Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2019, **29**, 421–423
Mendeleev Communications

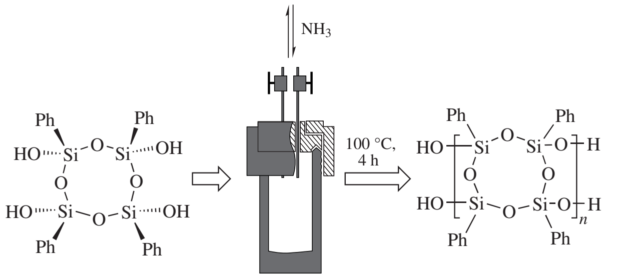
Condensation of all-*cis*-tetraphenylcyclotetrasiloxanetetraol in ammonia: new method for preparation of ladder-like polyphenylsilsesquioxanes

Anton A. Anisimov,[a] Natalia V. Polshchikova,[a] Yuliya S. Vysochinskaya,[a,b] Pavel A. Zader,[c] Galina G. Nikiforova,[a] Alexander S. Peregudov,[a] Mikhail I. Buzin,[a] Olga I. Shchegolikhina*[a] and Aziz M. Muzafarov[a,b]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: olga@ineos.ac.ru*
[b] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation*
[c] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2019.07.022

One-step method for the preparation of polyphenylsilsesquioxane by condensation of all-*cis*-1,3,5,7-tetraphenyl-1,3,5,7-tetrahydroxycyclotetrasiloxane in liquid ammonia has been developed. This method makes it possible to produce high molecular weight polymers with regular structure in the absence of organic solvent. The structure of the polymer product was confirmed by ^{1}H and ^{29}Si NMR spectroscopy, GPC, IR spectroscopy, powder X-ray diffraction and viscosimetry.



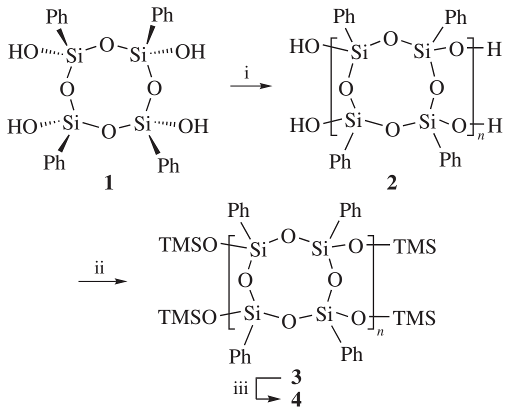
Ladder-like polyorganosilsesquioxanes constitute an important class of materials, which exhibit promising physicochemical properties, including high thermal stability and good mechanical performance.[1] In particular, polyphenylsilsesquioxanes, since they were first described in 1960,[2] continue to draw attention to the investigation of their synthesis and properties.[3–13] Typically, for the synthesis of ladder-like polyphenylsilsesquioxanes, various organic solvents and catalysts are employed, for example triethylamine, octylamine, potassium hydroxide, benzyltrimethylammonium hydroxide, tetramethylammonium hydroxide or layered silicate materials, such as montmorillonite.

To control the proper structure of synthesized ladder-like polyphenylsilsesquioxanes, strict reaction conditions are required, which leads to high production cost and thereby hampers further application. Thus, there is a need for development of alternative synthetic methods to simplify cost-effective production of these polymers.

Compressed media, namely condensed gases and supercritical fluids, represent a new type of solvents for chemical synthesis drawing much attention.[14] The properties of supercritical fluids, including the dissolving capacity, can be tuned by variation of pressure or degree of compression. It is essential that the following decompression step results in instant removal of the active environment from the reaction zone.

Here we report a new method for preparation of ladder-like polyphenylsilsesqioxane by condensation of all-*cis*-1,3,5,7-tetraphenyl-1,3,5,7-tetrahydroxycyclotetrasiloxane in liquid ammonia at elevated pressure in the absence of organic solvent.

All-*cis*-1,3,5,7-tetraphenyl-1,3,5,7-tetrahydroxycyclotetrasiloxane **1** was synthesized[15] from sodium *cis*-tetraphenylcyclotetrasiloxanolate by known procedure[16,17] and used as starting compound. The regular structure of this cyclic precursor allowed us to produce ladder-like polyphenylsilsesquioxanes in a directional way. Condensation of compound **1** was carried out in an autoclave according to Scheme 1.[†]



Scheme 1 *Reagents and conditions*: i, liq. NH_3, 100 °C, 4 h; ii, Me_3SiCl, pyridine, THF, room temperature, 24 h; iii, fractional precipitation.

