



# POLY(SILOXANE–PROPYLENE OXIDE–URETHANE–UREAS) BASED ON CYCLOALIPHATIC DIISOCYANATES: SYNTHESIS AND PROPERTIES

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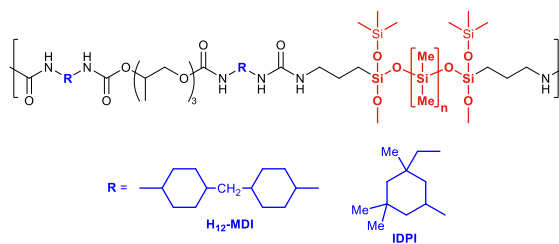
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## Abstract

New network poly(siloxane–propylene oxide–urethane–ureas) based on  $\alpha,\omega$ -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxanes, oligo(propylene oxide), and cycloaliphatic diisocyanates are synthesized. The resulting polymers are studied by differential scanning calorimetry and thermogravimetric analysis; their stress–strain characteristics are elucidated. These polymers are found to feature microphase separation and, consequently, two glass transition temperatures, defined by the chemical structures of the microphases. It is shown that an increase in the molecular weight and mass content of siloxane blocks leads to a decrease in the elastic modulus and tensile strength.

**Key words:** network poly(siloxane–urethane–ureas), oligosiloxane diamines, cycloaliphatic diisocyanates, stress–strain characteristics, thermal properties, microphase separation.



## Introduction

Polyurethanes (PUs) based on cycloaliphatic diisocyanates (DIs) comprise a rapidly developing area of polymer chemistry and find extensive use as coatings and elastomers. The main advantage of PUs based on cycloaliphatic DIs, compared to polyurethanes based on aromatic DIs, is high weather resistance and a much lower propensity to stain. Furthermore, materials obtained from these diisocyanates feature increased optical transparency, a fairly high glass transition temperature, as well as high resistance to different chemical reagents [1].

Among the variety of these polymers, of growing interest are poly(siloxane–urethanes) (PSUs) which represent unique polymers that combine the properties of polysiloxanes (hydrophobicity, high gas permeability, low surface energy, bioinertness, thromboresistance) and polyurethanes (high mechanical strength, abrasion resistance, relatively low cost) [2]. Poly(siloxane–ureas) (PSUrS) are very close in their properties to poly(siloxane–urethanes). An important advantage of the former is, as a rule, the absence of a toxic catalyst during their production [3–6].

The cited reports deal with linear poly(siloxane–urethanes) based on aliphatic and cycloaliphatic diisocyanates, while there is almost no literature data on network PSUs featuring a similar composition. Linear PSUs hold great promise, but the emerging data on cross-linked systems of this type require further evaluation and comparison [7].

The goal of this work was to synthesize and study the properties of new network poly(siloxane–propylene oxide–urethane–ureas) (PSPOUUs) based on  $\alpha,\omega$ -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxanes (DASs),

cycloaliphatic DIs H<sub>12</sub>-MDI and IPDI, and oligo(propylene oxide) (OPO).

## Experimental section

The synthesis of DASs ( $M_n = 1150, 1600, \text{ and } 2260 \text{ g/mol}$ ) was carried out according to the published methods [8, 9]. The presence of two types of functional groups in the resulting DASs enables the production of network poly(siloxane–urethanes), but at the same time complicates the definition of their molecular weights and may lead to undesirable gelation during the synthesis of polymers. The use of several methods, for example, gel permeation chromatography (GPC), NMR spectroscopy, and elemental microanalysis allowed for specifying the molecular weights. The results of GPC analysis allowed us to estimate the length of a siloxane moiety in oligosiloxanediols which served as intermediates in the synthesis of DASs. The <sup>1</sup>H NMR spectroscopic data provided the characterization of oligodiamines by the ratio of total integral intensities of the signals of all  $-(CH_2)-$  groups (3-aminopropyl moiety) and  $-SiMe_2O-$  groups (siloxane moiety) [9]. The gravimetric determination of carbon and hydrogen and spectrophotometric determination of silicon afforded a more accurate value of the length of the siloxane moiety based on the ratio of carbon and silicon contents. Thus, the molecular weight of the siloxane block can be determined both in the oligodiamine itself and in the polymers based on it. In PSPOUUr2 and PSPOUUr3, the length of the siloxane moiety was calculated from the ratio of the C/Si contents in the resulting polymers. In PSPOUUr4, this value was determined directly from the ratio of the element contents in the DAS oligodiamine, which can be difficult in

some cases due to its hydrolytic instability. In the case of PSPOUUr1, the model poly(siloxane–urea) PSUr1 was synthesized by reacting oligodiamine with H<sub>12</sub>-MDI in a 1:1 molar ratio in methyl ethyl ketone (MEK), and the molecular weight was calculated from the C/Si ratio in it. The advantage of this calculation method is that PSUr1 is a stable compound and has a simpler structure than PSPOUUr1 (Table 1).

