




Article

A Versatile Equilibrium Method for the Synthesis of High-Strength, Ladder-like Polyphenylsilsesquioxanes with Finely Tunable Molecular Parameters

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Abstract: A versatile equilibrium method for synthesizing ladder-like polyphenylsilsesquioxanes (L-PPSQs) with various molecular weights (from 4 to 500 kDa) in liquid ammonia was developed. The effect of diverse parameters, such as temperature, monomer concentration, reaction time, addition or removal of water from the reaction medium, on the polycondensation process was determined. The molecular weight characteristics and structure of the L-PPSQ elements obtained were determined by GPC, ¹H, ²⁹Si NMR, IR spectroscopy, viscometry, and PXRD methods. The physicochemical properties of L-PPSQs were determined by TGA and mechanical analyses.

Keywords: ladder-like polyphenylsilsesquioxanes; ammonia; condensation

1. Introduction

Polyphenylsilsesquioxanes (PPSQs) are important organosiloxanes with unique physicochemical properties, for instance, high thermal and radiation resistance, high refractive index, mechanical properties, and solubility in organic solvents such as chloroform, benzene, toluene, dichlorobenzene, xylene, and tetrahydrofuran (THF) [1,2]. Due to these properties, they are widely used as protective, dielectric, hydrophobic, heat-resistant coatings, modifiers of organic and organoelement formulations [3–8], and materials for optoelectronics [9,10].

The regular structure is yet another feature of PPSQs. PPSQs are usually obtained by polycondensation of phenyltrichloro- or -trialkoxysilanes. The reaction conditions determine the final structure of the PPSQ molecule [11]. As a result, it is possible to obtain PPSQs whose molecules have polyhedral, hyperbranched, statistical, or ladder-like structures.

Ladder-like PPSQs were first described by Brown et al. in 1960 [12], but their synthesis and study of their properties have continued to attract the attention of scientists for many decades. Such polymers having a molecular weight in the range of 10⁶ Da can form strong transparent films, with a high refractive index, and may find application as promising polymer matrices, membranes, materials for waveguides, etc. [3,6,13–19].

There are several approaches to the synthesis of L-PPSQs. The first approach involves the high-temperature (250 °C) polymerization of phenyltrichlorosilane hydrolysis products in the presence of a strong base [1]. Soviet scientists also performed studies in this area.

They identified various factors that affect the molecular weight and structural characteristics of the resulting polymers [20,21]. An important result was obtained in a study that demonstrated the reversible nature of the polymerization reaction and the stability of the most thermodynamically stable form of polyhedral octaphenylsilsesquioxane. The search for more efficient alternative approaches for synthesizing L-PPSQs continues. For example, Zhang et al. [22] suggested a method that involves the condensation of a preorganized 1,1,3,3-tetraphenyldisiloxane-1,3-diol monomer. This method assumes mild synthesis conditions; however, it is a multistage method similar to that described above. It should also be noted that the L-PPSQ elements obtained had relatively low molecular weights (up to 2×10^3 Da). This approach was developed further [23,24] using ethylenediamine as a template for the preorganization of PPSQs. After hydrolysis of this structure, L-PPSQs with $M_w = 5 \times 10^4$ Da were formed. Choi [25] suggested the simplest method for synthesizing L-PPSQs that involved the hydrolysis of phenyltrimethoxysilane in the presence of K_2CO_3 . The key factor in this reaction is the concentration of the initial monomer. In fact, T10 polyhedral decamer was formed at low monomer concentrations, while L-PPSQs with M_w up to 1.5×10^4 Da were formed at high concentrations. It can be observed from the above data that a versatile directed method for the synthesis of L-PPSQs with a predetermined molecular weight (M_w) has not been found to date.

In recent decades, there has been a growing interest in compressed gas media as new solvents for chemical reactions, including condensed gases and supercritical fluids [26–29]. The main advantages of these media include the possibility of adjusting their dissolving capacity and their instant removal from the reaction media. The latter feature is most important since the product obtained in this way does not require expenses for purification from the solvent.

Earlier, we developed a new method for the synthesis of phenyl-containing siloxanes in ammonia media. The advantage of this method is that ammonia plays the role of both a solvent and a catalyst. At the same time, the reaction products do not require purification, since ammonia is removed from the reaction medium and can be reused in the future. We have shown that phenylcyclotrisiloxanes, disiloxanes, and L-PPSQs with a molecular weight of $M_w = 164$ kDa can be obtained in an ammonia medium [30,31]. This method is promising because it employs an active medium—namely, ammonia whose properties can be altered in a wide range by varying the external conditions: pressure, temperature, and concentration of initial reagents.

Ammonia is a large-scale product from the chemical industry [32] that can be applied in various fields: fertilizers, refrigeration, medicine, etc. [33,34]. It should also be noted that ammonia can be used in organic and inorganic synthesis as a reagent and solvent [35–38]. Therefore, it is actively used in the synthesis of amides and amines [39]. It is worth noting separately that ammonia is used in the treatment and modification of polymers [37]. In organosilicon chemistry, ammonia is a key reagent in the synthesis of silazanes, an important class of organosilicon compounds [40].

This article presents the results of our studies on the effect of various factors on the condensation of *cis*-tetraphenylcyclotetrasiloxanetetraol (*cis*-tetraol) in ammonia. The structure and molecular weight characteristics of the resulting L-PPSQs, as well as physicochemical properties of the obtained samples, allow us to state that the process is versatile in terms of controlling the structure and properties of the reaction products.

2. Results and Discussion

2.1. Synthesis

The condensation of *cis*-tetraphenylcyclotetrasiloxanetetraol (*cis*-tetraol) was performed in high-pressure steel reactors (see Figure 1).

