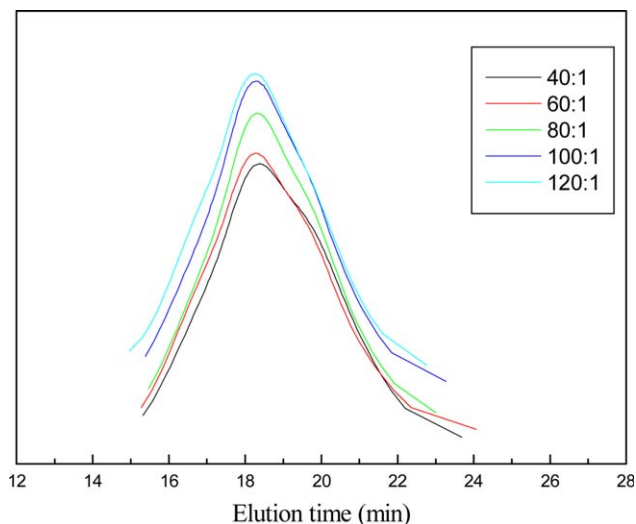
Entry	$n_{\text{CL}}/n_{\text{OH}}$	Mn/kg·mol <sup>-1a</sup>	Mw/Mn <sup>a</sup>	The conversion of CL/%	$n_{\text{CL}}/n_{\text{PhSiO}_{1.5}}$ <sup>b</sup>	$T_m$ /°C <sup>c</sup>	$\Delta H_m$ /(J/g) <sup>c</sup>
1	40	42.8	2.21	82.5	4.95: 1	55.7	63.3
2	60	44.5	2.26	79.6	5.25: 1	56.6	63.0
3	80	46.5	1.99	89.5	11.13: 1	56.9	71.7
4	100	48.5	2.02	83.7	17.03: 1	57.2	72.7
5	120	52.7	2.17	81.6	17.25: 1	57.3	90.7

Conditions:  $n_{\text{CL}}/n_{\text{OH}}=80$ , Polymerizations were carried out at 120°C for 4 h.

<sup>a</sup>The Mn and PDI were measured by GPC calibrated with polystyrene standards.

<sup>b</sup>The molar fraction ratio of CL to PhSiO<sub>1.5</sub> ( $n_{\text{CL}}/n_{\text{PhSiO}_{1.5}}$ ) in copolymers, calculated from <sup>1</sup>H-NMR.

<sup>c</sup> $T_m$  and  $\Delta H_m$  were determined by DSC.

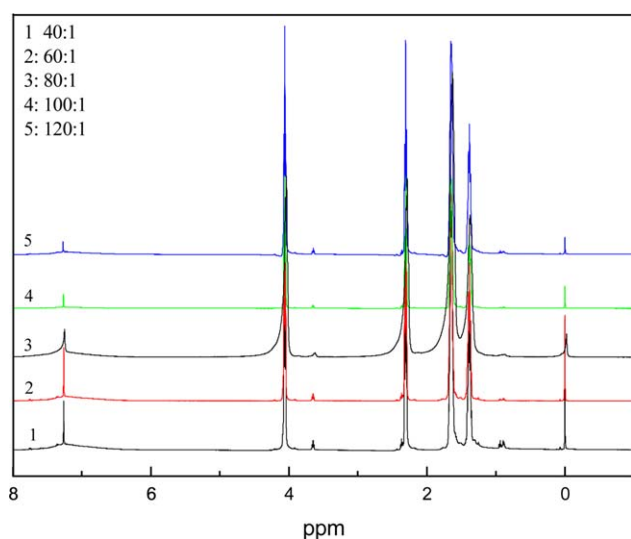


**Figure 4.** The SEC curves for the block copolymers obtained with various  $n_{\text{CL}}/n_{\text{OH}}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