The microanalysis data are presented in Table 1. The calculated element contents were derived from the results of <sup>1</sup>H NMR spectroscopic studies. The number of dimethylsiloxane units (*n*) was determined from the following proportion

$$(n + 2) \times M_{Si} = \frac{(2n + N) \times M_C}{C_C} \times c_{Si}$$

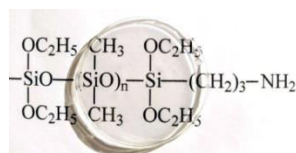
where *c<sub>c</sub>* and *c<sub>Si</sub>* are the mass concentrations of carbon and silicon, *M<sub>C</sub>* and *M<sub>Si</sub>* are the relative atomic masses of carbon and silicon, and *N* is the number of carbon atoms in the compound excluding the carbon atoms in the siloxane moiety.

**Table 1.** Compositions of the compounds used to calculate the length of the siloxane unit in the PSPOUUr3

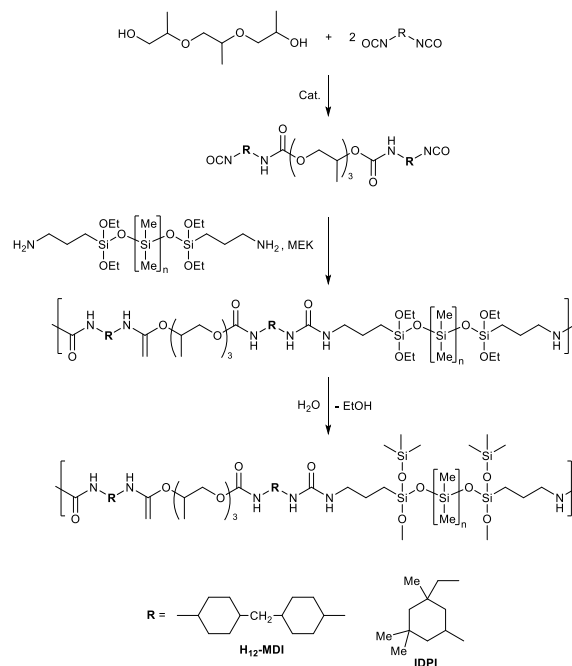
Comp.	Elemental analyses, %			
	H <sub>found</sub> /H <sub>calc</sub>	C <sub>found</sub> /C <sub>calc</sub>	Si <sub>found</sub> /Si <sub>calc</sub>	N <sub>found</sub> /N <sub>calc</sub>
DAS	8.38/8.43	34.33/34.52	33.96/34.24	1.40/1.22
PSUr	8.61/8.08	39.62/40.56	26.77/27.28	3.46/4.56
PSPOUUr2	8.57/8.44	45.56/44.42	21.14/22.92	5.21/3.65
PSPOUUr3	9.06/8.32	43.67/41.42	23.42/25.37	5.42/3.62

The synthesis of PSPOUUr3 was carried out using a two-step procedure (Scheme 1). At the first step, a prepolymer was prepared by introducing OPO (*M<sub>n</sub>* = 200 g/mol) into the diisocyanate under vigorous stirring. The OPO/DI molar ratio was 1:2.1. Dibutyltin dilaurate (DBTDL) was used as a catalyst (2 wt %). The prepolymer was colorless transparent viscous masses. The reaction course was monitored by titration of free isocyanate groups and IR spectroscopy. In all cases, the reaction proceeded completely, which was confirmed by the appearance of a characteristic absorption band of the carbonyl stretches (1697 cm<sup>-1</sup>) and NH stretches of the urethane group (3329 cm<sup>-1</sup>). The absence of a broad band in the range of 3100–3700 cm<sup>-1</sup> indicated that all the OH groups of oligodiols also reacted.

