2130 *Macromolecules* **2010**, *43*, 2130–2136
DOI: 10.1021/ma100145j

Macromolecules
ARTICLE

Study of the Supramolecular Architecture-Directed Synthesis of a Well-Defined Triple-Chain Ladder Polyphenylsiloxane

Zhongjie Ren,[†] Ping Xie,[‡] Shidong Jiang,[†] Shouke Yan,*,[†] and Rongben Zhang*,[‡]

[†]*State Key laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China, and* [‡]*Laboratory of Polymer Science and Material, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Received December 5, 2009; Revised Manuscript Received February 4, 2010

ABSTRACT: High molecular weight (M_w) triple-chain ladder polyphenylsiloxane (**TCLP**) was synthesized by a supramolecular architecture-directed approach. First, a bis(phenyldihydroxysiloxy)dimethoxysilane ladder monomer was self-assembled via hydrogen bonding interactions in acetonitrile/toluene (1:1, v/v) solution to form a ladder superstructure (**LS**). Then the **LS** was used as a template to direct the whole polymerization process. Lyophilization and surface-enhanced synchronous growth polycondensation process of the LS gave a ladder dimethoxysiloxy-bridged polyphenylsiloxane (**DCLP**) with gaseous triethylamine as condensation catalyst. Then **DCLP** was hydrolyzed to form a triple-chain ladder superstructure (**TCLS**), which was further converted into the target **TCLP** via subsequent in situ dehydration condensation. The three ladder entities formed during the polymerization, that is, **LS**, **DCLP**, and **TCLP**, have been well characterized. X-ray diffraction shows two Bragg reflections representing the ladder width and ladder thickness, respectively. ^{29}Si NMR analysis illustrates narrow peaks with the peak width at half-height of 0.5−2.5 ppm for the repeat units of the entities, indicating fine ladder regularity. In addition, an investigation of the dependence of the intrinsic viscosity [η] on molecular weight (M_w) in Mark−Houwink−Sakurada equation gave the exponent factor $\alpha = 1.19$, suggesting the target **TCLP** had a semirigid ladder structure. Meanwhile, high-resolution transmission electron microscopy observations showed a regular morphological structure for **TCLP** with a molecular width of ca. 1.4 nm. This value is quite close to the X-ray diffraction data. Dynamic mechanical analysis experiments also indicated **TCLP** has high storage modulus and high thermal stability.

Introduction

High molecular weight (M_w) ladder polymers bring about the persistent interests to scientists for their unique structures as well as their superior mechanical, thermoresistant, and electroluminescent properties compared with their single chain counterparts.[1] Among the ladder polymers, ladder polysiloxanes have been especially emphasized due to their hybrid composite and excellent resistances to thermal and irradiation degradations caused by the stronger bond energy of Si−O linkages than that of the common C−C and C−O ones.[2−4] Brown et al.[5] has first reported a high M_w ladder polyphenylsilsesquioxane (**Ph-LPSQ**) in the early 1960s. The reported structure was, however, refuted later by Frye et al.,[6] who indicated that the so-called **Ph-LPSQ** was actually "partially opened polycyclic cages", and Brook,[7] who claimed that the reported high M_w ladder polysilsesquioxanes are generally random networks. The difficulty stems from the fact that the preparation of ladder polysiloxane needs multifunctional monomers and therefore requires precise configuration control during polymerization process. Otherwise, cyclization and gelation reactions will take place, resulting in the formation of very complicated products with cyclic, ladder, cage and cross-linked structures.[8] As proposed by Bailey,[9] the most desirable type of reaction for preparing perfect ladder polymers is the one in which both sides of the ladder grow synchronously. This is, however, quite difficult to control during polymerization.

Supramolecular template-directed polymerization, which is of particular interest in the field of polymer synthesis, provides an effective method to synthesize polymers with designed structures.[10] As examples, while Stupp et al.[11] has prepared the first two-dimension planar polymer, Harada et al.[12] has successfully prepared the cyclodextrins-based tube polymers. Moreover, a series of polymers with peculiar structures, such as nanosphere and nanotube, have also been prepared by combining lyophilization with surface confined synthesis.[13−15] Taking this into account, we have put forward a supramolecular template strategy named "supramolecular architecture-directed stepwise coupling and polymerization" to realize the synchronous growth polymerization. As a result, a series of ordered double-chain ladder polymers, such as, organo-bridged polysiloxanes and polysilsesquioxanes, have been successfully prepared.[16−21]

It should be pointed out that triple-chain ladder polymers are expected to have even superior chemical and physical properties comparing to the double-chain ladder polymers. For example, the well-known fiberlike collagen protein, which exhibits a unique barlike three-ply spiral structure formed through hydrogen bonding between the polypeptides chains, shows excellent physical and mechanical properties (e.g., high-tensile strength etc.) in addition to its important biochemical functions.[22] Taking the excellent properties into account, the triple-chain ladder polymers may find many applications.[23−25] Therefore, the synthesis of triple-chain ladder polymers is of great significance both from scientific and practical view points. Recently, Swarger et al.[26] have achieved the synthesis of three-strand conducting ladder polymers by two-step electropolymerization of metallorotaxanes. Dehydration condensation-based synthesis of the triple-chain

---

*To whom correspondence should be addressed. E-mail: (S.Y.) skyan@mail.buct.edu.cn; (Z.R.) zhangrb@iccas.ac.cn. Tel. +86-10-6445 5928. Fax +86-10-6445 5928.

ladder polysiloxane (**TCLP**) is, however, even more difficult than the synthesis of the double-chain analogues considering hexafunctional monomers should be used. From the viewpoint of polymer chemistry, the preparation of triple-chain ladder polymers requires precisely confined synthesis of multifunctional monomer, which has not been touched so far. Herein, we report the details about the supramolecular architecture-directed synchronous growth polymerization for preparing the soluble high M_w well-defined **TCLP**.

Experimental Section

Materials. Toluene, 1,4-dioxane, hexane, and tetrahydrofuran (THF) were distilled over sodium and benzophenone; triethylamine was distilled over sodium before use. All other reagents were purchased without further purification.

Characterizations. Fourier transform infrared (FTIR) spectra were recorded using a NICOLET spectrophotometer in the range of 400−4000 cm^{-1}.

^{1}H and ^{29}Si NMR spectra were obtained at room temperature by using Bruker DX400 and Bruker DX300 spectrometers at 400 MHz and 59.6 MHz, respectively, with tetramethylsilane as the reference.