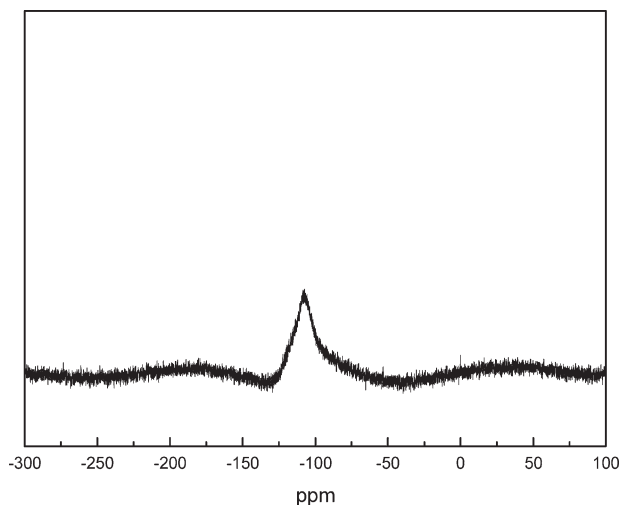
and much narrow molecular weight distribution ( $M_w/M_n$ ). It suggests that the products obtained were block copolymers, not a composite of PCL and LPPSQ.

A further structure analysis of the products was performed by  $^1\text{H-NMR}$  and  $^{29}\text{Si-NMR}$ .  $^1\text{H-NMR}$  spectra of the copolymers obtained are shown in Figure 5. The chemical shift  $\delta=7.26$  was ascribed to the proton of  $-\text{C}_6\text{H}_5$  in the block segment of LPPSQ. The chemical shift at 4.04, 2.29, 1.63, and 1.39 ppm were ascribed to the characteristic peaks of  $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ,  $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ ,  $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ , and  $\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  of CL units respectively.

The  $^{29}\text{Si-NMR}$  spectrum for the product Entry 3 in Table III was given by Figure 6, which denotes that the chemical shift at  $-104.22$  was ascribed to the ladder like structure of LPPSQ,



**Figure 5.**  $^1\text{H-NMR}$  spectra for the copolymer obtained with various  $n_{\text{CL}}/n_{\text{OH}}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

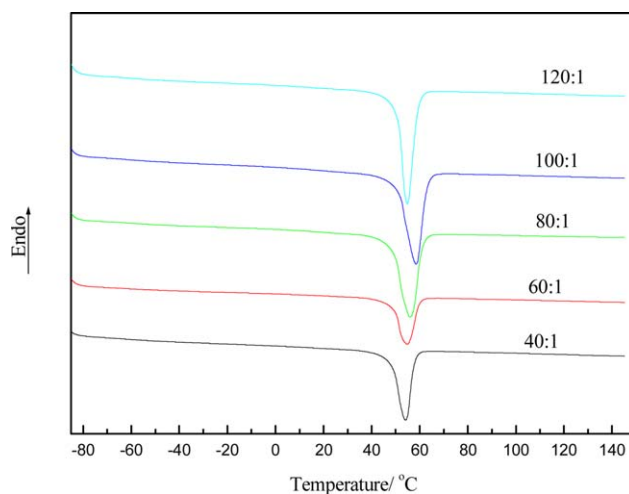


**Figure 6.**  $^{29}\text{Si-NMR}$  spectrum for the copolymer obtained (Entry 3 in Table III).

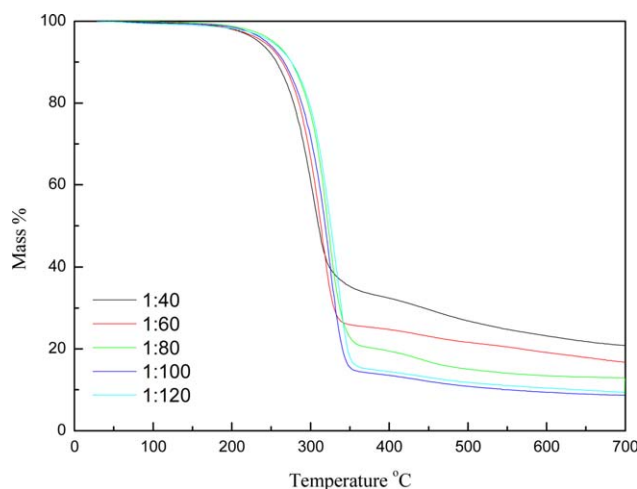
which indicated that the well-defined ladder-like structure of LPPSQ was not damaged.

The thermal behaviors of the LPPSQ based hybrid star-shaped copolymers of CL were characterized by DSC as shown in Figure 7 and summarized in Table III. The melting points and enthalpies of the copolymers both increased with the increasing of the CL content, declaring higher crystallinity of the LPPSQ based hybrid star-shaped copolymers of CL with high CL content. Each copolymer has only one thermal transition, predicating singular crystalline in copolymers and the block structure of copolymers.