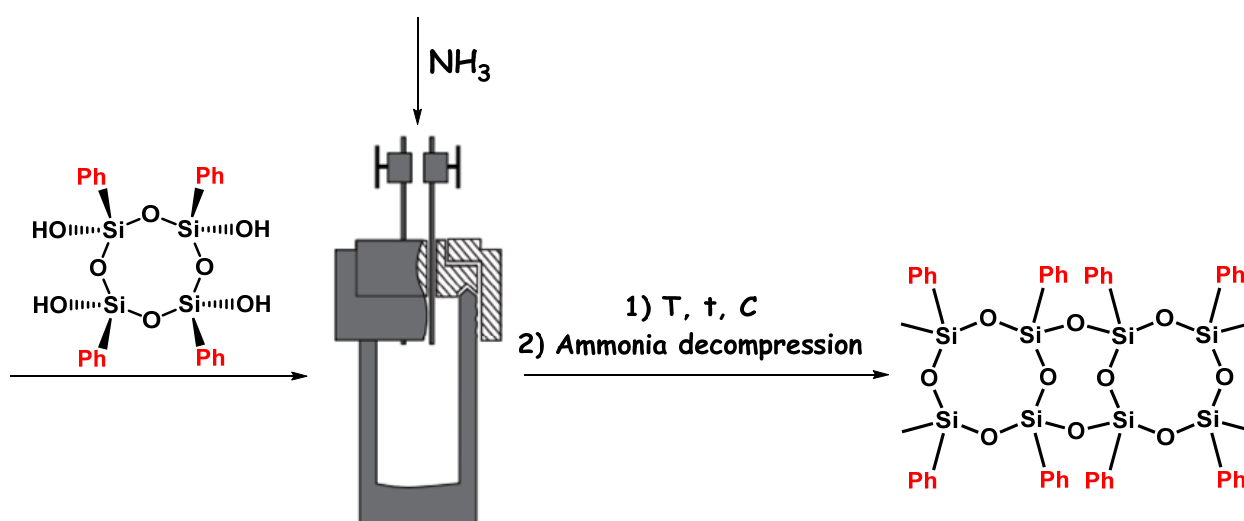


Figure 1. General scheme of L-PPSQ synthesis in ammonia medium.

A certain amount of *cis*-tetraol was loaded into a high-pressure reactor, which was then cooled to $-50\text{ }^{\circ}\text{C}$, and ammonia was pumped using a flow controller. Then, the reactor was immersed into a thermostatic bath at a given temperature. After a certain time, the reactor was cooled to room temperature, ammonia was decompressed, and the polymer was isolated.

To assess the solubility of the initial monomer and visualize the reaction, we carried out an experiment in test tubes at room temperature (see Figure 2). As can be seen from Figure 2a, the monomer dissolves in ammonia to form an ideal solution. The condensation products begin to precipitate from the solution after 15 min (Figure 2b). The polymer precipitated as a separate phase can be distinctly observed an hour later (Figure 2c).

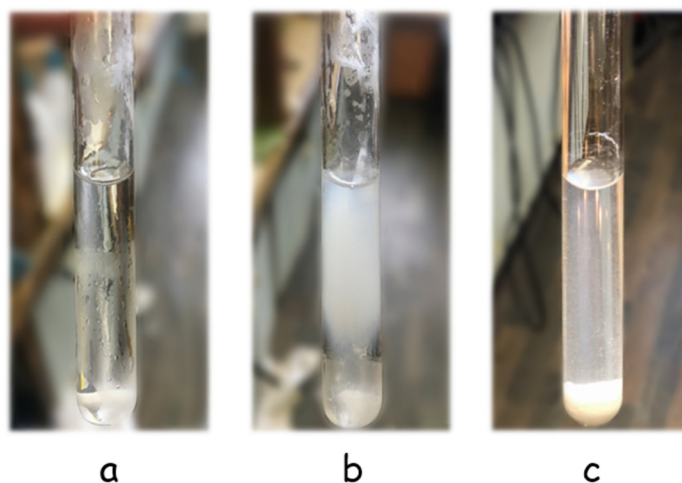


Figure 2. (a) Solubility of the monomer in ammonia, (b) 15 min after dissolution, and (c) 1 h after dissolution.

The reaction products were analyzed by GPC, NMR, IR spectroscopy, PXRD, and viscometry in solution.

2.2. Monomer Concentration Effect

The effect of monomer concentration on the condensation process was studied at a temperature of $30\text{ }^{\circ}\text{C}$ using a reaction time of 4 h (Figure 3, Table 1, Experiments 1–4).

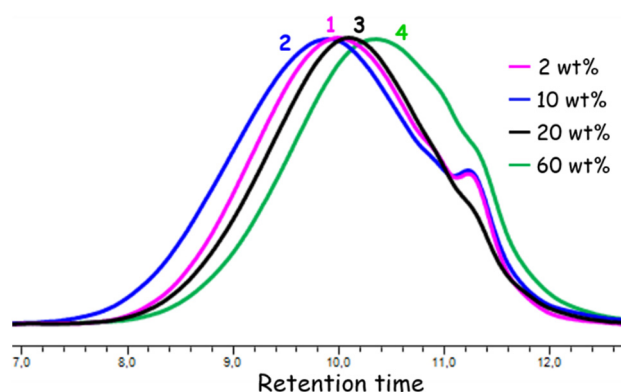


Figure 3. GPC curves obtained in Experiments 1–4.

Table 1. Experimental data on the effect of monomer concentration, reaction time, and temperature.

