

Synthesis of Ladder-like Polyphenylsilsesquioxanes with Fairly High Regularity Using 1,2-Ethylenediamine as Endo-template*

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Abstract Ladder-like polyphenylsilsesquioxanes with fairly high regularity were synthesized using an endo-template 1,2-ethylenediamine at mild temperature *via* direct co-hydrolysis and condensation reactions in the presence of acid catalysts in the mixture of 1,4-dioxane/H₂O. The features for synthesis of ladder-like polyphenylsilsesquioxanes were investigated in detail. The products obtained were characterized by FTIR, SEC, XRD and NMR.

Keywords: Ladder-like; Poly(phenyl silsesquioxanes); Endo-template.

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INTRODUCTION

Ladder-like polysilsesquioxanes ((RSiO_{3/2})_n, LPSQs) with high regularity have attracted considerable attention because of their special performances such as excellent thermo-resistant and mechanical properties, good solubility, low dielectric constant and favorable chemical resistance^[1–6]. Such properties have made LPSQs one of research focuses for applications not limited to fabricate organic-inorganic hybrid materials^[7–10], semiconductor devices^[4, 11], organic light-emitting diodes^[10, 12], molecular silicas^[13], nano-patterning in lithography^[14] and drug delivery^[15]. However, LPSQs with high regularity can not be easily prepared because of the fact that some uncontrolled side reactions were encountered in polycondensation of silanol-containing monomers, such as cyclization and gelation reactions^[6] resulting in complicated products with cyclic, ladder, cage, cube and cross-linked structures^[16].

The most-efficient method to prepare materials with controlled shape and size is using supramolecular templates to restrict their shape and size^[17]. Based on the supramolecular template polymerization technique proposed by Zhang *et al.*, many regular LPSQs were designed and synthesized. Firstly, LPSQs containing side chain methacrylate groups^[18], lateral bromophenyl groups^[19], perfect phenelenediimino- bridged LPSQs^[20] and 3-methyl-1,5-diphenylbenzene groups^[21] were prepared using *p*-phenylene diamine as a template respectively. Later, soluble quadruple-chain LPSQs with high molecular weight^[22] and a LPSQ with high regularity^[23] were

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synthesized using *m*-phenylenediamine as a template. Recently, polyhydrosilsesquioxane^[24], polyphenylsilsesquioxane and alkoxy substituted polyisophthalamide^[25] with perfect ladder were synthesized with a supramolecular architecture-directed approach by “synchronous cleavage” of the bridge and *in situ* condensation reaction.

However, the synthesis methods of LPSQs mentioned above were all using exo-templates. To the best of our knowledge, there is no LPSQ synthesized by the supramolecular template polymerization technique with an endo-template. In this work, ladder-like polyphenylsilsesquioxanes (LPPSQs) with fairly high regularity were synthesized by an endo-template 1,2-ethylenediamine at mild temperature *via* direct co-hydrolysis and condensation using sequential one batch, two-step reactions in the presence of acid catalysts in 1,4-dioxane/H₂O. The features for synthesis of LPPSQs were investigated and the LPPSQs were characterized in detail.

EXPERIMENTAL

Materials

PhSiCl₃ (99.9 %) was obtained from Xin'an Chemicals Co. Ltd.. The other reagents and solvents used were analytical grade and commercially available. Toluene and 1,4-dioxane were distilled over sodium benzophenone ketyl before use. All other reagents were used as purchased.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE AV400 (400 MHz) spectrometer in acetone at room temperature without tetramethylsilane (TMS) as the internal reference. Fourier-transform infrared (FTIR) spectroscopic analysis was carried out using a Perkin-Elmer FTIR 2000 spectrometer over the frequency range of 4000–400 cm⁻¹ using KBr pellets. 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. X-ray diffraction (XRD) analysis was carried out using a D/Max 2550V/PC X-ray diffractometer with Cu-K α radiation operated at 40 kV and 40 mA in the 2 θ range of 0°–80° at a sweep rate of 0.04 (°)·s⁻¹. Differential scanning calorimetry (DSC) curves were recorded using a DSC Q100 apparatus under a nitrogen atmosphere with a carrier gas flow rate of 20 mL·min⁻¹. The samples were heated to 100 °C, held for 2 min to erase the thermal history, then cooled to –100 °C at a rate of 10 K·min⁻¹, and finally heated again to 200 °C at a heating rate of 10 K·min⁻¹.