[†] All-*cis*-1,3,5,7-tetraphenyl-1,3,5,7-tetrahydroxycyclotetrasiloxane **1** (1.0 g, 1.9 mmol) was loaded into an autoclave equipped with a magnetic stirrer, then the autoclave was filled with NH_3 under chill-down using a Bronkhorst IN-FLOW mass flow meter. The reaction mixture was heated at 100 °C for 4 h and then decompressed. The condensation product **2** was obtained as a white powder. Yield 0.961 g (96%). A solution of polymer **2** (0.961 g, 1.8 mmol) in THF (15 ml) was added to a solution of trimethylchlorosilane (1.56 g, 14.4 mmol) and pyridine (1.14 g, 14.4 mmol) in THF (15 ml). The reaction mixture was stirred at room temperature for 24 h, then filtered through silica gel to remove precipitated material. The solvent was evaporated *in vacuo* (10 Torr, 40 °C, then 1 Torr, 100 °C, 6 h). The capped product **3** was obtained as white film-forming polymer. Yield

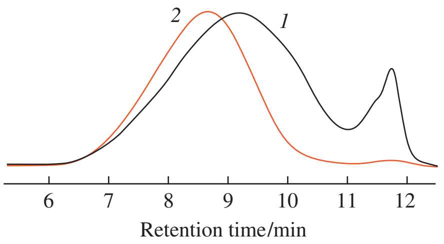


Figure 1 GPC analysis of (*1*) polymer **3**: major component M_n 43000, M_w 115000, *Đ* 2.6, 86% area; minor component M_n 1800, M_w 2500, *Đ* 1.4, 14% area and (*2*) high molecular weight polymer **4**: M_n 86000, M_w 164000, *Đ* 1.9.

We assume that liquid ammonia serves both as a solvent and as a catalyst: water formed from condensation of silanol groups reacts with ammonia resulting in the formation of NH_4OH, which in turn causes a rearrangement of initially formed polymer chain. The course of the reaction in concentrated solution promotes the formation of a polymer instead of octaphenylsilsesquioxane. After decompression of ammonia, condensation product **2** was obtained in 96% yield. Then it was treated with trimethylchlorosilane for capping the residual OH groups to form polymer **3** (see Scheme 1). The GPC analysis of compound **3** (Figure 1) exhibited bimodal molecular weight distribution with high-molecular component area 86%.

Fractional precipitation of polymer **3** in THF–ethanol gave high molecular weight polymer **4** in 75% yield (see Figure 1).[‡] The structure of polymer **4** was confirmed by ^{1}H and ^{29}Si NMR spectroscopy, IR spectroscopy, powder X-ray diffraction and viscosimetry.

Its ^{29}Si NMR spectrum exhibited two main chemical peaks at 10 and –80 ppm assigned to Me_3SiO groups, or *M*-units according to the established siloxane groups labeling, and to $PhSiO_3$, or *T*-units, respectively (Figure S5, see Online Supplementary Materials).[18,19]

The bulk structure of polymer **4** was analyzed by X-ray diffraction (XRD). Figure 2 shows the XRD pattern with intensive main diffraction maximum at $2\theta = 7°$ (d_1) and the second broad and weak peak with a center at $2\theta \approx 20°$ (d_2). The results are similar to those reported for organosilicon ladder polymers.[20,21]

To confirm the structure of polymer **4**, its intrinsic viscosity $[\eta]$ was determined in toluene (Figure 3). The molecular mass *M* was calculated from the formula $[\eta] = 1.77\times10^{-5} M^{0.895}$ and found to be *ca.* 86500.[22]

The thermogravimetric analysis of polymer **4** revealed its thermo-oxidative degradation in air having two distinguished stages with temperatures of the maximum rate of decomposition

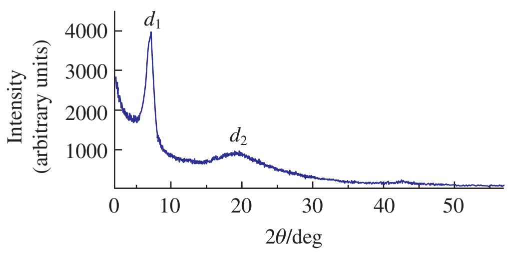


Figure 2 XRD pattern for polymer **4**.

0.711 g (74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: –0.76 to 0.32 (br. s), 6.21–7.80 (br. s). ^{29}Si NMR (150 MHz, $CDCl_3$) δ: –80 to –75 ($PhSiO_3$), 10.6 (Me_3SiO). IR (KBr, ν/cm^{-1}): 3094–3008, 1595, 1430, 1101–997, 842, 725, 692, 477–407.