Experiment	Monomer Concentration, wt%	Temperature, °C	Reaction Time, h	Mn, kDa	Mw, kDa	Mp, kDa	Mw/Mn
1	2	30	4	4.6	9.1	6.1	1.9
2	10	30	4	5.1	11.1	6.8	2.2
3	20	30	4	4.2	8.1	5.1	1.9
4	60	30	4	3.8	7.1	4.0	1.9
5	20	30	4	4.2	8.1	5.1	1.9
6	20	30	8	5.1	10.4	6.3	2.0
7	20	30	13	5.8	12.7	7.8	2.2
8	20	30	24	6.4	14.5	8.5	2.3
9	20	30	168	6.3	14.9	8.7	2.4
10	20	30	4	4.0	7.6	5.1	1.9
11	-	30	4	8.2	18.2	10.6	2.2
12	-	30	4	9.4	22.1	12.0	2.4
13	20	30	4	7.8	15.5	9.4	1.9
14	20	50	4	14.4	34.1	14.7	2.4
15	20	100	4	60.1	144.1	95.3	2.4
16	20	150	4	189.9	477.9	461.7	2.5
17	20	200	4	145.5	461.6	361.6	3.2
18	20	300	4	13.0	95.2	56.4	7.3

It can be observed from the data presented in Table 1 (Experiments 1–4) that the monomer concentration does not significantly affect the molecular weight characteristics of the polymers obtained. It can be concluded from the above data that 10 wt% is the optimal concentration of the monomer to produce a polymer with a higher molecular weight under these reaction conditions. It should also be noted that a decrease in the monomer concentration below 20 wt% results in low molecular weight products, as it can be observed from the bimodal nature of the curves obtained in experiments 1 and 2. It can be assumed that polyhedral compounds containing few hydroxy groups are formed in this case. The effect of monomer concentration on the structure of the products was also previously [24].

2.3. Reaction Time Effect

The effect of reaction time on the condensation process was studied at 30 °C and a monomer concentration of 20 wt% (see Figure 4, Table 1, Experiments 5–9). The reaction was performed for 4 to 168 h.

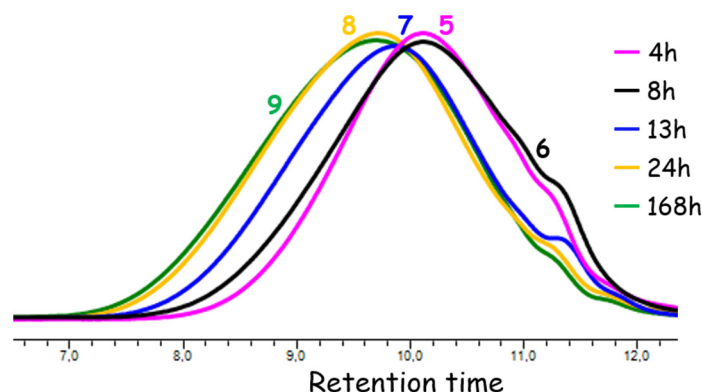


Figure 4. GPC curves obtained in Experiments 5–9.

It can be observed from GPC data that the molecular weight of condensation products ceases to increase after 24 h. Probably, the polycondensation reaction reaches dynamic equilibrium due to the release of water in the condensation of *cis*-tetraol in the first stage. After the release of water, M_W growth occurs by the polymerization–condensation mechanism. The growth of M_W stops upon reaching an equilibrium. To confirm this assumption, we carried out experiments using the “condensation–decompression–condensation” consequent cycle. In this case, water resulting from the reaction is removed along with ammonia from the reactor. It can be observed from Figure 5 that after the second condensation (Experiment 12), the molecular weight ceases to increase significantly in comparison with Experiment 11 (Table 1, Experiments 10–12), i.e., the condensation processes naturally slow down as the concentrations of reacting groups decrease.

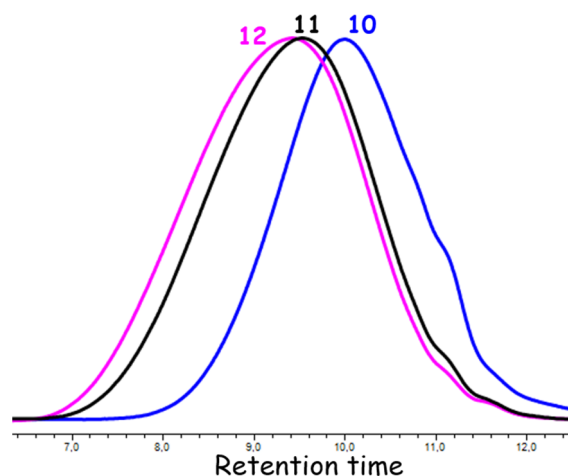


Figure 5. GPC curves obtained in experiments 10—L-PPSQ synthesis; 11—synthesis after first decompression; 12—synthesis after second decompression.

The reaction time does not significantly affect the molecular weight characteristics of L-PPSQs, as it can be observed from the data obtained.

2.4. Temperature Effect

The condensation of *cis*-tetraol was performed at temperatures from 30 to 300 °C for 4 h at 20% monomer concentration (Figure 6, Table 1, Experiments 13–18).

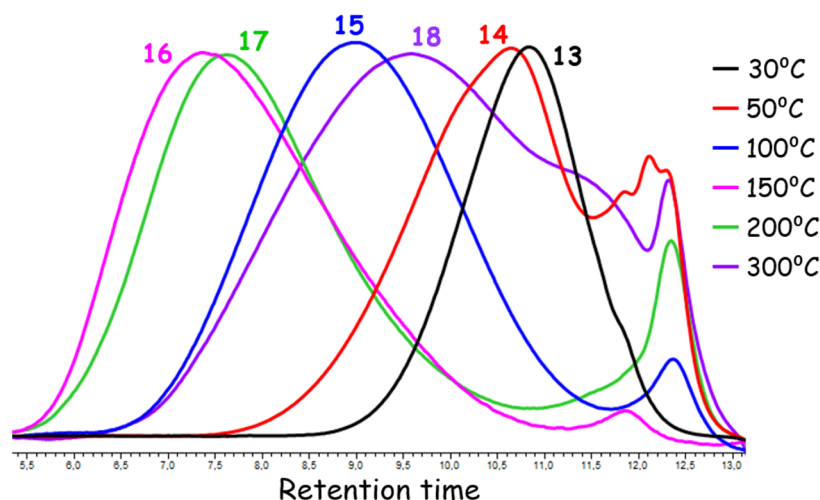


Figure 6. GPC curves obtained in Experiments 13–18.