Synthesis of Ladder-like Diethylamine-bridge Polyphenylsilsesquioxane (LDABPPSQ)

As the essential precursor of the LPPSQs, LDABPPSQ was produced according to Fig. 1. A mixture of 1,2-ethylenediamine (20.08 mL, 0.03 mol), triethylamine (TEA) (8.36 mL, 0.06 mol) and toluene (100 mL) was added slowly into a three-neck flask containing PhSiCl₃ (9.62 mL, 0.06 mol) and toluene (150 mL) under an atmosphere of dry argon and stirred quickly at –10 °C over 6 h. 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), toluene (50 mL) and dioxane (100 mL) for 6 h. To give the maximum opportunity for all the Si–OH groups formed to condense with the neighboring excess Si–Cl ones, the dropping speed of water should be controlled strictly. Subsequently, the measured pH value of the reaction system was adjusted to 8–9 with TEA. Then the reaction mixture was filtered using a Buchner funnel to remove solid byproducts after continuous stirring for 4 h at 40 °C. The filtrate was washed with deionized water until measured pH 7 was achieved. Later, a white solid was precipitated after the filtrate was mixed with an equal mass of *n*-hexane. Finally, the precipitate was collected by a Buchner funnel and dried at 60 °C about 24 h under vacuum and a solid white powder of LDABPPSQ (10.135 g) obtained with a yield of 86.8%. SEC analyses showed that the LDABPPSQ obtained has a fairly high molecular weight of 5.03×10^4 with a narrow molecular weight distribution of 1.88. FTIR (KBr, cm⁻¹): 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). The XRD pattern of LDABPPSQ demonstrates two distinct peaks at approximately 7.4° and 19.4°, standing for the ladder width ($w = 2.34$ nm) and thickness ($t = 5.74$ nm), respectively^[26].