X-ray diffraction (XRD) was performed on a Rigaku D/max 2400 diffractometer with Cu Kα radiation.

Elemental analysis was conducted by Heraeus CHN-RAPID, DATEL System, Inc. (Germany).

Vapor pressure osmometry (VPO) analysis was measured in dry toluene at 40 °C on a Knauner VPO instrument at 20% relative humidity.

The DSC investigation was carried out on a Mettler Toledo Star 822 differential scanning calorimeter at a heating rate of 10 °C/min under nitrogen atmosphere.

Thermogravimetric analysis (TGA) of **TCLP** was performed on Perkin-Elmer TGA7 thermal analyzer under a 50 mL/min nitrogen flow. The samples were heated from 25 to 800 °C at a rate of 10 °C/min.

Laser light scattering (LLS) measurements were performed on an ALV/DLS/SLS-5022F spectrometer equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He−Ne Laser (λ_0 = 632.8 nm) as the light source. The spectrometer has a high coherence factor of $\beta \sim 0.95$ because of a novel single-mode fiber optical coupled with an efficient avalanche photodiode. The LLS cell was held in a thermostat index matching vat filled with purified and dust-free THF with the temperature controlled to within ±0.02 °C. The details of the LLS instrumentation and theory can be found elsewhere.[27]

Gel permeation chromatography (GPC) analysis was also performed by a set of a Hitachi/Merck L-7100 pump, a Waters 2414 refractive index detector, and a Waters 486 ultraviolet detector, the combination of Hersteller MZ-Gel SDplus 5 μm, porosity 100 Å, 10^3 Å, 10^4 Å, and 10^6 Å. THF with 1 g/L LiBr was used as eluent at flow rate of 1 mL/min at 35 °C.

Elemental analysis was conducted by Heraeus CHN-RAPID, DATEL System, Inc. (Germany).

The viscosity was determined with Ubbelohde viscometers using toluene as solvent at 23 °C. The flow time of pure solvent was maintained at least 100 s and thus the kinetic correction could be negligible.

For transmission electron microscopy (TEM) observation, 1% solution of **TCLP** in toluene was dropped onto the carbon-coated mica surface. After evaporation of the solvent, the carbon film together with the sample was then floated onto the surface of distilled water and transferred onto 400 mesh copper grids for TEM observation. A JEOL JEM-2100F TEM operated at 200 kV was used in this study.

Dynamic mechanical analysis (DMA) was performed on the sample of 5 × 5 × 1 mm in size using a dynamic mechanical analyzer from Mettler Toledo (DMA/SDTA861^e) under shear mode in a temperature range of −60 to 350 °C at a frequency of 1 Hz and 3 °C /min. Storage modulus and tg δ were recorded as a function of temperature.

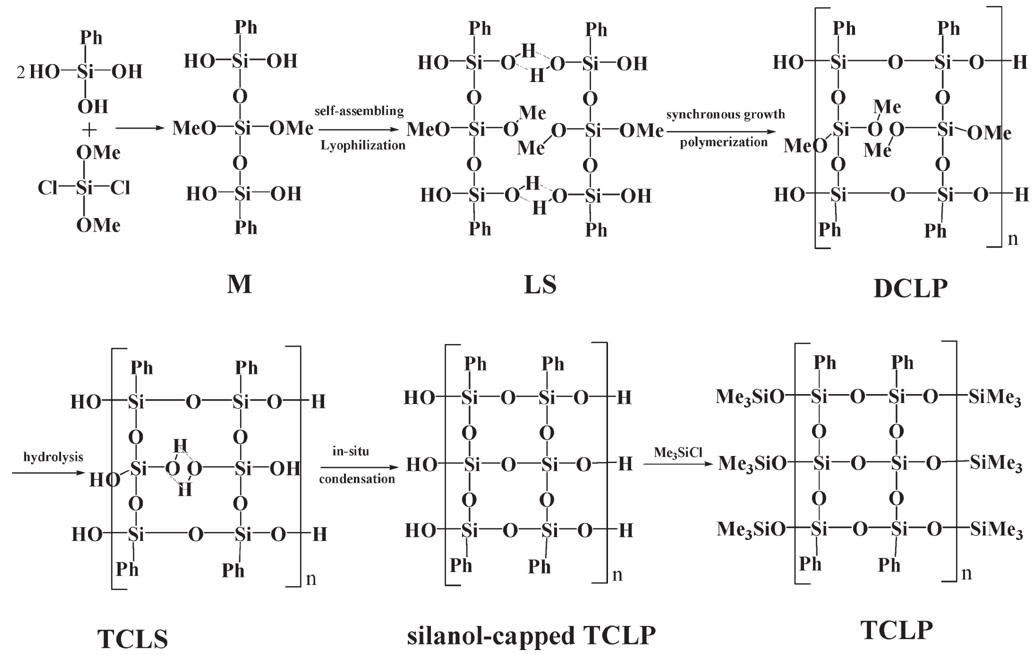
Synthesis. *Preparation of Phenylsilanetriol.*[28] A mixture of phenylamine (14.02 g, 150 mmol), deionized water (2.7 g, 50 mmol) and 350 mL of anhydrous ether was placed into a 500 mL round bottom flask in ice bath. Then phenyltrichlorosilane (10.58 g, 50 mmol) and 50 mL anhydrous ether were added stepwise over 5 h. The reaction was continued for a further 2 h at room temperature after addition of phenyltrichlorosilane. After removing the sediment through filtration, the solution was then condensed and precipitated with *n*-hexane to give the white product (6.1 g, 78%). ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm): 7.44 (dd, 2H), 7.36 (q, 3H), 5.55 (s, 3H). FT-IR (cm^{-1}): 3000−3600 (Si−OH), 1430 (−Ph) and 907 (Si−OH). ^{29}Si NMR (59.6 MHz, 1,4-dioxane), δ = −52.7 ppm. Elem. Anal. Calcd for $C_6H_8O_3Si$: C, 46.13; H, 5.16. Found: C, 46.21; H, 5.10.