‡ A solution of blocked polymer **3** (1.2 g) in THF–ethanol (C = 1%) was fractionated at room temperature to give high molecular weight polymer **4**. Yield 0.9 g (75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: –0.78 to 0.19 (br. s), 6.04–7.79 (br. s). ^{29}Si NMR (150 MHz, $CDCl_3$) δ: –80 to –75, 10.5. IR (KBr, ν/cm^{-1}): 3074–2851, 1748, 1596, 1463, 1432, 1379, 1134, 1042, 732, 697, 506.

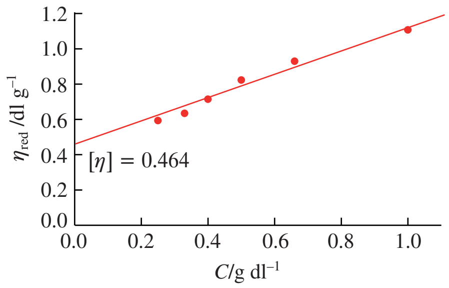


Figure 3 Reduced viscosity *vs.* concentration for dilute solutions of polymer **4** in toluene (T = 37 °C).

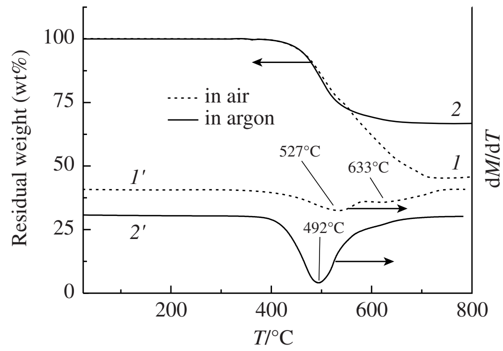


Figure 4 Thermogravimetric curves for polymer **4**: (*1*) TG in air, (*2*) TG in argon, (*1′*) DTG in air, (*2′*) DTG in argon; heating rate 10 K min^{-1}.

527 and 633 °C (Figure 4, curves *1* and *1′*). Thermal destruction in argon occurred in one stage (see Figure 4, curves *2* and *2′*) with temperature of the maximum rate of decomposition 492 °C, which is slightly lower than that for the destruction in air. The decrease of sample weight was complete at *ca.* 700 °C and the solid residue weights were 67 and 45% for air and argon conditions, respectively. The weight of the solid residue in air was close to the calculated content of silicon dioxide in the polymer. Under an argon atmosphere, the solid residue contained more carbon due to decomposition of phenyl groups.[13,23]

In summary, one-step method for the preparation of polyphenylsilsesquioxane by condensation of cyclic polyol in liquid ammonia medium at elevated pressure has been developed. The new method can be potentially used for the production of various polysiloxanes.

This study was supported by the Russian Science Foundation (grant no. 14-23-00231). The NMR, IR spectroscopic data and X-ray data were obtained using the equipment of Center for Molecule Composition Studies of A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.022.

References

1 (*a*) R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 1995, **95**, 1409; (*b*) D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431; (*c*) Q. Zhou, S. Yan, C. C. Han, P. Xie and R. Zhang, *Adv. Mater.*, 2008, **20**, 2970; (*d*) H. S. Lee, S.-S. Choi, K.-Y. Baek, E. C. Lee, S. M. Hong, J.-C. Lee and S. S. Hwang, *Macromol. Res.*, 2012, **20**, 1131.

2 J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kiser and K. W. Krantz, *J. Am. Chem. Soc.*, 1960, **82**, 6194.

3 (*a*) K. A. Andrianov, S. A. Pavlova, I. I. Tverdokhlebova, V. N. Emel'yanov, T. A. Larina and A. Yu. Rabkina, *Polym. Sci. U.S.S.R.*, 1972, **14**, 2628 (*Vysokomol. Soedin.*, 1972, **A14**, 2246); (*b*) K. A. Andrianov, I. I. Tverdokhlebova, N. N. Makarova, I. I. Mamaeva, A. K. Chekalov, V. M. Men'shov and S. A. Pavlova, *Polym. Sci. U.S.S.R.*, 1978, **20**, 425 (*Vysokomol. Soedin.*, 1978, **A20**, 377).