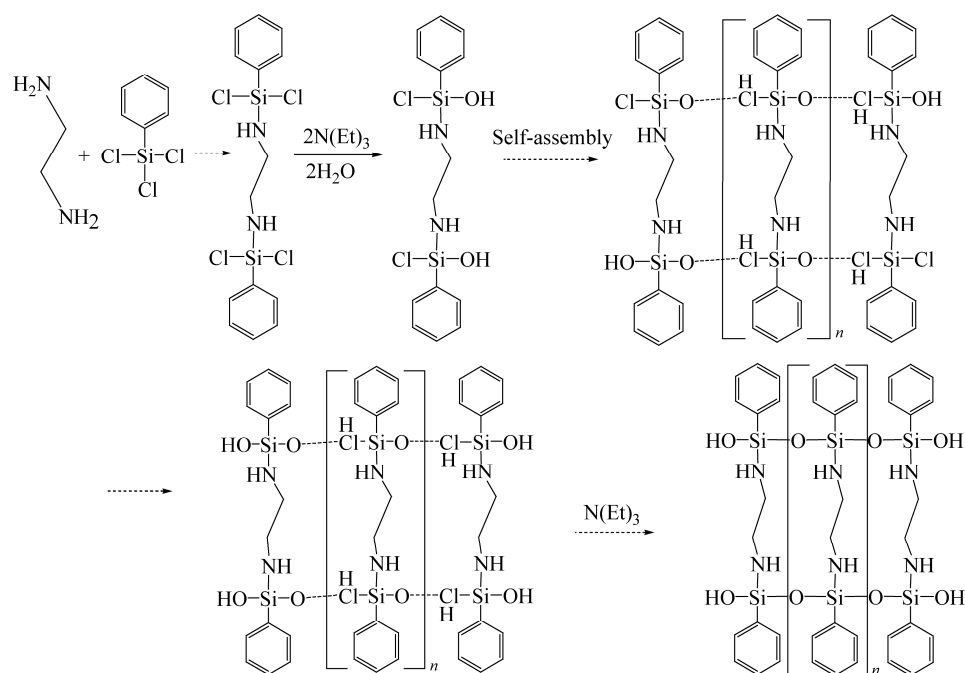


Fig. 1 Synthetic route for the LDABPPSQ

Synthesis of LPPSQs

To synthesize the LPPSQs, the 1,2-ethylenediamine bridge of LDABPPSQ must be removed (Fig. 2). Typically, LDABPPSQ (1.875g, 0.015 mol $\text{SiO}_{3/2}$) was dissolved into 100 mL toluene. Then mineral acid such as HCl, H_2SO_4 and H_3PO_4 was added to catalyze the reaction of removing the 1,2-ethylenediamine bridge. The mixture was neutralized after stirred at 45 °C for 4 h. After removal of the precipitate by a Buchner funnel, the filtrate was evaporated to dryness, and a white powder product of LPPSQ was produced. FTIR (KBr, cm^{-1}): 3688–3100 (s, $-\text{SiOH}$), 2997–3095 (m, $\text{Ph}-\text{H}$), 1593, 1430 (m, $\text{Si}-\text{Ph}$), 950–1132 (s, $\text{Si}-\text{O}-\text{Si}$).

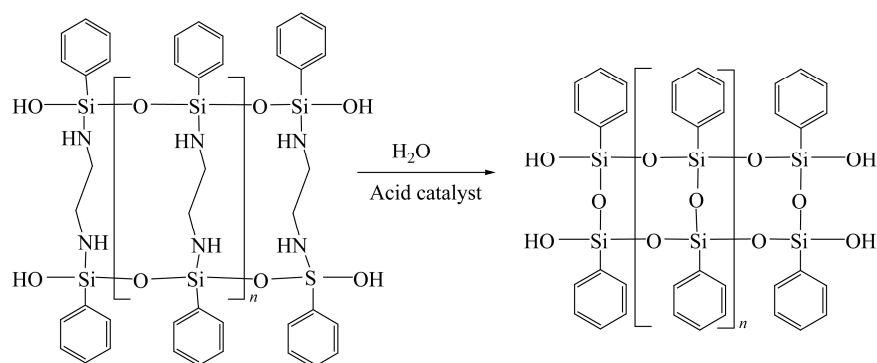


Fig. 2 Synthetic route for the LPPSQs

Synthesis of Random Phenyl Silicone Resin

PhSiCl_3 (105.6 g, 0.5 mol) was dropped into a three-necked bottle containing a mixture of deionized water (40.5 g, 2.25 mol) and toluene (100 mL) at 50 °C for 0.5 h under vigorous stirring and then the reaction was continuously carried out at 50 °C for 2 h. Subsequently, the system was neutralized and evaporated to dryness, and a white rigid solid random phenyl silicone resin (54.825 g) with a yield of 85.0% was obtained.

RESULTS AND DISCUSSION

Synthesis and Characterization of LDABPPSQ

The LDABPPSQ obtained was characterized by SEC, FTIR, DSC and XRD respectively. SEC analyses (Fig. S1) show that the LDABPPSQ obtained has a fairly high molecular weight of about 5.0×10^4 with a narrow molecular weight distribution of 1.88. The FTIR spectrum of LDABPPSQ obtained is shown in Fig. S2. The bands at $3697\text{--}3568\text{ cm}^{-1}$, 3368 cm^{-1} and 1421 cm^{-1} were ascribed to be the characteristic peaks of —SiOH , NH and —Si—N respectively while the bands at $3000\text{--}3080\text{ cm}^{-1}$ and 1431 cm^{-1} were assigned to Ph—H and Si—Ph respectively. The absorbance at $990\text{--}1190\text{ cm}^{-1}$ was the characteristic peak of Si—O—Si . The XRD pattern of LDABPPSQ in Fig. S3 demonstrates two distinct peaks at approximately 7.4° and 19.4° , identified as the ladder thickness ($t = 5.74\text{ nm}$) and width ($w = 2.34\text{ nm}$), respectively.