Preparation of Dimethoxydichlorosilane.[29] A mixture of tetramethyl orthosilicate (51.7 mL, 348 mmol), silicon tetrachloride (40 mL, 348 mmol) was added into an autoclave and heated to 150 °C for 30 h. After that, the mixture was then separated by fractional distillation. The boiling point of the product is 100−102 °C (62.6 g, 61%). ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm): 3.68 (s, 6H). ^{29}Si NMR (59.6 MHz, 1,4-dioxane), δ = −55.2 ppm. Elem. Anal. Calcd for $C_2H_6O_2Cl_2Si$: C, 14.91; H, 3.75; Cl, 44.02. Found: C, 14.88; H, 3.82; Cl, 44.09.

*Preparation of Monomer (**M**), Bis(phenyldihydroxysiloxy)-dimethoxysilane.* A mixture of phenylsilanetriol (1.35 g, 8.6 mmol) and 40 mL anhydrous 1.4-dioxane was added into a three-neck flask protected by Argon atmosphere. The flask was equipped with two constant pressure funnels, which contain dimethoxydichlorosilane (0.644 g, 4 mmol), 15 mL of 1,4-dioxane, and triethylamine(0.808, 8 mmol), 15 mL of 1,4-dioxane, respectively. First, 1 mL of dimethoxydichlorosilane solution was added dropwise at room temperature, and then dimethoxydichlorosilane and triethylamine were added dropwise at the same speed over 6 h. The reaction was continued for another 2 h at the room temperature after addition. The sediment was removed by filtration and then the solvent was removed by reduced pressure at room temperature. After that, the mixture was dissolved in ether and washed three times by deionized water. The solution was dried over anhydrous sodium sulfate to get the product (1.0 g, 81%). ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm): 7.7 (dd, 4H), 7.36 (q, 6H), 5.53 (s, 6H), 3.53 (s, 6H). ^{29}Si NMR (59.6 MHz, 1,4-dioxane), δ = −62.4, −71.7 ppm. Elem. Anal. Calcd for $C_{14}H_{20}O_6Si_3$: C, 45.62; H, 5.47. Found: C, 45.75; H, 5.39.

*Preparation of Dimethoxysiloxy-Bridged Double-Chain Ladder Polyphenylsiloxane (**DCLP**) Precursor via Self-Assembly and Surface-Enhanced Synchronous Growth Polycondensation.* A saturated solution of bis(dihydroxyphenylsiloxy)dimethoxysilane in toluene/acetonitrile (1/1) (0.25 mol/L) was slowly stirred at 0 °C for about 15 min for self-assembling the bis(dihydroxyphenylsiloxy)dimethoxysilane into ladder superstructure. Then, 0.5 mL of this solution was added into a 250 mL flask. The flask was rotated rapidly to spread the sample solution on its inner surface. Following that, the flask was frozen instantly. After removal of the solvent under a vacuum, ladder superstructures were coated on the inner surface of the flask as a thin solid layer. The solid phase polycondensation of the ladder superstructure was then initiated when TEA vapor (catalyst) was drawn into the flask at room temperature. The in situ surface enhanced confined polycondensation was allowed to proceed for 48 h. Subsequently, the in situ polymerized product on the inner surface of reaction flask was dissolved in toluene/acetonitrile (1/1) and the dehydration polycondensation was continued for another 20 h at 45 °C in the presence of several drops of TEA. The byproduct water was removed by azeotropic distillation under reduced pressure to increase the

Scheme 1. Synthetic Route to TCLP



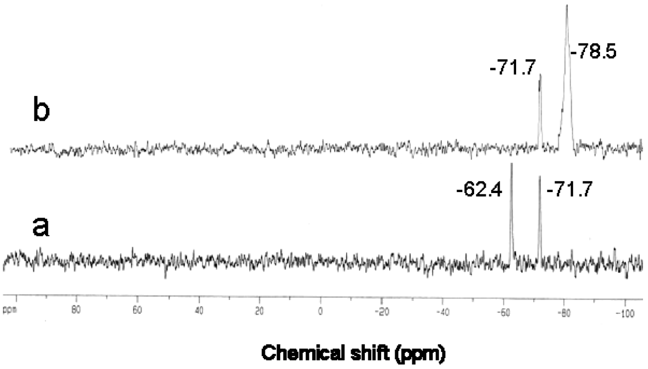


Figure 1. ^{29}Si NMR of (a) ladder superstructure **LS**; (b) intermediate dimethoxysiloxy-bridged double-chain ladder polysiloxane **DCLP**.

molecular weight of the final polymer. The final mixture was precipitated by methanol and filtered to give white solid **DCLP** (47 mg, 94%). ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm): 7.7−7.4 (b, 4H), 7.4−7.25 (b, 6H), 3.56 (s, 6H). ^{29}Si NMR (59.6 MHz, toluene), δ = −71.7, −78.5 ppm.

Preparation of the Target ***TCLP***. A mixture of 1.6 g **DCLP**, 40 mL of THF, 1 mL of water, and 5d 0.1 mol/L hydrochloric acid was stirred 24 h at room temperature, until the methyl group absorbance peak disappeared in FTIR. The solvent then was removed by reduced pressure. The product was dissolved in toluene/acetonitrile (1/1) again. The solution was added into 1 mL of TEA and stirred for 24 h at room temperature, and the polycondensation was then continued for another 24 h at 45 °C. Finally, the solution of trimethylchlorosilane (0.1 mL, 0.1 mol/L) in toluene was added, and the end-capping reaction was allowed to proceed for 6 h. The final mixture was precipitated by methanol and filtered to give white solid (1.47 g, 96%).^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm): 7.7−7.4 (b, 4H), 7.4−7.25(b, 6H). ^{29}Si NMR (59.6 MHz, toluene), δ = −76.8, −109.4 ppm.

Results and Discussion

As sketched in Scheme 1, the whole polymerization process was realized through four steps including the following: (1) the preparation of monomer bis (phenyldihydroxysiloxy) dimethoxysilane (**M**); (2) ladder monomer **M** was self-assembled via hydrogen bonding interactions in acetonitrile/toluene (1:1, v/v) solution to form a ladder superstructure (**LS**); (3) the **LS**, which was used as a template to direct the whole polymerization process, underwent first a lyophilization and surface-enhanced synchronous growth polycondensation process to get ladder dimethoxysiloxy-bridged polyphenylsiloxane (**DCLP**) with gaseous triethylamine as condensation catalyst; (4) the **DCLP** was then hydrolyzed to form a triple-chain ladder superstructure (**TCLS**), which was further converted into the target **TCLP** via subsequent in situ dehydration condensation. In the following paragraphs, we will describe each step in details.

