



SYNTHESIS AND PROPERTIES OF LADDER POLYPHENYLSILSESQUIOXANES OBTAINED FROM *CIS*-HEXAPHENYLCYCLOHEXASILOXANEHEXAOL AND PHENYLSILANETRIOL

Cite this: *INEOS OPEN*, 2024, 7 (1–3), 91–93
DOI: 10.32931/io2438a

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Received 21 May 2024,
Accepted 11 August 2024

http://ineosopen.org

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Abstract

The condensation of *cis*-hexaphenylcyclohexasiloxanehexaol and phenylsilanetriol in an ammonia medium was studied. The soluble high-molecular ladder polyphenylsilsesquioxanes (L-PPSSs) were obtained, which are capable of forming transparent and strong films. The structure and properties of the resulting L-PPSSs were investigated using different physicochemical methods, including ¹H NMR spectroscopy, UV-vis and IR spectroscopy, viscometry in solution, GPC, TGA, mechanical analysis.

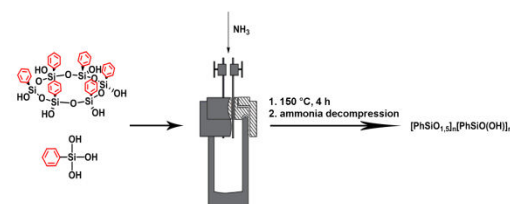
Key words: polyphenylsilsesquioxanes, ammonia, *cis*-hexaphenylcyclohexasiloxanehexaol, phenylsilanetriol.

Introduction

Among the variety of organosilicon polymers, polyphenylsilsesquioxanes, the structure of which depends on the synthesis method, attract special attention. Among the variety of structural forms of polyphenylsilsesquioxanes, ladder-like polymers are of particular interest. They feature high thermal and thermo-oxidative stability, good dielectric characteristics, high refractive index, and solubility in a wide range of organic solvents. A classical method for obtaining ladder polyphenylsilsesquioxanes is a multi-stage process which involves energy-consuming reactions conditions, significantly restricting its wide application [1]. Earlier, a method for obtaining L-PPSSs from *cis*-tetraphenylcyclotetrasiloxanetetraol (*cis*-tetrol) in an ammonia medium was developed at the Laboratory of Organosilicon Compounds of INEOS RAS [2, 3]. The advantage of this approach is that ammonia used in the synthesis acts as both a solvent and a catalyst for the condensation process. In addition, it can be instantly removed from the reaction mixture by decompression, so the resulting polymers do not require further purification. It is also noteworthy that, by varying the reaction conditions, it is possible to regulate the molecular weight characteristics of the resulting product.

The goal of this study was to obtain L-PPSSs in an ammonia medium from the precursors of various structures, namely, *cis*-hexaphenylcyclohexasiloxanehexaol (*cis*-hexol) and phenylsilanetriol, as well as to study the properties of the resulting polymers.

General scheme for L-PPSS synthesis in ammonia



Results and discussion

The initial monomers were obtained by the published methods [4, 5]. The condensation of silanols was carried out in steel autoclaves (Fig. 1).

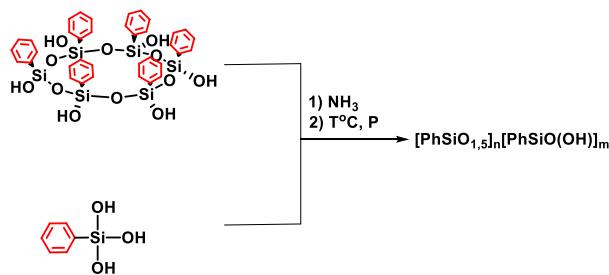


Figure 1. Condensation of silanols in ammonia.

The required amount of *cis*-hexaphenylcyclohexasiloxanehexaol or phenylsilanetriol was loaded into an autoclave, then the autoclave was cooled to -50 °C, and ammonia was injected using a flow controller. The reaction was carried out at 150 °C and 50 atm for 4 h, analogously to the experiment with *cis*-tetrol [3]. After the reaction completion, ammonia was decompressed and the polymer was recovered. The resulting samples were separated from the low-molecular components by reprecipitation, after which the residual silanol groups were blocked with Me_3SiCl in the presence of pyridine. The blocking was performed for further investigation of the physicochemical properties in order

to avoid the condensation of residual silanol groups. The amount of the residual silanol groups was extremely low, which did not allow their content to be adequately determined using NMR spectroscopy.

The GPC analysis showed that the resulting polymers have high molecular weights (Table 1, Fig. 2).

Table 1. Molecular weight characteristics of polymers **1** (based on *cis*-hexol) and **2** (based on phenylsilanetriol)

Polymer	M_w , kDa	M_n , kDa	M_p , kDa	PDI	M_n , kDa $[\eta]$, dL/g
1	561	202	689	2.7	442 1.50
2	319	137	266	2.3	349 1.34

^a reaction conditions: 150 °C, monomer 20 wt %, 5g NH₃.

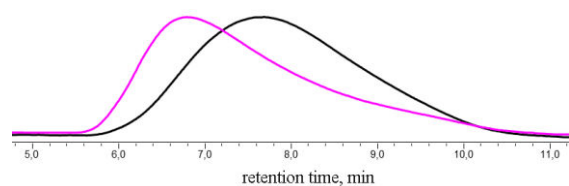


Figure 2. GPC curves of polymers **1** and **2**.