The Features for Preparation of LPPSQs

LPPSQs were synthesized with LDABPPSQ as the precursor. The 1,2-ethylenediamine acts as an endo-template, which was self-assembled by concerted interaction of hydrogen bonding and aromatic $\pi\text{--}\pi$ stacking^[27]. As is known that H-bonding is highly susceptible to the ambient environment such as temperature and polarity or donor-electron capability of solvents^[28]. To prepare LPPSQs, the 1,2-ethylenediamine bridge of LDABPPSQ must be removed. The features for removing template catalyzed by various acids are list in Table 1. As can be seen that when the same molar equivalents of acids were utilized to catalyze the removing template reaction, the yield of the products was in order of $\text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{HCl}$.

Table 1. LPPSQs prepared by various acids

Entry	Catalysts	Yield (%)	Appearance	$M_n (10^4)$	PDI
1	H_2SO_4	25.5	White powder	4.96	1.86
2	H_3PO_4	20.5	Brown powder	5.11	1.81
3	HCl	12.7	Light yellow powder	2.02	2.99

Conditions: LDABPPSQ 1.875 g, the catalysts were all 1.5 mL.

All reactions were carried out at 45°C for 4 h.

The XRD patterns of LPPSQs prepared by various acids are shown in Fig. 3 and the results according to the Bragg's equation are list in Table 2. It can be seen that the ladder superstructure catalyzed by H_2SO_4 exhibited the narrowest half peak width. This implies that the LPPSQ catalyzed by H_2SO_4 possesses higher regularity than those formed by the other acid catalysts. From the results, it can be concluded that H_2SO_4 has a moderate donor-electron capacity and does not interrupt the hydrogen-bonds of silanols.

Table 2. Results from the XRD patterns of LPPSQs prepared by various acids according to the Bragg's equation

Entry	Peak height of $2\theta_1$ (nm)	Width of LPPSQs (Half peak width of $2\theta_1$) (nm)	Peak height of $2\theta_2$ (nm)	Thickness of LPPSQs (Half peak width of $2\theta_2$) (nm)
LPPSQ-HCl	27.8	2.23	12.0	5.46
LPPSQ- H_3PO_4	33.6	2.18	11.6	5.79
LPPSQ- H_2SO_4	36.8	2.09	11.7	5.28
LDABPPSQ	42.5	2.34	12.8	5.74

To discuss and verify the 1,2-ethylenediamine bridged structure of LDABPPSQ, the ^{13}C -NMR spectra of LDABPPSQ and LPPSQ are exhibited by Fig. 4. The signals $\delta = 124\text{--}134$ were ascribed to be C of $\text{C}_6\text{H}_5\text{—}$. It can be obviously seen that the chemical shift of C in $\text{C}_6\text{H}_5\text{—}$ migrated to higher field, which may be attributed to the interaction of H-bonding and electron-donating of amino group in the 1,2-ethylenediamine bridged structure of LDABPPSQ. The signals $\delta = 56.0$ in the spectrum of LDABPPSQ can be ascribed to C in 1,2-ethylenediamine bridged structure ($\text{—NHCH}_2\text{CH}_2\text{NH—}$), while the signals $\delta = 56.0$ in the spectrum of LPPSQ vanished. It can be easily concluded that the 1,2-ethylenediamine bridged structure was removed completely and a LPPSQ with fairly high regularity was synthesized.