Preparation of the Bis(phenyldihydroxysiloxy) Dimethoxysilane Monomer. The monomer bis(phenyldihydroxysiloxy)-dimethoxysilane (**M**) was synthesized by dehydrochlorization coupling reaction of dimethoxydichlorosilane with phenylsilanetriol. In this process, the feed ratio, the addition order and speed of materials and the reaction temperature are the important parameters for getting the desired monomer. For this reaction, the phenylsilanetriol must be excessive. Therefore, we set the feed ratio of phenylsilanetriol and dimethoxydichlorosilane as 2.15:1. The excessive phenylsilanetriol can be removed by washing with water. Moreover, the dimethoxydichlorosilane and TEA solutions should be added dropwise into the phenylsilanetriol solution simultaneously with the drop speed of TEA slightly slower than that of dimethoxydichlorosilane to avoid the TEA induced condensation of phenylsilanetriols or/and the produced monomers **M**. In addition, the reaction under room temperature with slow material addition speed is preferred. The ^{29}Si NMR spectrum of the obtained monomer **M** is presented in Figure 1a. The appearance of two peaks at δ = −62.4 and −71.7 ppm, respectively (as shown Table 1), indicates the existence of two kinds of silicon atoms corresponding to the two repeat structures of $Ph(OH)_2\underline{Si}{-}O{-}$ and $-O(OCH_3)\underline{Si}(OCH_3)O-$, respectively.

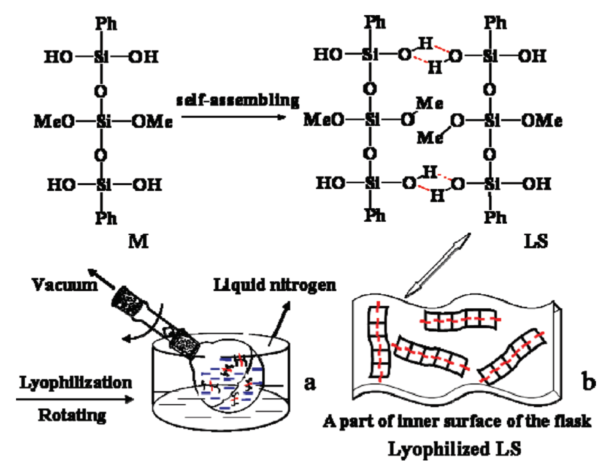
Formation and Characterization of Self-Assembled Ladder Superstructure (LS) in Solution. Kakudo and Watase et al.[30,31] have reported a series of crystal structures of organosilanols, which provided clear information regarding the H-bonding

Table 1. Characterization Data of Three Ladder Entities, LS, DCLP, and TCLP

sample	DP/M	polydisperse index (PDI)	W^a/T^b by XRD (nm) found	W^a/T^b by XRD (nm) calcd.	$\delta^d/w_{1/2}{}^e$ (ppm) by ^{29}Si NMR
LS	5/1,970^f		1.33/0.41	−c	−62.4/0.5; −71.7/0.5
DCLP	−/66,028^g	1.37^h	1.34/0.45	1.34/0.39	−71.7/0.5; −78.5/2.5
TCLP	−/63,600^g	1.42^h	1.36/0.43	1.36/0.39	−76.4/2.5; −109.4/2.5

[a] W, the ladder width. [b] T, the ladder thickness. [c] −, absence. [d] δ, chemical shift. [e] $w_{1/2}$, peak width at half-height. [f] M_n determined by VPO. [g] M_w determined by SLLS. [h] PDI determined by GPC.

Scheme 2. Schematic Illustration of Ladder Superstructure LS Alignment (a) in Solution and (b) on the Glass Surface



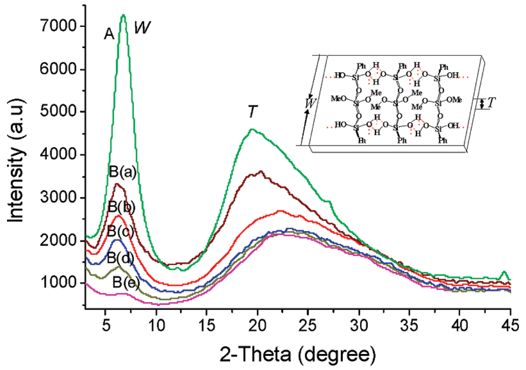


Figure 2. XRD spectra of (A) **DCLP** and (B) **LS** in different solvents by lyophilization (a) toluene/acetonitrile, (b) acetonitrile, (c) dioxane/acetonitrile, (d) dioxane, and (e) toluene/acetonitrile at 80 °C. The inserted chart illustrates the ladder width (W) and ladder thickness (T) of the **LS**.

between Si−OH groups. They found that these crystal structures consist of molecular chains with square-planar (parallelogram-type) hydrogen bonding between the two nearest intermolecular Si−OH neighbors as linkages. It is also confirmed that this type of Si−OH association exists not only in crystalline phase but also in solution. Recently, Gunji et al.[32] have reported the crystal structure of 1,3-diphenyl-tetrahydroxy-disiloxane, in which four Si−OH groups face each other to form a ladder-type network caused by the intermolecular H-bonding. On the basis of these studies, it was proposed that ladder superstructure **LS** could be formed from the self-assembly of the monomer **M** via square-planar H-bonding interactions of silanols in solution (Scheme 2).

To confirm the presence of **LS** in solution, we conducted a series of controlled experiments. As a weak supramolecular dynamic assembly based-on the hydrogen-bonding of Si−OH groups, **LS** displayed an apparent molecular weight of 1,970 measured by vapor pressure osmometry (VPO) at 40 °C, corresponding to ca. 5 repeat units of the monomer (as shown Table 1). This suggests the existence of H-bonding induced supramolecular aggregates. To further confirm the formation of ladder superstructures, that is, **LS** shown in Scheme 2, different solutions of the obtained monomer were lyophilized by quick freezing in liquid nitrogen. In this way, thin films on glass slides can be obtained by removing the solvent under reduced pressure. X-ray diffraction (XRD), which has been widely used in the structure analysis of ladder polymers,[33,34] was performed. As shown in Figure 2, the XRD of the above lyophilized samples shows two distinct diffraction peaks with 2θ at about 6.6 and 20.2°, representing the ladder width (W) and thickness (T) of the ladder superstructure, respectively.[5] This result is very similar to that of the usual ladder polymers[16] and indicates the presence of **LS** in solution.