The second step was carried out in MEK at 20 °C. The solutions of the prepolymer and α,ω-bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane (in a 1:1 molar ratio) in MEK (*c* = 10 g/dL) were mixed and filtered. Then the film was cast onto a Teflon substrate. Under the action of air moisture, the Si–O–C bonds cleaved, resulting in the release of ethanol and its subsequent evaporation with the solvent. The formation of the cross-linked PSPOUUr3 occurred due to the condensation of the resulting silanol groups. This afforded colorless transparent films (Fig. 1), which were dried to constant mass, first, under ambient conditions and then under vacuum.



**Figure 1.** PSPOUUr image.



**Scheme 1.** Synthesis of PSPOUUr3.

## Physicochemical methods

The quantitative chemical analysis was carried out by gravimetry and spectrophotometry.

The GPC analysis was performed on a Shimadzu instrument (Japan, Germany) using a RID-20 A refractive index detector, PSS SVD 10E3A column (sizes 300×7.8 mm), polystyrene standards, and toluene as an eluent at –40 °C and the flow rate of 1 mL/min.

The IR spectra were registered on a Bruker Tensor 37 FTIR-spectrometer for liquid samples in a thin layer.

The <sup>1</sup>H and <sup>29</sup>Si NMR spectra were recorded on a Bruker Avance 400 spectrometer in CDCl<sub>3</sub> at *T* = 298 K. The chemical shifts were measured relative to TMS.

The content of a gel fraction in the samples was determined using a standard method in a Soxhlet extractor in MEK.

The stress–strain characteristics of the resulting polymer films were determined on a LLOYD Instruments LR5K Plus versatile testing machine at a stretching rate of 100 mm/min.

The glass transition temperatures of the films were determined by DSC using a DSC-3 instrument (Mettler-Toledo, Switzerland) at a heating rate of 10 °C/min in an argon atmosphere.

The thermogravimetric analysis was performed on a Shimadzu-DTG60H thermal analyzer (Japan) at a heating rate of 10 °C/min in an argon atmosphere.

## Results and discussion

Table 2 presents the main characteristics of the resulting PSPOUUr3 featuring different contents of the siloxane component *W<sub>sil</sub>* (mass fraction of total siloxane including terminal groups after the network formation). All the poly(siloxane–propylene oxide–urethane–ureas) were characterized by a high content of the gel fraction. In the case of PSPOUUr1, the content of the gel fraction was lower, presumably, due to the side processes of macrocycle formation.

**Table 2.** Main characteristics of the resulting PSPOUUrS

Comp.	DAS, $\frac{n}{M_n}$	OPO, $\frac{m}{M_n}$	DI	$W_{\text{sil}}$ , wt %	Gel fraction content, %	$T_g$	$\varepsilon_b$ , %	$\sigma_b$ , MPa	$E$ , MPa	$T_d^{5\%}$ , °C argon
PSPOUUr1	$\frac{11}{1150}$	$\frac{3}{200}$	H <sub>12</sub> -MDI	42	71	68	30 ± 3	15 ± 2	160	251
PSPOUUr2	$\frac{17}{1600}$	$\frac{3}{200}$	H <sub>12</sub> -MDI	56	80	–118/58	90 ± 9	10 ± 1	60	265
PSPOUUr3	$\frac{17}{1600}$	$\frac{3}{200}$	IPDI	62	79	–110/40	230 ± 23	9 ± 1	30	265
PSPOUUr4	$\frac{25}{2260}$	$\frac{3}{200}$	H <sub>12</sub> -MDI	71	96	–112/53	80 ± 8	7 ± 0.7	50	267