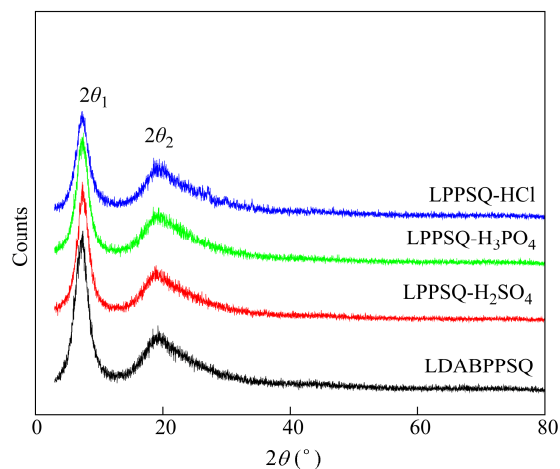


Fig. 3 The XRD patterns of LPPSQs prepared by various acids

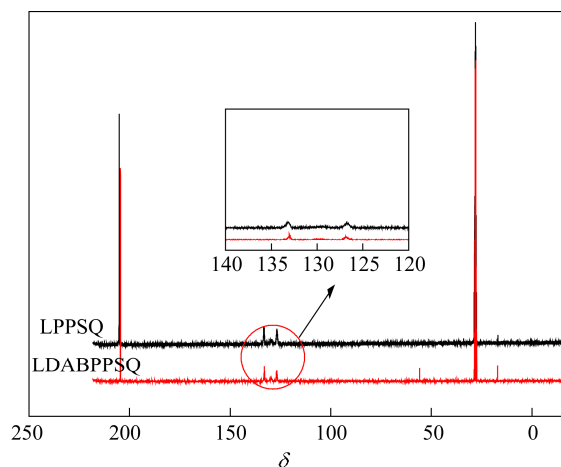


Fig. 4 The ^{13}C -NMR spectra of LDABPPSQ and LPPSQ of entry 1 in the Table 1

To better clarify the regularity of LPPSQ prepared, the LDABPPSQ, LPPSQ and the random phenyl silicone resin were characterized by ^{29}Si -NMR analysis (Fig. 5). It was known that the higher the regularity of ladder polymer, the narrower the resonance peak of silicon atoms in polymer skeleton^[5, 29]. Figure 5 shows that a highest single signal at $\delta = -107.6$ ascribed to the ladder-like structure of LDABPPSQ. The ^{29}Si -NMR spectrum of LPPSQ in Fig. 5 also shows only a relative narrower single signal at $\delta = -79.3$ ascribed to the $\text{Ph-SiO}_{3/2}$. However, the ^{29}Si -NMR spectrum of random phenyl silicone resin with a quite small signal at $\delta = -69.4$. The ^{29}Si -NMR analysis indicates that the product obtained possesses fairly regular ladder-like structure^[29].

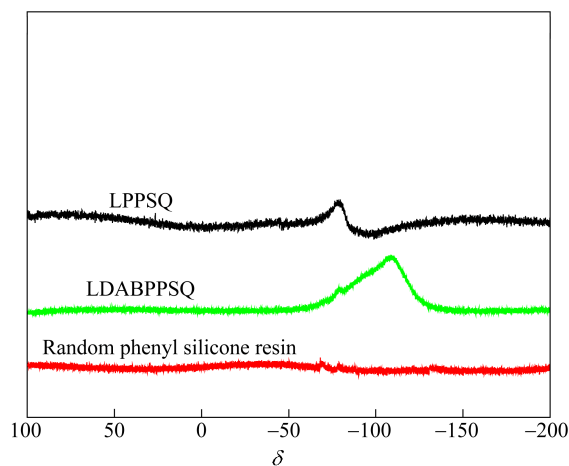


Fig. 5 The ^{29}Si -NMR spectra of LDABPPSQ, LPPSQ of entry 1 in the Table 1 and the corresponding synthesized random phenyl silicone resin

Moreover, it is known that the glass transition temperatures (T_g) can be used to reflect the rigidity and regularity of ladder chain. The higher the T_g , the higher the ladder rigidity and regularity. The single T_g value of LPPSQs measured by DSC is in order of $\text{LPPSQ-H}_2\text{SO}_4 > \text{LPPSQ-HCl} > \text{LPPSQ-H}_3\text{PO}_4$ exhibited by Fig. 6, which also suggests the product catalyzed by H_2SO_4 with the greatest rigidity and the highest ladder regularity^[29].