It is well-known that the H-bonding is very susceptible to the ambient environment such as temperature and polarity or donor-electron capability of solvents.[35,36] In this work, we focused on the influence of solvents on the regularity of ladder superstructure. To achieve this, we chose four kinds of solvents, that is, acetonitrile, 1,4-dioxane, acetonitrile/toluene (1:1, v/v), and acetonitrile/1,4-dioxane (1:1,v/v), which may promote the formation of maximum hydrogen-bonding according to the literature.[35,37] The XRD patterns of the samples lyophilized from different solutions with monomer concentration of 0.25 mol/L and initially at 0 °C are shown in Figures 2B(a−d). One can see that the ladder superstructure self-assembled in acetonitrile/toluene (1:1, v/v) at 0 °C showed a sharper and more intense peak in the small-angle region than that self-assembled in 1,4-dioxane, acetonitrile, and acetonitrile/1,4-dioxane solutions. This implies that **LS** formed in acetonitrile/toluene (1:1, v/v) solution at 0 °C possesses a higher regularity than those formed in other solution. A possible reason is that acetonitrile/toluene solvent has low donor-electron capacity and does not interrupt the hydrogen-bonds of silanols. To demonstrate the foregoing explanation, the acetonitrile/toluene solution of the monomer was first heated to 80 °C and then lyophilized quickly. As illustrated in Figure 2B(e), this treatment approximately leads to the disappearance of Bragg diffraction corresponding to the ladder width. This indicates that hydrogen-bonded ladder superstructures have been greatly destroyed upon heating the solution to 80 °C. According to the above experimental results, we have chosen the acetonitrile/toluene (1:1, v/v) as solvent in the follow-up polymerization process.

Preparation of the Dimethoxysiloxy-Bridged Ladder Polyphenylsiloxane (DCLP) via Self-Assembly and Surface-Enhanced Synchronous Growth Polycondensation. In situ surface-confined polycondensation was an important step for preparing well-defined ladder **DCLP** and consequent the final target triple-chain polymer **TCLP**. At first, a thin layer of the self-assembled ladder superstructure was coated on the inner surface of the reaction flask via rotating the flask and lyophilization, and then polycondensation was initiated when TEA vapor was drawn into the flask. The inner surface condition of the reaction flask, for example, the hydrophilic or hydrophobic property, was an important factor for the polycondensation, influencing the adsorption of ladder superstructure **LS** onto the inner surface. It was found in our previous work,[37] as far as the regularity of the resultant **DCLP** was concerned, that the octadecyl-terminated inner surface was poorly suited for the in situ surface-confined polycondensation, whereas both the ordinary and the hydroxyl-terminated inner surfaces were similarly effective for the polycondensation process. Thus, the ordinary inner surface was chosen. Moreover, the rotating speed of the reaction flask also affects the surface-confined polycondensation. The continuous rotation of the flask led to the alignment of the ladder superstructure along the rotation direction. A faster rotating speed resulted in a better spreading of the liquid phase and consequently a thinner layer of the ladder superstructure. In principle, a thinner layer would be more favorable for the fabrication of a polymer with high regularity. It was found that a combination of a 500 mL reaction flask, 0.5 mL of saturated solution of monomer **M** in acetonitrile/toluene (1:1, v/v) (0.25 mol/L), rotating speed of ca. 270 rpm, and a vacuum rate of 0.05 mbar during the lyophilization process were optimal for this stage of polycondensation.

Compared with the usual solution polycondensation, the in situ surface-confined polycondensation could efficiently restrain the cyclization and random gelation side reactions. This greatly reduced the fractions of cyclo-oligomers and cages and increased the ladder regularity of the **DCLP**. The product obtained at this stage of polycondensation was HO-terminated **DCLP** oligomer. Under mild conditions, the oligomers readily self-organized into a new extended ladder superstructure. Therefore, a follow-up condensation in toluene/acetonitrile (1/1) solution was carried out under suitable conditions to further increase the molecular weight of **DCLP**, while the ladder regularity of polymer was effectively maintained.

As shown in Figure 1b, the ^{29}Si NMR spectrum of the resulting **DCLP** consists of two peaks at $\delta = -71.7$ with a narrow peak width at half-height of 0.5 ppm and $\delta = -78.5$ ppm with a narrow peak width at half-height of 2.5 ppm, suggesting the existence of two kinds of silicon skeletons. The former peak is assigned to Si-atom of the middle repeat structure $-O(OCH_3)\underline{Si}(OCH_3)O-$, and the latter is associated to the side $Ph\underline{Si}O_{3/2}$. In addition, the XRD profile of **DCLP** (see Figure 1A) also display two distinct peaks at 2θ around 6.4° (ladder width, $W = 1.34$ nm) and 19.5° (ladder thickness, $T = 0.45$ nm), respectively. XRD and ^{29}Si NMR results indicate the **DCLP** possesses a regular ladder structure. Generally, the gel permeation chromatograph (GPC) using polystyrene as the standard samples is only suitable to characterize the flexible single-chain polymers. For this reason, molecular weight of the **DCLP** was determined by static light scattering in THF solution as $M_w = 6.60 \times 10^4$. But polydisperse index still was determined by GPC as shown in table 1.

Preparation of the Target Triple-Chain Ladder Polymer (TCLP). The target **TCLP** was prepared via hydrogen bonding-aided in situ dehydration condensation of triple-chain ladder superstructure (**TCLS**) derived by hydrolysis of **DCLP**. It is realized by hydrolyzing the methoxy groups of the **DCLP** into the hydroxyl groups and follow-up condensation of them. In this step, 0.1 mol/L hydrochloric acid and THF were used to hydrolyze the methoxy groups into hydroxyl groups. Polar solvent THF favors the hydrolysis of the methoxy groups. In addition, the 0.1 mol/L hydrochloric acid cannot break the formed Si−O−Si chains of **DCLP**. FTIR measurement was conducted to follow the kinetics of the hydrolysis process by monitoring the intensity of characteristic absorption bands relevant to the Si−OMe (2910, 2850 cm^{-1}) and Si−OH (3300 cm^{-1}) groups. After hydrolysis for 24 h at 25 °C, the peak associated to the Si−OH groups increased remarkably, while the peak corresponding to the Si−OMe groups disappeared completely. Also the ^{1}HNMR signal of Si−OMe at $\delta = 3.6$ ppm disappeared. All these indicate unambiguously the completion of the hydrolysis reaction. Because the condensation of Si−OH groups unavoidably happened partly during the hydrolysis process under acid condition, the triple-chain ladder superstructure (**TCLS**) derived from **DCLP** cannot be separated.