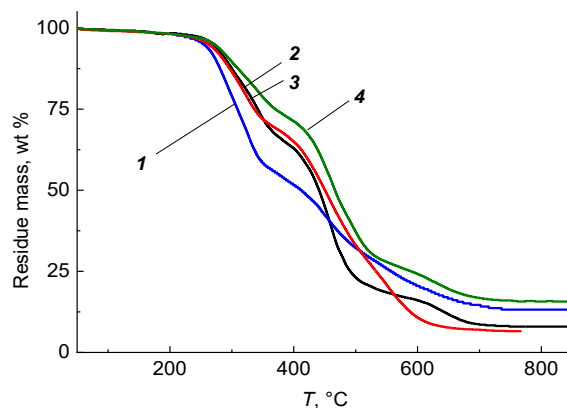
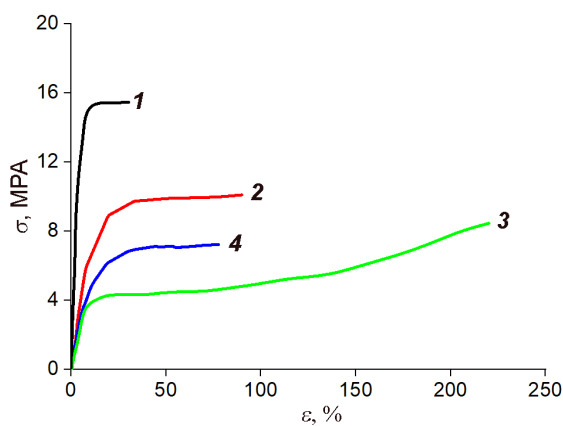
It is well known that a characteristic feature of poly(siloxane–urethanes) is their propensity for microphase separation due to the thermodynamic incompatibility of the components, which can be judged, in particular, from a significant difference in their solubility parameters (oligo(propylene oxide)  $\delta = 17.4$  (MPa)<sup>0.5</sup> and oligodimethylsiloxane  $\delta = 14.9$  (MPa)<sup>0.5</sup>) [1, 10, 11].

PSPOUUr1, which contains shorter siloxane blocks in its structure, displays one glass transition temperature  $T_g = 68$  °C. Presumably, this is a result of kinetic/thermodynamic hindrances that prevent separation of dimethylsiloxane blocks into a separate phase at their lower content and the low molecular weight.

As the value of  $W_{\text{sil}}$  increases (PSPOUUr2, PSPOUUr3, PSPOUUr4), the phase separation is observed, which follows from the appearance of two  $T_g$ : in the range of negative temperatures—the glass transition temperature of the siloxane component, and in the range of positive temperatures—that of the organic component. Of note is the mutual influence of the siloxane and oligo(propylene oxide) phases in the PSPOUUrS explored on their glass transition temperatures:  $T_g$  of the siloxane component increases, while  $T_g$  of the organic component decreases (Table 2) with the increasing content of the siloxane component. It can be assumed that the lower glass transition temperature of the siloxane phase in PSPOUUr2 compared to that of PSPOUUr3 with the same size of the siloxane block is a combination of all these factors. It should also be mentioned that an increase in the content of the siloxane component leads to a drastic increase in the content of the gel fraction (Table 2).

The results of the TGA studies are presented in Table 2 and Fig. 2. The temperature of the PSPOUUr decomposition beginning lies within the ranges typical for PUs [12–15]. The decomposition proceeds in two stages, the first one is observed in the range of 240–300 °C, while the second one—at 300–420 °C. Note that the higher the siloxane content in the system, the lower the mass loss value during the first stage of decomposition (Fig. 2). It is obvious that an increase in the content of the siloxane units in the PSPOUUrS improves their thermal stability. This can be seen when comparing the values of  $T_d^{5\%}$  for PSPOUUr1 and other PUs in Table 2.

Figure 3 shows the stress–strain curves of the PSPOUUrS explored. It can be seen that an increase in the molecular weight and mass content of the siloxane blocks, characterized by lower intermolecular interactions, affects the stress–strain characteristics of the polymers. This is manifested in a decrease in the elastic modulus and tensile strength (Table 2, Fig. 3). PSPOUUr2 and PSPOUUr3, which feature close compositions,

**Figure 2.** TGA curves for PSPOUUr1 (1), PSPOUUr2 (2), PSPOUUr3 (3), and PSPOUUr4 (4) obtained at a heating rate of 10 °C/min in an argon atmosphere.**Figure 3.** Stress–strain curves for PSPOUUr1 (1), PSPOUUr2 (2), PSPOUUr3 (3), and PSPOUUr4 (4).

differ only in the included diisocyanates, but in the case of PSPOUUr3, a much higher relative elongation at break is observed than in PSPOUUr2. It should be noted that for PSPOUUr3, the material strengthening is observed during its deformation. This difference may be due to a decrease in the volume of rigid segments and an increase in the chain sections between cross-links [1] and requires further investigation.