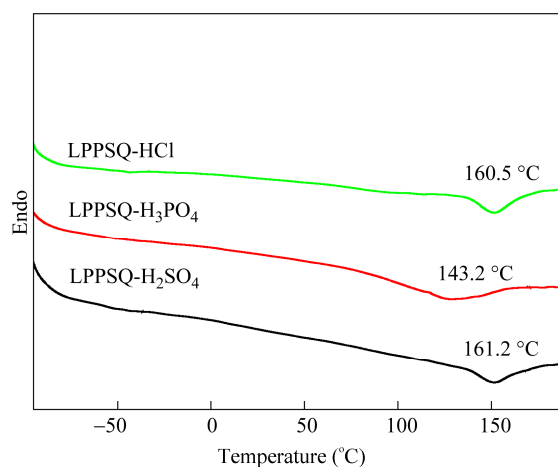


Fig. 6 The DSC curves of LPPSQs prepared by various acids

The results above demonstrated that H_2SO_4 was good acidic catalyst for preparation of LPPSQs, consequently the effect of various amount of H_2SO_4 was studied (Table 3 and Fig. 7). As can be seen, the products prepared were all with moderate high molecular weights from 3.64×10^4 to 5.21×10^4 with fairly narrow molecular weight distributions. The appropriate amount of H_2SO_4 was 1.5 mL. When the amount of H_2SO_4 was less than 1.5 mL, the yield and molecular weight of the products increased with the increasing of H_2SO_4 . A further increment of H_2SO_4 will result in a product with lower yield and lower molecular weight.

Table 3. Effect of H_2SO_4 amount on preparation of LPPSQs

Entry	The amount of H_2SO_4 (mL)	Yield (%)	Appearance	M_n (10^4)	PDI
1	0.5	22.3	White powder	3.64	2.27
2	1	25.5		4.96	1.86
3	1.5	29.6		5.21	1.66
4	2.0	27.4		4.86	1.54

Conditions: LDABPPSQ 1.875 g. All reactions were carried out at 45 °C for 4 h.

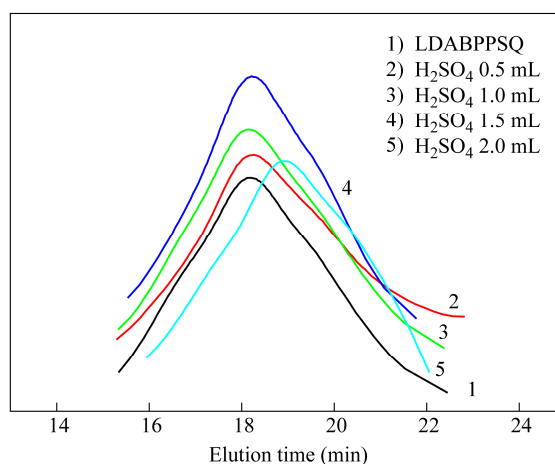
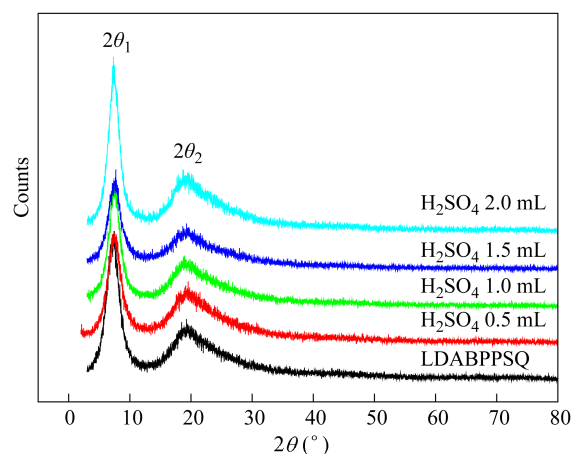


Fig. 7 The SEC curves of LPPSQs prepared with different amounts of H_2SO_4

Additionally, the regularity of the products was also investigated by XRD analysis (Table 4 and Fig. 8). It can be seen that when the amount of H_2SO_4 was 1.5 mL, the ladder superstructure prepared exhibited the most sharpest and intensive peak. It denotes that an appropriate amount of H_2SO_4 will help to form well defined structure of LPPSQs.