The temperature of *cis*-tetraol condensation in ammonia has a significant effect on this process as can be seen from the data obtained. As the temperature rises from 30 to 150 °C, the M_W of the product increases. The largest M_W of the polymer was obtained at 150 °C (16). A further increase in temperature results in a decrease in the M_W of the reaction products. This is due to the fact that the equilibrium is shifted towards the formation of low-molecular-weight products at temperatures of 200 and 300 °C, which agrees with the data published earlier [41,42].

Thus, we showed for the first time that it is possible to obtain ladder polyphenyl-silsesquioxane with a certain molecular weight in the range of 8–500 kDa. To this end, it is sufficient to vary the reaction temperature within 30–150 °C. A further increase in temperature activates depolymerization processes, and hence, the M_W decreases.

2.5. Water Effect

It appears that the presence of water in the system is an important factor affecting the condensation of *cis*-tetraol in ammonia. Water is formed upon homofunctional condensation of silanol groups and limits the growth of L-PPSQ molecular weight, as shown above. Its removal leads to a shift of equilibrium and an increase in the M_W of the resulting polymer. We found that an additional amount of water in the system also affects the polycondensation process. Experiments with the addition of 3×10^{-2} , 15×10^{-2} , and 30×10^{-2} mmol% water (Experiments 19–21) into the reaction system were performed. An increase in the water amount results in the formation of polymers with a lower molecular weight, as can be observed from the data shown in Figure 7 and Table 2.

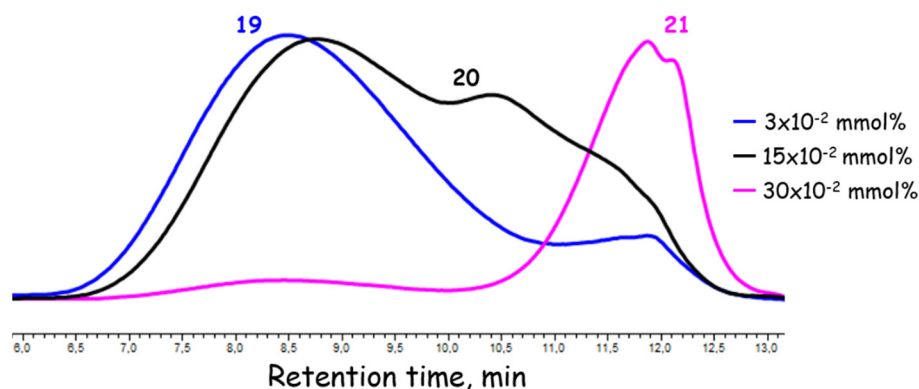


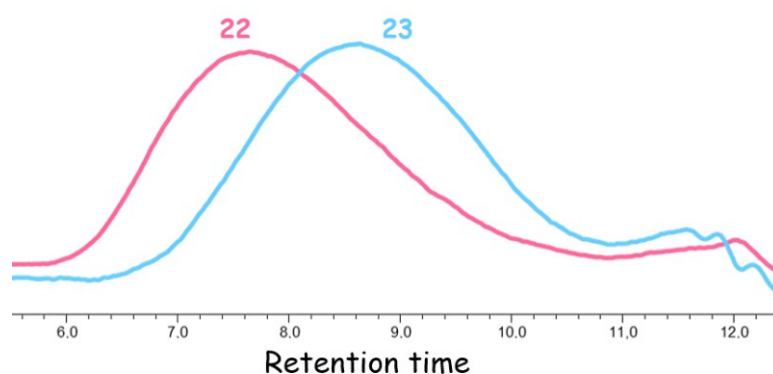
Figure 7. GPC curves obtained in experiments 19–21.

Table 2. Data of experiments on the water effect.

Experiment	Monomer Concentration, wt%	H ₂ O Concentration, mmol%	Temperature, °C	Reaction Time, h	HMWF ^[a]		Mw/Mn	LMWF ^[b]		Mw/Mn
					Mn, kDa	Mw, kDa		Mn, kDa	Mw, kDa	
19	20	3×10^{-2}	150	4	51.4	134.1	2.6	0.8	2.0	2.6
20	20	15×10^{-2}	150	4	72.3	120.7	1.7	2.2	8.6	3.8
21	20	30×10^{-2}	150	4	95.5	150.0	1.6	1.2	2.9	2.5

^[a] HMWF—high molecular weight fraction; ^[b] LMWF—low molecular weight fraction.

It is likely that this effect may be associated with the reaction mechanism. We assume that the mechanism of L-PPSQ formation in the system in question is largely similar to the mechanism of high-temperature polymerization first suggested by Brown and subsequently studied in detail by Soviet scientists [41]. It involves the anionic polymerization of phenyltrichlorosilane hydrolysis products, where potassium hydroxide acts as the initiating agent. Accordingly, an increase in its amount should lead to a decrease in the product's M_w and an increase in the fraction of side processes (depolymerization, chain transfer). In our case, the addition of more water results in the formation of a larger amount of NH_4OH in the system. This compound may have an effect similar to potassium hydroxide under liquid ammonia conditions. On the other hand, water is also released in the homocondensation of silanol groups. In this case, its additional amount displaces the equilibrium towards the formation of low-molecular products. This assumption was proved by the following experiment. At first, the residual silanol groups in the L-PPSQ sample were blocked with trimethylchlorosilane, then its reaction with water was carried out. It can be observed from Figure 8 that in this case, the siloxane bond is broken and a product with a smaller molecular weight is formed.

**Figure 8.** GPC curves obtained in Experiments 22—L-PPSQ with silanol groups blocked by trimethylchlorosilane; 23—condensation product of sample 22 with addition of water.