4 E. Leśniak, Z. M. Michalska and J. Chojnowski, *J. Inorg. Organomet. Polym.*, 1998, **8**, 1.

5 J. H. Harreld, K. Su, D. E. Katsoulis, M. Suto and G. D. Stucky, *Chem. Mater.*, 2002, **14**, 1174.

6 X.-f. Yang, C. Cao, Z.-h. Chen, J. Liu, M.-x. Luo and G.-q. Lai, *Chin. J. Polym. Sci*., 2015, **33**, 1305.

7 Y. Abe and T. Gunji, *Prog. Polym. Sci.*, 2004, **29**, 149.

8 S. Yamamoto, N. Yasuda, A. Ueyama, H. Adachi and M. Ishikawa, *Macromolecules*, 2004, **37**, 2775.

9 Z.-X. Zhang, J. Hao, P. Xie, X. Zhang, C. C. Han and R. Zhang, *Chem. Mater.*, 2008, **20**, 1322.

10 (*a*) I. M. Petrova, A. K. Buryak, F. M. Dolgushin, A. S. Peregudov, Z. S. Klemenkova and N. N. Makarova, *Russ. Chem. Bull., Int. Ed.*, 2014, **63**, 2395 (*Izv. Akad. Nauk, Ser. Khim.*, 2014, 2395); (*b*) I. M. Petrova, A. K. Buryak, A. S. Peregudov, T. V. Strelkova, E. G. Kononova, I. S. Bushmarinov and N. N. Makarova, *Mendeleev Commun.*, 2015, **25**, 229; (*c*) N. N. Makarova, Yu. I. Lyakhovetsky, I. M. Petrova, F. M. Dolgushin, N. S. Ikonnikov, A. S. Peregudov, T. V. Strelkova and Z. S. Klemenkova, *Polymers*, 2018, **10**, 422.

11 S.-S. Choi, A. S. Lee, S. S. Hwang and K.-Y. Baek, *Macromolecules*, 2015, **48**, 6063.

12 M. Nowacka, A. Kowalewska and T. Makowski, *Polymer*, 2016, **87**, 81.

13 K. A. Andrianov, S. V. Bushin, M. G. Vitovskaya, V. N. Yemel'yanov, P. N. Lavrenko, N. N. Makarova, A. M. Muzafarov, V. Ya. Nikolayev, G. F. Kolbina, I. N. Shtennikova and V. N. Tsvetkov, *Polym. Sci. U.S.S.R.*, 1977, **19**, 536 (*Vysokomol. Soedin.*, 1977, **A19**, 469).

14 J. Walkowiak, G. Franciò and W. Leitner, in *Applied Homogeneous Catalysis with Organometallic Compounds*, eds. B. Cornils, W. A. Herrmann, M. Beller and R. Paciello, Wiley-VCH, Hoboken, NJ, 2018, vol. 4, pp. 1221–1258.

15 J. F. Brown, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 4317.

16 O. I. Shchegolikhina, Yu. A. Pozdnyakova, Yu. A. Molodtsova, S. D. Korkin, S. S. Bukalov, L. A. Leites, K. A. Lyssenko, A. S. Peregudov, N. Auner and D. E. Katsoulis, *Inorg. Chem.*, 2002, **41**, 6892.

17 Yu. S. Vysochinskaya, A. A. Anisimov, S. A. Milenin, A. A. Korlyukov, F. M. Dolgushin, E. G. Kononova, A. S. Peregudov, M. I. Buzin, O. I. Shchegolikhina and A. M. Muzafarov, *Mendeleev Commun.*, 2018, **28**, 418.

18 H. Ban, A. Tanaka, Y. Kawai and S. Imamura, *Polymer*, 1990, **31**, 564.

19 S. Hayashida and S. Imamura, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 55.

20 K. A. Andrianov, G. L. Slonimsky, A. A. Zhdanov, D. Ya. Tsvankin, V. Yu. Levin, V. S. Papkov, Yu. P. Kvachev and E. M. Belavtseva, *J. Polym. Sci., Part A: Polym. Chem.*, 1976, **14**, 1205.

21 D. Ya. Tsvankin, V. Yu. Levin, V. S. Pankov, V. P. Zhukov, A. A. Zhdanov and K. A. Andrianov, *Polym. Sci. U.S.S.R.*, 1979, **21**, 2348 (*Vysokomol. Soedin.*, 1979, **A21**, 2126).

22 T. E. Helminiak, C. L. Benner and W. E. Gibbs, *Polym. Prepr.*, 1967, **8**, 284.

23 A. Fina, D. Tabuani, F. Carniato, A. Frache, E. Boccaleri and G. Camino, *Thermochim. Acta*, 2006, **440**, 36.

Received: 12th December 2018; Com. 18/5773