The TGA results for thermal degradation of copolymers plotted in Figure 8 exhibited that the degradation temperature decreased with the increasing of CL unit content.  $T_{d5}$  points of all the copolymers are around  $260^\circ\text{C}$ , which illustrated that the products obtained have excellent thermal stability.



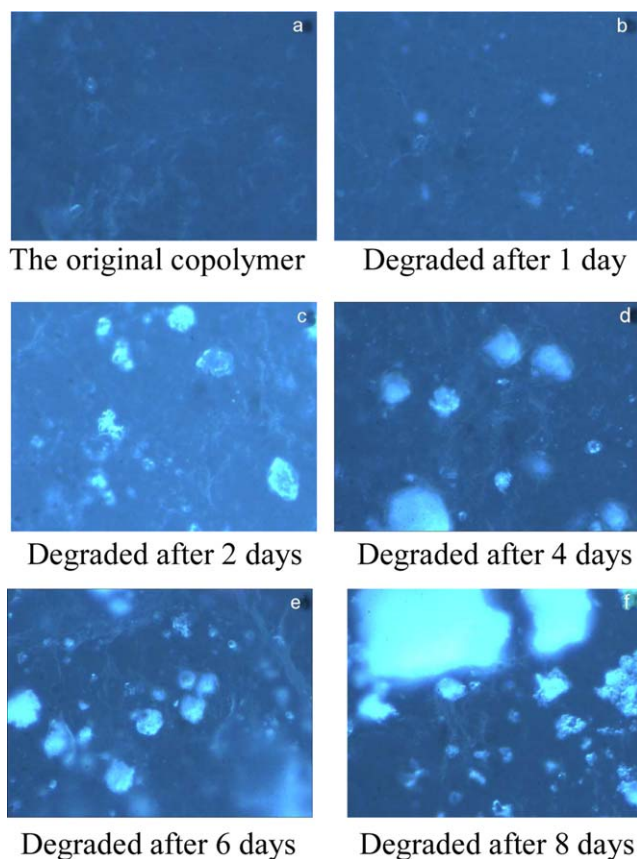
**Figure 7.** DSC curves for the products obtained with various  $n_{\text{CL}}/n_{\text{OH}}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** TGA curves for the products obtained with various  $n_{\text{CL}}/n_{\text{OH}}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Degradation Properties of the LPPSQ Based Hybrid Star-Shaped Copolymers of CL

The degradation property of the block copolymer investigated in an enzyme-containing buffer with pH 7.0 at 37°C and 180 rpm. The degradation profiles for the product Entry 3 in



**Figure 9.** Photos of the block copolymer enzymatic degradation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** The Residual Mass of the Degraded Product

Entry	Degradation time/d	Residual mass/%
1	0	100
2	1	98.5
3	2	93.3
4	4	90.1
5	6	87.7
6	8	80.4

Conditions: An enzyme-containing buffer with pH 7.0 at 37°C and 180 rpm.

Table I is shown by Figure 9. The results of the residual mass are also summarized in Table IV. It obviously exhibited that the copolymer began to degrade after 1 day. With the prolongation of degradation time, the copolymer degrades faster and faster. It can be seen from the microscopy that the copolymer even cannot remain the original morphology after 8 days while the control sample without enzyme was still not degraded. It is shown by all these results that the products are with good biodegradable property.

### CONCLUSIONS

Ladder-like poly(phenyl silsesquioxane) based hybrid star-shaped copolymers of CL were prepared by ring opening polymerization of CL catalyzed by  $\text{Sn}(\text{Oct})_2$  with hydroxyl terminated LPPSQ as initiator. The thermal behaviors of products characterized by DSC declared that the melting points and enthalpies of the copolymers both increased with the increasing of the CL content. Furthermore, the TGA results exhibited that the products have excellent thermal stability with degradation temperature decreased with the increasing of CL unit content. The good biodegradable property was also confirmed by the enzymatic degradation experiment. Branched star-polymers of aliphatic polyesters such as PCL have attracted much attention for their unique architectures for environmentally packing materials such as implantable polymeric scaffold materials for tissue engineering and internal bone xation. Aroused by the investigation above, we are continuing to explore the synthesize, performance, and applications of the LPPSQ hybrid star copolymers and miktoarm star copolymers of CL with other cyclic esters (such as lactide, cyclic carbonate) catalyzed by salen or salan complexes of rare earth and late transition metals.

### ACKNOWLEDGMENTS

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