It can be observed from Table 3 that the molecular weight of the L-PPSQ sample decreases twofold.

Table 3. Data from experiments 21–24 with water.

Experiment	Monomer Concentration, wt%	H ₂ O Concentration, mmol%	Temperature, °C	Reaction Time, h	Mn, kDa	Mw, kDa	Mp, kDa	Mw/Mn
22	20	-	150	4	102.7	283.2	276.5	2.8
23	-	30×10^{-2}	150	4	54.4	136.1	110.2	2.5
21	20	30×10^{-2}	150	4	1.2	2.9	1.5	2.45
24	-	-	150	4	16.9	61.7	46.8	3.6

It should be noted that if the low-molecular-weight product obtained in Experiment 21 is subjected to the polymerization reaction again without water addition, a high-molecular L-PPSQ can be obtained (see Figure 9, Table 3). In other words, the reaction is completely reversible and this fact emphasizes its versatility. By adjusting the process parameters, it is

possible to synthesize products with certain molecular parameters and also to convert the polymer into the starting compounds for reuse.

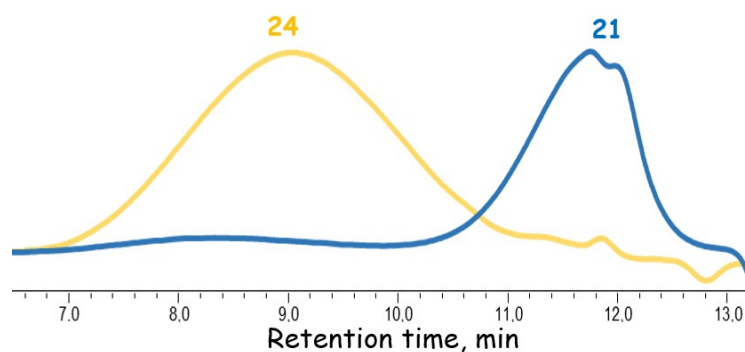
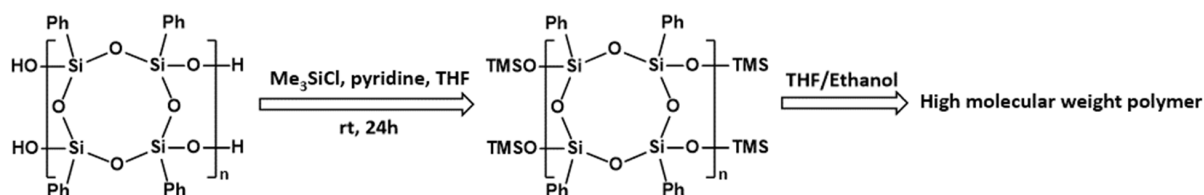


Figure 9. GPC curves obtained in Experiment 21 is the low molecular weight condensation product of *cis*-tetraol with addition of water; Experiment 24 is the product of condensation of sample 21.

2.6. Isolation and Study of L-PPSQ Structure

To determine the structure and properties of the L-PPSQ samples obtained, we blocked the residual silanol groups with trimethylchlorosilane in the presence of pyridine. After that, the products were reprecipitated in the ethanol/THF system (Scheme 1) and analyzed.



Scheme 1. Blocking of residual silanol groups in L-PPSQ and followed by reprecipitation of the resulting polymers.

In this way, three samples of polymers synthesized at 30, 100, and 150 °C were prepared (25–27). Their molecular weight characteristics are shown in Figure 10 and in Table 4.

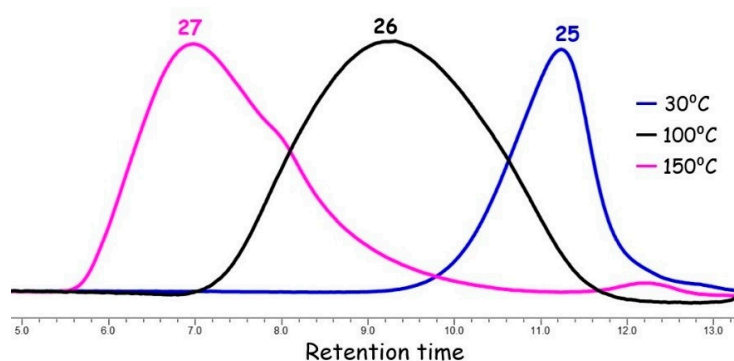


Figure 10. GPC curves obtained in Experiments 25–27.

Table 4. Molecular weight characteristics of polymers 25–27.

Experiment	Monomer Concentration, wt%	Temperature, °C	Reaction Time, h	Mp, kDa	Mw, kDa	Mn, kDa	Mw/Mn	Wt OH, %w	WnmrOH, %w	Wt/W nmr
25	20	30	4	14.2	22.4	12.3	1.8	0.550	0.62	1.1
26	20	100	4	116.6	161.9	67.2	2.4	0.100	0.14	1.4
27	20	150	4	558.4	549.2	196.8	2.4	0.035	0.07	1.9

It is known that L-PPSQ samples obtained by the classic high-temperature method have a defective structure [43,44], i.e., the content of SiOH groups in the polymers exceeds the theoretical value. The ratio of the measured and calculated values of the content of hydroxy groups can provide information about the defectiveness of the polymers obtained. It can be seen from the data in Table 4 that the defectiveness of the structure of the synthesized polymers increases in proportion to the molecular weight. At the same time, this value of sample 25 obtained under the mildest conditions is close to the theoretical one. The content of SiOH groups regularly decreases with an increase in the MW of samples, which indicates its predominantly linear-ladder structure. The results obtained from the analysis of functional groups allow us to use L-PPSQ samples as accessible blocks for synthesizing block copolymers as an alternative to linear/ladder-like polysiloxane block copolymers used previously [7,45,46].