## Conclusions

New network poly(siloxane–propylene oxide–urethane–ureas) based on  $\alpha,\omega$ -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxanes, cycloaliphatic

diisocyanates H<sub>12</sub>-MDI and IPDI, and oligo(propylene oxide) were synthesized. An increase in the content of the siloxane units in the structures of the resulting PSPOUUs improves their thermal stability.

It was shown that the PSPOUUs obtained represent two-phase systems with at least 56 wt % content of the siloxane component, and both phases have a mutual impact on the glass transition temperature of each other:  $T_g$  of the siloxane component increases, while  $T_g$  of the organic component decreases with the increasing content of the siloxane component.

A comparison of the stress–strain characteristics of the PSPOUUs of different compositions revealed that an increase in the molecular weight and mass content of the siloxane blocks leads to a decrease in the elastic modulus and tensile strength.

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## References

1. M. F. Sonnenschein, *Polyurethanes. Science, Technology, Markets, and Trends*, Wiley, **2015**.
2. C.-A. Xu, M. Lu, Z. Tan, Z. Qu, K. Wu, J. Shi, *Colloid Polym. Sci.*, **2020**, 298, 1215–1226. DOI: 10.1007/s00396-020-04695-4
3. E. Delebecq, J.-P. Pascault, B. Boutevin, F. Ganachaud, *Chem. Rev.*, **2013**, 113, 80–118. DOI: 10.1021/cr300195n
4. I. K. Shundrina, I. V. Oleinik, V. I. Pastukhov, L. A. Shundrin, V. S. Chernonosova, P. P. Laktionov, *Polym. Sci., Ser. B*, **2020**, 62, 385–393. DOI: 10.1134/S1560090420040090
5. M. Shaikh, N. R. Choudhury, R. Knott, J. R. Kanwar, S. Garg, *Eur. J. Pharm. Biopharm.*, **2016**, 101, 82–89. DOI: 10.1016/j.ejpb.2016.01.015
6. N. Riehle, K. Athanasopulu, L. Kutuzova, T. Götz, A. Kandelbauer, G. E. M. Tovar, G. Lorenz, *Polymers*, **2021**, 13, 212. DOI: 10.3390/polym13020212
7. T. R. Salikhov, Synthesis of 1-aza-2-silacyclopentanes, aminosiloxanes and poly(siloxane–ureas) on their basis, *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Mendeleev University of Chemical Technology, Moscow, Russia, **2015**.
8. A. Kalinina, N. Strizhiver, N. Vasilenko, N. Perov, N. Demchenko, A. Muzafarov, *Silicon*, **2015**, 7, 95–106. DOI: 10.1007/s12633-014-9233-z
9. I. B. Meshkov, A. A. Kalinina, V. V. Gorodov, A. V. Bakirov, S. V. Krashennikov, S. N. Chvalun, A. M. Muzafarov, *Polymers*, **2021**, 13, 2848. DOI: 10.3390/polym13172848
10. R. Benrashid, G. L. Nelson, *J. Polym. Sci., Polym. Chem.*, **1994**, 32, 1847–1865. DOI: 10.1002/pola.1994.080321006
11. L. I. Makarova, G. G. Nikiforova, L. V. Filimonova, M. I. Buzin, V. G. Vasil'ev, E. S. Afanas'ev, M. N. Il'ina, O. V. Sinitsina, E. G. Kononova, I. O. Volkov, N. N. Samsonova, S. P. Novikova, V. S. Papkov, *Polym. Sci., Ser. B*, **2019**, 61, 20–27. DOI: 10.1134/s156009041901007x
12. G. Trovati, E. A. Sanches, S. C. Neto, Y. P. Mascarenhas, G. O. Chierice, *J. Appl. Polym. Sci.*, **2010**, 115, 263–268. DOI: 10.1002/app.31096
13. A. Z. Mohd-Rus, T. J. Kemp, A. J. Clark, *Prog. React. Kinet. Mech.*, **2009**, 34, 1–41. DOI: 10.3184/146867809X425749
14. D. Filip, D. Macocinschi, S. Vlad, *Composites, Part B*, **2011**, 42, 1474–1479. DOI: 10.1016/j.compositesb.2011.04.050
15. Y. Cai, Y. Hu, L. Song, L. Liu, Z. Wang, Z. Chen, W. Fan, *J. Mater. Sci.*, **2007**, 42, 5785–5790. DOI: 10.1007/s10853-006-0634-2

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