Table 4. Results from the XRD patterns of LPPSQs prepared by different amount of H_2SO_4 according to the Bragg's Equation

The amount of H_2SO_4 (mL)	Peak height of $2\theta_1$ (nm)	Width of LPPSQs (Half peak width of $2\theta_1$) (nm)	Peak height of $2\theta_2$ (nm)	Thickness of LPPSQs (Half peak width of $2\theta_2$) (nm)
0.5	4.93	1.98	14.7	5.02
1	2.46	2.19	9.9	5.01
1.5	3.68	2.09	11.7	5.28
2.0	3.08	2.44	12.7	5.71
LDABPPSQ	4.25	2.34	12.8	5.74

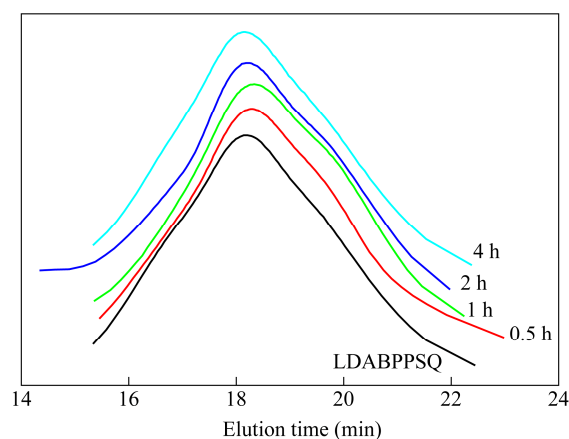
**Fig. 8** The XRD patterns of LPPSQs prepared with different amounts of H_2SO_4

Furthermore, the effects of reaction time on the LPPSQs were discussed (Table 5 and Fig. 9). Table 5 and Fig. 9 exhibited that there were almost no variation of the yield when the reaction time was shorter than 2 h. The products prepared were also with moderate high molecular weights with fairly narrow molecular weight distributions.

Table 5. The LPPSQs prepared with different reaction time

Run	Reaction time (h)	Yield (%)	Appearance	M_n (10^4)	PDI
1	0.5	33.4	white powder	4.87	1.97
2	1	33.5		4.94	1.90
3	2	31.1		5.52	2.46
4	4	25.5		4.96	1.86

Conditions: All reactions were carried out at 45 °C.

**Fig. 9** The SEC curves of LPPSQs prepared with different reaction time

CONCLUSIONS

Ladder-like polyphenylsilsesquioxanes with fairly high regularity were synthesized with an endo-template 1,2-ethylenediamine at mild temperature *via* direct co-hydrolysis and condensation reactions in the presence of acid catalysts in the mixture of 1,4-dioxane/H₂O. The investigation exhibited that the endo-template 1,2-ethylenediamine can be completely removed when the reaction of 1.875 g LDABPPSQ was carried out at 45 °C for 4 h catalyzed by 1.5 mL H₂SO₄, and the product synthesized had fine ladder regularity.