The three polymer samples isolated by this method were used to obtain films from 1% solutions in toluene by casting onto cellophane support. PPSQ samples obtained at 100 °C (26) and 150 °C (27) form hard transparent films, whereas the polymer sample with a lower molecular weight obtained at 30 °C (25) is unable to form continuous films (see Figure 11).

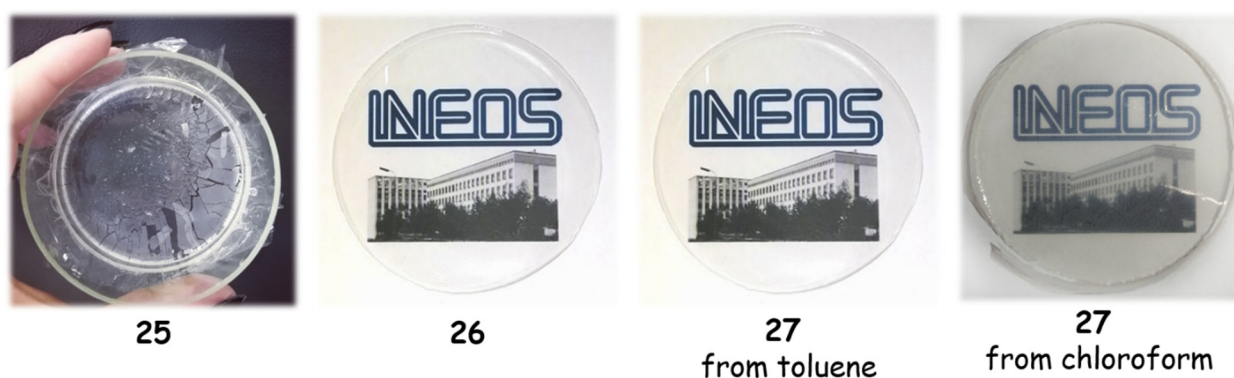


Figure 11. Polymer films 25–27.

The ladder structure of polymers was confirmed by a set of physicochemical methods—namely, NMR, IR spectroscopy, and PXRD.

2.7. NMR and IR Spectroscopy

The L-PPSQ samples synthesized (25–27) were studied by NMR and IR spectroscopy. ^1H NMR spectra contain two main peaks at 6.2–7.8 ppm and -0.67 – 0.08 ppm belonging to the $\text{PhSiO}_{1.5}$ and terminal $\text{Me}_3\text{SiO}_{0.5}$ groups, respectively. Their ^{29}Si NMR spectra exhibit two peaks corresponding to $\text{PhSiO}_{1.5}$ groups (-80 ppm) and $\text{Me}_3\text{SiO}_{0.5}$ terminal groups (10 ppm).

The IR spectra of the L-PPSQ samples obtained show absorption bands typical of phenyl groups (691 , 727 cm^{-1}), Si-O-Si bonds (1020 – 1120 cm^{-1}), and $\text{Me}_3\text{SiO}_{0.5}$ groups (1254 cm^{-1}). There are no stretching bands typical of $-\text{SiOH}$ groups in the region of 3100 – 3500 cm^{-1} . This fact confirms that silanol groups are completely blocked with trimethylchlorosilane (see Figure 12).

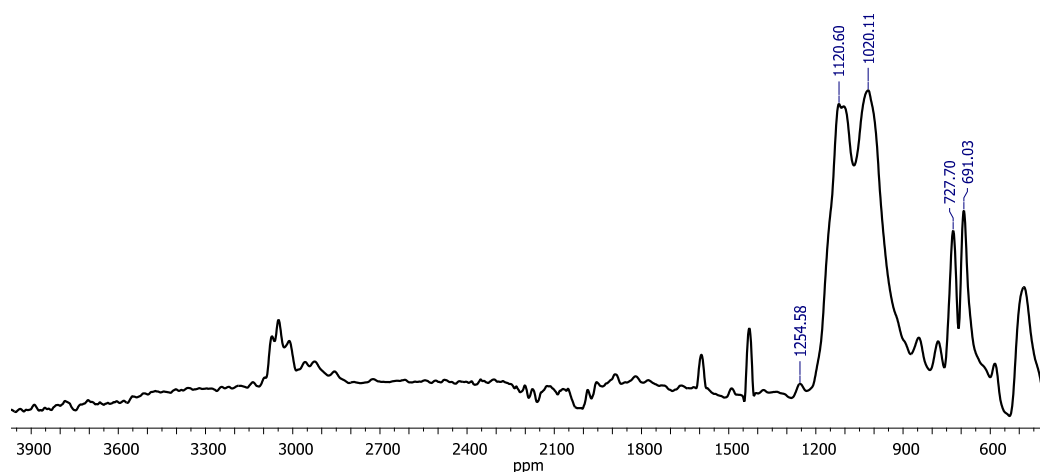


Figure 12. IR spectra of L-PPSQ 27.

The NMR and IR spectroscopy data obtained agree with the results previously published for L-PPSQ samples [47].

2.8. Powder X-ray Diffraction Analysis (PXRD)

Powder X-ray phase analysis (XRD) for samples 25–27 shows two distinct diffraction halos, in good agreement with previous works. The first halo at $7.2\text{--}7.3^\circ$ (d_1), indicating the intramolecular chain-to-chain distance (i.e., the width of each double chain) in the double-chained, ladder-like molecule is narrow and sharp. It is indicated that L-PPSQs have a sufficiently rigid skeleton in which there is limited movement around the longitudinal axis, and the conformation is practically invariable. The second diffuse halo indicates that the average thickness of the ladder-like polymer chain is $19.7\text{--}19.8^\circ$ (d_2) (see Figure 13, Table 5). These values agree with the results described in the literature for L-PPSQs [48].