The samples obtained were studied by viscometry in solution. The concentration dependence of the intrinsic viscosity of the polymer solutions was studied in toluene at 37 °C. Based on the resulting dependences, the values of the characteristic viscosities of the solutions explored and M_n were calculated using the following formula: $[\eta] = 1.77 \cdot 10^{-5} \cdot M^{0.895}$ (Fig. 3, Table 1) [6]. The results obtained are in good agreement with the literature data for L-PPSSs [7].

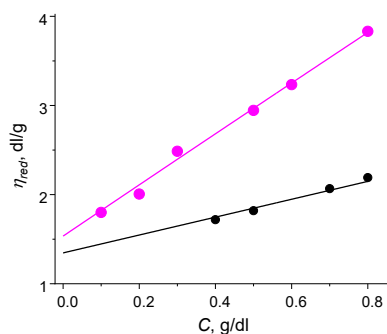


Figure 3. Dependence of the intrinsic viscosity on the solution concentration for polymers **1** and **2**.

The thermal and thermo-oxidative stability of the polymers obtained were studied by thermogravimetric analysis. From the data obtained, it is obvious that the temperatures of the decomposition of the resulting L-PPSSs exceeds 500 °C both in air and in argon and are practically independent of the structure of the initial monomer (Table 2, Figs. 4, 5).

Table 2. TGA data for polymers **1** and **2**

Polymer	Air		Argon	
	$T_d^{5\%}$, °C	Residue, %	$T_d^{5\%}$, °C	Residue, %
1	525	48	550	72
2	556	66	525	74

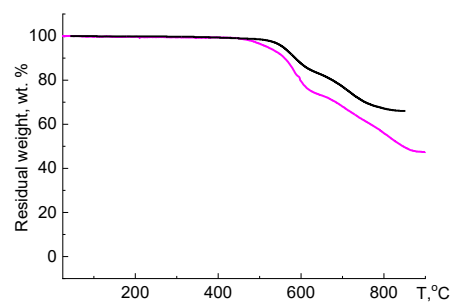


Figure 4. TGA curves in air for samples **1** and **2**.

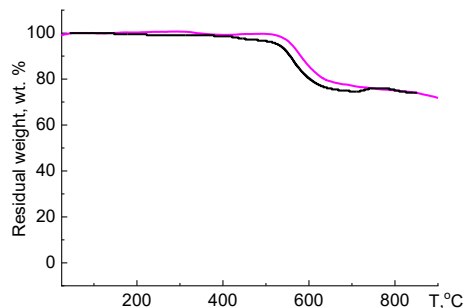


Figure 5. TGA curves in argon for samples **1** and **2**.

The mechanical properties of the resulting polymers were studied by uniaxial tension. It was found that the L-PPSSs obtained have high mechanical characteristics for silicones (Table 3, Fig. 6). It is worth noting that samples **1** and **2** are capable of forming transparent, strong and flexible films. This property is a distinctive feature of the L-PPSSs obtained in this work from brittle L-PPSSs synthesized by the alternative methods [8].

Table 3. Mechanical characteristics of polymers **1** and **2**

Sample	E , MPa	σ , MPa	ϵ , %
1	1530	38 ± 3.8	5 ± 0.5
2	1517	39 ± 3.9	7 ± 0.7

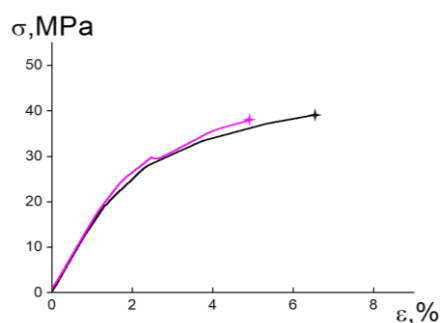


Figure 6. Stretching curves of polymers **1** and **2**.

The UV-Vis spectra (Fig. 7) of the resulting polymers indicate high optical homogeneity and transparency ($T \sim 90\%$ in the visible region) of the materials.

Conclusions

The ladder PPSSs were obtained from precursors of different structures by the condensation of silanols in an ammonia medium. It was shown that the resulting polymers are

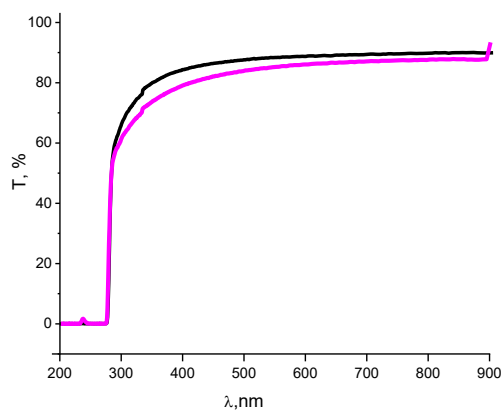


Figure 7. The UV-vis spectra for polymer **1** and **2**.

capable of forming transparent ($T = 90\%$), strong and flexible films ($E = 1530$ MPa, $\sigma = 38$ MPa, $\varepsilon = 5\%$ for L-PPSS **1** and $E = 1517$ MPa, $\sigma = 39$ MPa, $\varepsilon = 7\%$ for L-PPSS **2**), featuring improved thermal ($T_d^{5\%} = 520$ °C and 525 °C for **1** and **2**, respectively) and thermo-oxidative ($T_d^{5\%} = 525$ °C and 556 °C for **1** and **2**, respectively) properties. The combination of these properties of the resulting L-PPSSs makes them promising objects for use in materials science.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 21-73-20225).

The characterization of the resulting compounds was performed with financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of the Center for Molecular Composition Studies of INEOS RAS (viscosity, mechanical, optical measurements). The GPC and NMR spectroscopic studies were performed with financial support from the Ministry of Science and Higher

Education using the equipment of the collaborative access center "Center for Polymer Research" of ISPM RAS.

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