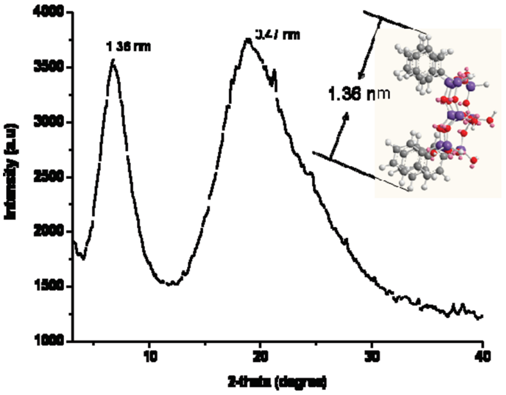


Figure 3. XRD of the target triple-chain ladder **TCLP**. The inserted chart is the molecular simulated **TCLP** by Chemoffice 2006.

Follow-up in situ condensation of Si−OH groups was conducted in acetonitrile/toluene (1:1, v/v) and catalyst TEA. The mixed solvent acetonitrile/toluene (1:1, v/v) favors the formation of ladder superstructure **TCLS** through hydrogen-bonding of the neighboring Si−OH groups. Since the condensation of Si−OH groups was carried out in a confined environment composed by two ladder Si−O−Si chains, new triple-chain ladder polymer structure could form effectively. After a 48 h polycondensation, the peak associated to the Si−OH groups disappeared almost completely in FT-IR spectrum. A small peak at ca. 3600 cm^{-1} is associated to free terminal Si−OH groups. These terminal Si−OH groups were then end-capped by adding trimethylchlorosilane to avoid cross-linking of the molecular chains.

Characterization of TCLP. As the target triple-chain ladder polymer is prepared via hydrogen bonding-aided in situ dehydration condensation of triple-chain ladder superstructure (**TCLS**), the structure of the final **TCLP** has a close resemblance of the ladder superstructure **LS** obtained in solution. As shown in Figure 3, the XRD profile of the final **TCLP** exhibits also two distinct peaks at 2θ around 6.3 and 19.4°. These two peaks correspond to the ladder width ($W = 1.36$ nm) and thickness ($T = 0.46$ nm), respectively, as predicted by the molecular simulation with Chemoffice 2006 simulation software. If **TCLP** has a cis-isotactic structure, the adjacent phenyl groups are arranged on the same side of the ladder backbone and the width of the ladder is about 1.36 nm (inset of Figure 3), which is in excellent agreement with the XRD result. However, if **TCLP** has a cis-syndiotactic structure as shown in Figure S10, the width of the ladder is about 1.51 nm, which is inconsistent with the XRD result. So it is reasonable that **TCLP** is of cis-isotactic configuration.

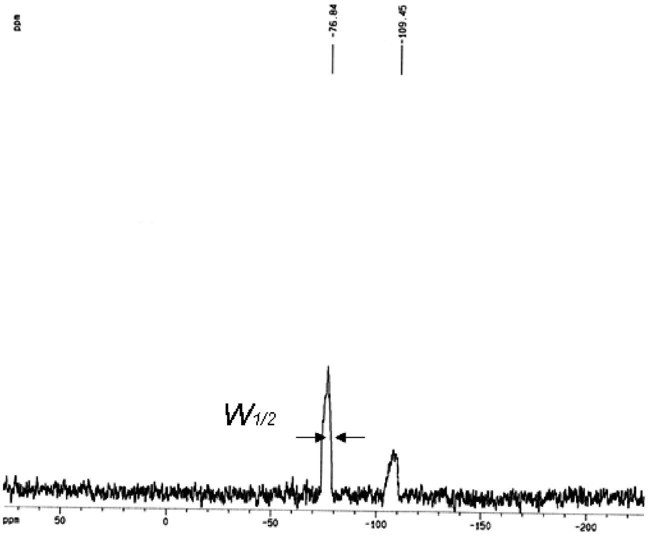


Figure 4. ^{29}SiNMR of **TCLP**.

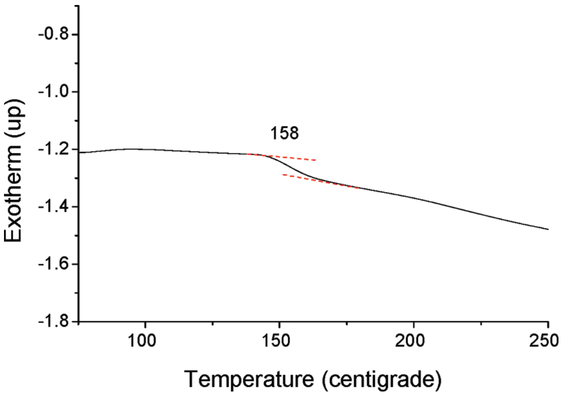


Figure 5. DSC curve of **TCLP**.

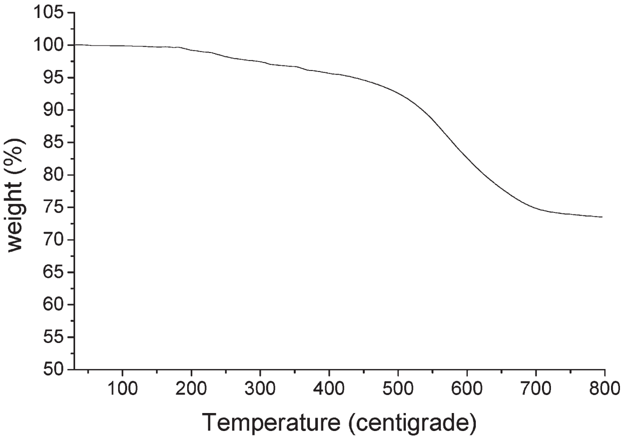


Figure 6. TGA curve of **TCLP**.