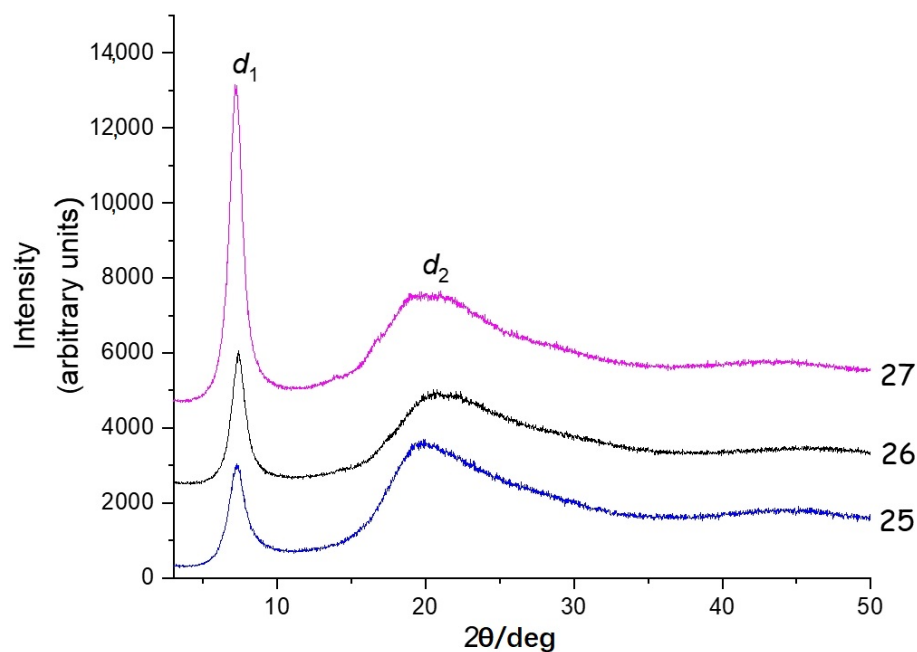


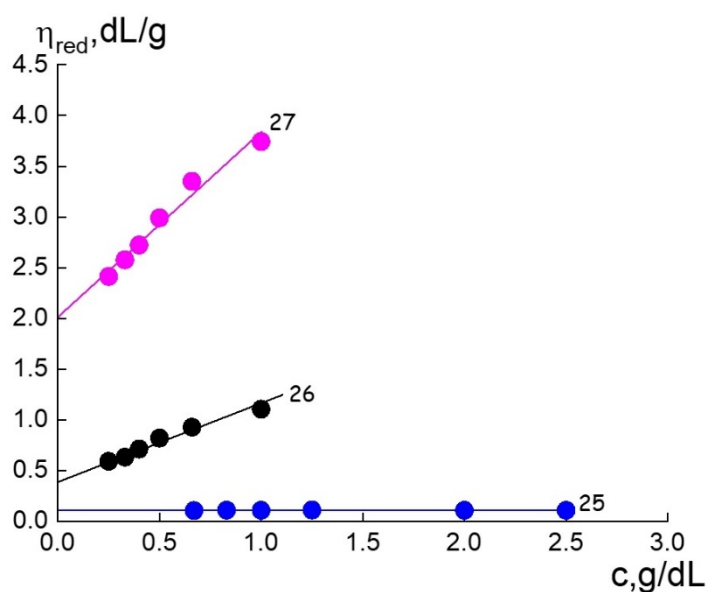
Figure 13. Diffraction data for polymers 25–27.

Table 5. Values of PXRD parameters for polymer samples 25–27.

Experiment	d ₁ , nm	d ₂ , nm
25	12.2	4.5
26	12.3	4.4
27	12.2	4.5

2.9. Viscosity Measurements

Figure 14 and Table 6 show the values of the intrinsic viscosity of solutions of the polymers in toluene at 37 °C and their molecular weights M_n calculated by the formula $[\eta] = 1.77 \times 10^{-5} \times M^{0.895}$. The formula was derived from a study of 18 molecular weights $(0.26\text{--}4.88) \times 10^5 M_n$ of polymer fractions¹ and is applicable in a wide range of molecular weights.

**Figure 14.** Reduced viscosity vs. concentration for dilute solutions of polymers 25–27 in toluene (T = 37 °C).**Table 6.** Molecular weight characteristics of polymers 25–27.

Experiment	M _w , kDa	M _n , kDa	M _η , kDa	[η], dL/g
25	22.4	12.3	15.6	0.1
26	161.9	67.2	73.3	0.4
27	549.2	196.8	442.5	2.2

It is worth noting that the reduced viscosity of polymer 25 nearly does not depend on the concentration of the solutions studied. This dependence of the viscosity of L-PPSQ solutions on M_w coincides with literature data [49,50].

3. Exploration of L-PPSQ Properties

3.1. Thermal Characteristics

L-PPSQ samples were studied by the TGA method in air and in argon. The results obtained are shown in Figure 15a,b and Table 7. The decomposition onset temperature of the samples synthesized and the amount of solid residue after the end of thermal transformations are in good agreement with literature data [51,52]. The onset temperature of polymer samples grows with an increase in their molecular weight, both in air and in argon. While the percentage of solid residue in the air atmosphere for all L-PPSQ samples differs insignificantly (Figure 15a, Table 7), the percentage of solid residue in the

argon atmosphere changes appreciably (Figure 15b, Table 7) symbatically with an increase in the molecular weight. This effect may be due to the specifics of the elimination and decomposition of phenyl groups that are responsible for the carbonization of the solid residue of L-PPSQ with different molecular weights.