REFERENCES

- 1 Baney, R.H., Itoh, M., Sakakibara, A. and Suzuki, T., *Chem. Rev.*, 1995, 95: 1409
- 2 Li, G.Z., Wang, L., Toghiani, H., Daulton, T.L., Koyama, K. and Pittman, C., *Macromolecules*, 2001, 34(25): 8686
- 3 Kannan, R.Y., Salacinski, H.J., Butler, P.E. and Seifalian, A., *Acc. Chem. Res.*, 2005, 38(11): 879
- 4 Lee, H.J., Lin, E.K., Wang, H., Wu, W. and Moyer, E.S., *Chem. Mater.*, 2002, 14(4): 1845
- 5 Unno, M., Suto, A. and Matsumoto, H., *J. Am. Chem. Soc.*, 2002, 124: 1574
- 6 Zhang, Z.X., Hao, J.K., Xie, P., Zhang, X.J., Han, C.C. and Zhang, R.B., *Chem. Mater.*, 2008, 20: 1322
- 7 Lee, A.S.S., Choi, S.S., Lee, H.S., Jeon, H.Y., Baek, K.Y. and Hwang, S.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2012, 50(21): 4563
- 8 Gao, Q.S., Qi, S.L., Wu, Z.P., Wu, D.Z. and Yang, W.T., *Thin Solid Films*, 2011, 519(19): 6499
- 9 Feng, L.Q. and Iroh, J.O., *J. Inorg. Organomet. Polym.*, 2013, 23(3): 477
- 10 Ren, Z.J., Zhang, R.B., Wang, F. and Yan, S.K., *Polym. Chem.*, 2011, 2: 608
- 11 Choi, S.S., Lee, A.S., Lee, H.S., Jeon, H.Y., Baek, K.Y., Choi, D.H. and Hwang, S.S., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49(23): 5012
- 12 Choi, S.S., Lee, H.S., Hwang, S.S., Choi, D.H. and Baek, K.Y., *J. Mater. Chem.*, 2010, 20: 9852
- 13 Roll, M.F., Kampf, J.W., Kim, Y., Yi, E. and Laine, R.M., *J. Am. Chem. Soc.*, 2010, 132(29): 10171
- 14 Lee, B.K., Goo, N., Hong, L., Kim, D., Tanaka, H., Lee, H.Y. and Kawai, T., *Langmuir*, 2010, 26(18): 14915
- 15 Ni, C., Wu, G., Zhu, C. and Yao, B., *J. Phys. Chem. C.*, 2010, 114(32): 13471
- 16 Abe, Y. and Gunji, T., *Prog. Polym. Sci.*, 2004, 29: 149
- 17 Suzuki, K., Sato, S. and Fujita, M., *Nat. Chem.*, 2010, 2: 25
- 18 Krishnan, P.S.G. and Shang, C.T.S., *High Perform. Polym.*, 2007, 19: 21
- 19 Li, H., Yu, S.Y., Shen, Z.R., Zhang, Z.X., Duan, Q.H., Jiang, J.Q., Xie, P. and Zhang, R.B., *Chinese J. Polym. Sci.*, 2004, 22(5): 445
- 20 Zhang, T.Y., Deng, K.L., Zhang, P.P., Xie, P. and Zhang, R.B., *Chem. Eur. J.*, 2006, 12: 3630
- 21 Ren, Z.J., Chen, Z.Z., Fu, W.X., Zhang, R.B., Shen, F.Z., Wang, F., Ma, Y.G. and Yan, S.K., *J. Mater. Chem.*, 2011, 21: 11306
- 22 Chen, Z.Z., Li, Z.B., Guo, H.X., Zhang, J.T., Ren, Z.J., Yan, S.K., Xie, P. and Zhang, R.B., *Chem. Mater.*, 2012, 24: 1968
- 23 Lu, Z.B., Lv, Y.S., Wan, Y.Z., Xie, P. and Zhang, R.B., *Acta Polymerica Sinica (in Chinese)*, 2009, (12): 1287
- 24 Ren, Z.J., Cao, X.Y., Xie, P., Zhang, R.B., Yan, S.K. and Ma, Y.G., *Chem. Commun.*, 2009, 4079
- 25 Ren, Z.J., Tian, Y., Xie, P., Yan, S.K. and Zhang, R.B., *Polym. Chem.*, 2010, 1: 1095
- 26 Zhou, Q.L., Yan, S.K., Han, C.C., Xie, P. and Zhang, R.B., *Adv. Mater.*, 2008, 20(15): 2970
- 27 Lv, Y.S., Ren, Z.J., Wan, Y.Z., Xie, P. and Zhang, R.B., *Chinese J. Polym. Sci.*, 2009, 27(4): 525
- 28 Williams, E.A., Cargioli, J.D. and Larochelle, R.W., *J. Organomet. Chem.*, 1976, 108(2): 153
- 29 Ren, Z.J., Xie, P., Jiang, S.D., Yan, S.K. and Zhang, R.B., *Macromolecules*, 2010, 43(5): 2130