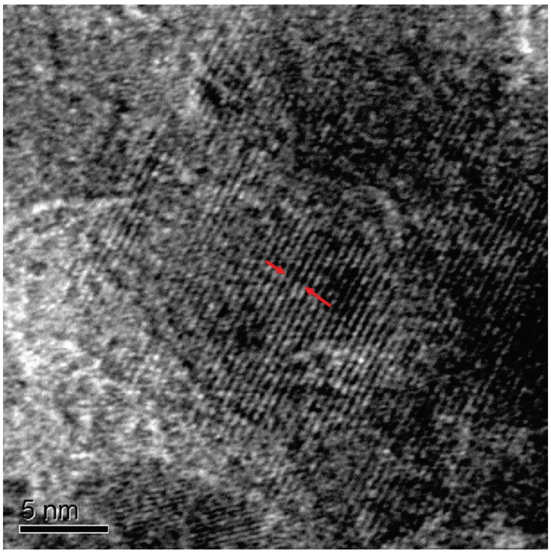


Figure 7. TEM image of **TCLP**.

In addition, the structural regularity of **TCLP** was further confirmed by ^{29}Si NMR analysis. It was known that the higher the regularity of ladder polymer, the narrower the resonance peak of silicon atoms in polymer skeleton.[5,38] As shown in Figure 4, the ^{29}Si NMR spectrum of **TCLP** showed two signals at $\delta = -76.4$ ppm and $\delta = -109.4$ ppm, corresponding to the $\text{Ph-}\underline{\text{Si}}\text{O}_{3/2}$ (side silicon atom of triple-chain) and $\underline{\text{Si}}\text{O}_{4/2}$ unit (middle silicon atom of triple-chain), respectively. The narrow peaks with a half-height width of 2.5 ppm indicate that the **TCLP** possess fine triple-ladder regularity. Moreover, it is known that the glass transition temperatures (Tg) can be used to reflect the rigidity and regularity of ladder chain. The higher the Tg, the higher the ladder rigidity and regularity. The Tg of **TCLP** measured by differential scanning calorimetry (DSC) is ca. 158 °C (Figure 5), suggesting great rigidity and fine ladder regularity.

The thermal decomposition temperature of **TCLP** is as high as ca. 600 °C and the weight loss at 800 °C is equal to 27 wt % of the initial amount, showing excellent thermal stability (Figure 6). However, the slight weight loss of 5% before 500 °C may be caused by condensation of some remaining silanol groups of the defected polysiloxane chains.

The relationship between the intrinsic viscosity $[\eta]$ and the absolute molecular weight of the polymers was studied to investigate the ladder conformational properties of the **TCLP**. Usually, the Mark−Houwink−Sakurada equation is used to express the intrinsic viscosity as a function of the molar mass.

$$[\eta] = KM^{\alpha} \qquad (1)$$

K and α are constants for a given polymer−solvent system at a given temperature. The exponent α is characteristic for the polymer topology and ranges from $\alpha = 0$ (solid spheres) over $\alpha = 0.5$ (random coil under θ conditions) to $\alpha = 2$ (rigid rod).[39,40] The viscosity index (α) of the **TCLP** estimated by the log $[\eta]$/log M_w plot (not shown here but can be found in Supporting Information as Figure S11) is 1.19, indicating a high stiffness of the ladder chain.

The high-resolution transmission electronic microscopy image, as shown in Figure 7, shows clear features (three parallel bright-dark alternative lines) of the extended ladder chains of **TCLP**. The width of three parallel bright-dark alternative lines, as marked by the arrows, is measured to be 1.4 nm, which is quite close to the ladder width of **TCLP** estimated by the XRD. Therefore, these dark lines may correspond to the stacked side phenyl groups and the main ladder Si−O−Si chains, respectively. This result is similar to that of the real double-chain ladder polytriphenylenesilsesquioxane.[19]

Dynamic mechanical analysis (DMA) is an efficient method to determine the relationship of polymer structure and materials' performance. Figure 8 shows the temperature

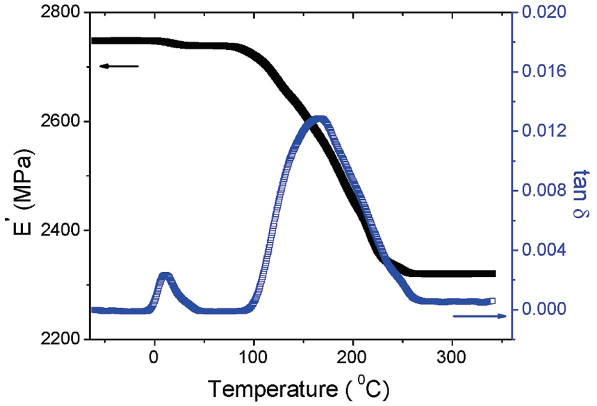


Figure 8. Temperature dependence of storage modulus and tan δ for of **TCLP**.

dependence of storage modulus (E') and tan δ, the ratio of loss modulus to storage modulus, of the **TCLP**. The α-relaxation process associated with the glass transition of the **TCLP** is determined. The α-relaxation temperature ($T\alpha$), taken at the maximum of tan δ peaks, is 167 °C. As expected, the $T\alpha$ values associated with the glass transition of **TCLP** is close to the Tg results (158 °C) obtained by DSC. Except the α-relaxation, a β-relaxation process was also observed at ca. 9.5 °C, which may be attributed to the inner rotation of the side phenyl groups or the Si−O−Si bonds. The value of E' of the **TCLP** is around 2740 MPa at 25 °C, which exhibits an obvious reduction around 170 °C corresponding to its' glass transition. In addition, the value of E' is 2320 MPa when the temperature is above 250 °C and it is almost constant with the temperature increasing. A few decrease of E' before and after the Tg indicates that the **TCLP** has high thermal stability.

Conclusions

A high M_w and well-defined triple-chain ladder polyphenylsiloxane **TCLP** with a narrow peak width at half-height of 2.5 ppm in ^{29}SiNMR spectrum was synthesized by a supramolecular architecture-directed approach. First, bis(phenyldihydroxysiloxy)dimethoxysilane was self-assembled to form ladder superstructure (**LS**). Then the **LS** underwent first a lyophilization and surface-enhanced synchronous growth polycondensation process to get intermediate ladder dimethoxysiloxy-bridged polyphenylsiloxane (**DCLP**). Finally, the in situ dehydration condensation of hydrogen bonded triple-chain ladder superstructure **TCLS** derived by hydrolysis of **DCLP** gave the target **TCLP**. The confined environment has prevented other side reactions such as the cyclization and gelation, which commonly occur in solution polycondensation of silanol-containing monomers. This strategy could be suitable to prepare a variety of well-defined triple-chain ladder polymers.