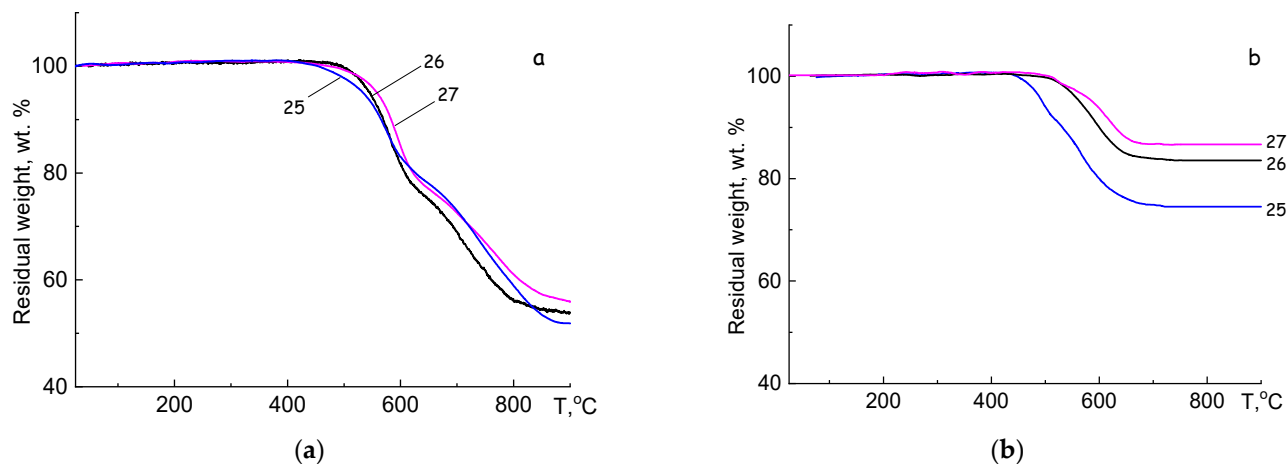


Figure 15. TGA curves of polymers 25–27 obtained at a heating rate of 10 degrees/min: (a) in air; (b) in argon.

Table 7. Thermal data of polymers 25–27.

Experiment	$T_d^{5\%, ^\circ\text{C}}$ Air	$M_{\text{res, wt\%}}$ Air	$T_d^{5\%, ^\circ\text{C}}$ Argon	$M_{\text{res, wt\%}}$ Argon
25	527	52	464	75
26	536	54	557	85
27	537	56	587	87

It should be noted that the thermal characteristics obtained for polymer 27 are superior to the results published previously [53].

3.2. Physical and Mechanical Measurements

The mechanical properties of polymers obtained at 100 and 150 °C (26 and 27) were studied by the uniaxial extension method.

A film obtained from the polymer synthesized at 150 °C that had the largest molecular weight (27) (see Figure 16, Table 8) showed the best mechanical characteristics. The values of ultimate tensile stress (σ) and elongation at break (ϵ) found for polymer 27 match the best characteristics of L-PPSQs reported in the recent literature [53].

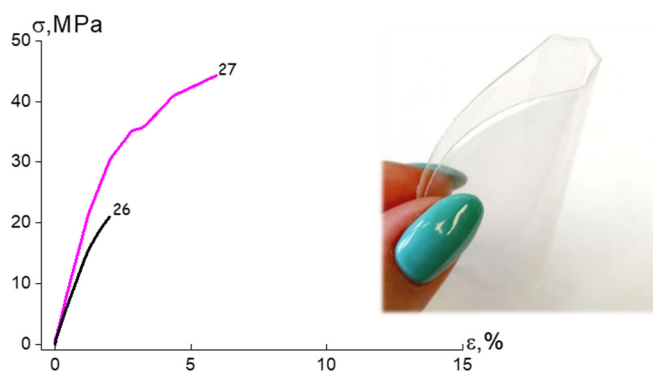


Figure 16. Stretching curves of polymers 26–27.

Table 8. Mechanical characteristics of polymers 26–27.

Experiment	E, MPa	σ_p , MPa	ϵ_p , %
26	1300	21	2
27	1700	44	6

Curve 26 is almost linear and corresponds to Hooke's deformation. This suggests that there is nearly no segmental mobility or mobility of macromolecules as a whole, which are responsible for elasticity and plasticity, respectively, in this polymer. At the same time, sample 27 behaves somewhat differently as it can be observed from the deviation of the tensile curve from Hooke's plot. It can be ascribed to the greater defectivity of sample 27 (Table 4). Defects can disrupt the structure of the double-stranded chain. So-called hinges, i.e., places where rotation around the siloxane bond is possible, appear in it. It is likely that segmental mobility appears in a molecule with a sufficient number of such hinges. As a result, the ultimate deformation of sample 27 increases to 6%, which is three times larger than that of sample 26.

4. Conclusions

A versatile method for the synthesis of L-PPSQs with controlled molecular weight characteristics was developed for the first time. The effect of various parameters (temperature, monomer concentration, reaction time, addition, and removal of water to/from the reaction medium) on the polycondensation process was studied. It was found that the reaction temperature and amount of water in the system are the main parameters determining the molecular weight characteristics of L-PPSQs. The molecular weight characteristics and structures of the polymers were confirmed by GPC, ^1H , ^{29}Si NMR, IR spectroscopy, viscosity measurements, and PXRD. The high-molecular-weight L-PPSQs obtained are capable of forming flexible transparent films with high mechanical and thermal characteristics. The important factors of the new process include the possibility to produce functional blocks with various molecular weights and high-strength samples with a very promising set of properties for critical practical applications. These processing characteristics, along with the previously shown [29] possibility of complete recycling of the reaction medium, i.e., ammonia, indicate their full compliance with the modern requirements for polymer materials and processes of their production within the framework of the sustainable development concept.

Author Contributions: T.O.E. carried out experiments and wrote the paper; A.A.A. and M.N.T. conceived, designed and wrote the paper; M.A.N. recorded the ^1H and ^{29}Si NMR spectra; M.I.B. conducted a study using the TGA and DSC methods; G.G.N. conducted physical and mechanical measurements; Y.S.D. carried out the synthesis of monomers; I.E.U. conducted powder X-ray diffraction analysis; O.I.S. wrote the paper and discussion of the results; A.M.M. led the research. All authors have read and agreed to the published version of the manuscript.

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