Acknowledgment. The financial supports of NSFC (No. 50833006, 50773088, 50973008) are gratefully acknowledged.

Supporting Information Available: Characterization data of the monomer and polymer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **1999**, *121*, 11538–11545.
(2) Zhou, Q.; Yan, S.; Han, C. C.; Xie, P.; Zhang, R. *Adv. Mater.* **2008**, *20*, 2970–2976.
(3) Sanchez, C.; Soler-Illia, G. J.; de., A. A.; Ribot, F.; Lalot, T.; Mayer, C. R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061–3083.
(4) Sanchez, C.; Arribart, H.; Guille, M. M. G. *Nat. Mater.* **2005**, *4*, 277–288.
(5) Brown, F., Jr.; Vogt, L. H., Jr.; Katchman, A.; Eustance, J. W.; Kiser, K. M.; Krantz, K. W. *J. Am. Chem. Soc.* **1960**, *82*, 6194–6195.
(6) Frey, C. L.; Klosowski, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4599–4601.
(7) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley-Interscience: New York, 2000; pp 309−311.
(8) Abe, Y.; Gunji, T. *Prog. Polym. Sci.* **2004**, *29*, 149–182.
(9) Baily, W. J. In *Concise Encyclopedia of Polymer Science & Engineering*; Kroschwitz, J. L., Ed.; John Willey & Sons, Inc.: New York, 1990; pp 516−528.
(10) Couet, J.; Samuel, S. J.; Kopyshev, A.; Santer, S.; Biesalski, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3297–3301.
(11) Stupp, S. I.; Son, S.; Lin, H. C.; Li, L. S. *Science* **1997**, *276*, 384–389.
(12) Harada, A.; Li, J.; Kamachi, M. *Nature* **1993**, *364*, 516–518.
(13) Keisuke, T.; Takuzo, A. *Chem. Commun.* **2000**, *24*, 2399–2412.
(14) Lin, S.; McCarley, R. L. *Langmuir* **1999**, *15*, 151–159.
(15) Gopireddy, D.; Husson, S. M. *Macromolecules* **2002**, *35*, 4218–4221.
(16) Zhang, T.; Deng, K.; Zhang, P.; Xie, P.; Zhang, R. B. *Chem.—Eur. J.* **2006**, *12*, 3630–3635.
(17) Wan, Y.; Yang, L.; Zhang, J.; Zhang, P.; Fu, P. F.; Zhang, T.; Xie, P.; Zhang, R. B. *Macromolecules* **2006**, *39*, 541–547.
(18) Tang, H.; Sun, J.; Jiang, J.; Zhou, X.; Hu, T.; Xie, P.; Zhang, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 10482–10488.
(19) Zhang, X.; Xie, P.; Shen, Z.; Jiang, J.; Zhu, C.; Li, H.; Zhang, T.; Han, C. C.; Wan, L.; Yan, S.; Zhang, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3112–3116.
(20) Ren, Z. J.; Cao, X. Y.; Xie, P.; Zhang, R. B.; Yan, S. K.; Ma, Y. M. *Chem. Commun.* **2009**, *27*, 4079–4081.
(21) Liu, C.; Liu, Y.; Shen, Z.; Xie, P.; Zhang, R. B.; Yang, J.; Bai, F. *Macromol. Chem. Phys.* **2001**, *202*, 1581–1585.
(22) Metzler, D. E. *Biochemistry*, 2nd ed.; Harcourt Academic Press: London, 2001.
(23) Stupp, S. I.; Lin, H. C.; Li, L. S.; Keser, M. *J. Am. Chem. Soc.* **1995**, *117*, 5212–5227.
(24) Liu, D. S.; Tang, Y. X.; Dai, D. R.; Zhang, R. B. *Sci. China, Ser. B: Chem.* **1997**, *40*, 568–573.
(25) Han, S. F.; Li, Z.; Ji, S. X.; Dai, D. R.; Zhang, R. B; Zhu, C. F.; Wang, C. *J. Sol-Gel Sci. Technol.* **2000**, *18*, 137–144.
(26) Buey, J.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 608–612.
(27) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1974.
(28) Takiguchi, T. *J. Am. Chem. Soc.* **1959**, *81*, 2359–2361.
(29) Terunuma, D.; Hatta, S.; Araki, T.; Ueki, T.; Okazaki, T.; Suzuki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1545–1548.
(30) Kakudo, M.; Watase, T. *J. Chem. Phys.* **1953**, *21*, 167–168.
(31) Kakudo, M.; Kasai, N.; Watase, T. *J. Chem. Phys.* **1953**, *21*, 1849–1850.
(32) Seto, I.; Gunji, T.; Kumagai, K.; Arimitsu, K.; Abe, Y. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1983–1987.
(33) Li, H.; Liu, C. Q.; Guo, G. Q.; Zhou, X. S.; Zhang, J. M.; Shen, D. Y.; Zhang, Z. X.; Xie, P.; Yu, S. Y.; Zhang, R. B. *J. Polym. Sci., Part A* **2002**, *40*, 3161–3170.
(34) Andrianov, K. A.; Pakhomov, V. I. *Dokl. Akad. Nauk. SSSR* **1965**, *162*, 79–81.
(35) Gutmann, V. *Chem. Ind.* **1971**, 102–107.
(36) Williams, E. A.; Cargioli, J. D.; Larochelle, R. W. *J. Organomet. Chem.* **1976**, *108*, 153–158.
(37) Zhang, Z. X.; Hao, J. K.; Xie, P.; Zhang, X. J.; Han, C. C.; Zhang, R. B. *Chem. Mater.* **2008**, *20*, 1322–1330.
(38) Unno, M.; Suto, A.; Matsumoto, H. *J. Am. Chem. Soc.* **2002**, *124*, 1574–1575.
(39) Vanhee, S.; Rulkens, R.; Lehmann, U.; Rosenauer, C.; Schulze, M.; Ko1hler, W.; Wegner, G. *Macromolecules* **1996**, *29*, 5136–5142.
(40) Okoshi, K.; Sakajiri, K.; Kumaki, J.; Yashima, E. *Macromolecules* **2005**, *38*, 4061–4064.