

Electronic supplementary information

EFFECT OF A CATALYST ON the SYNTHESIS AND PROPERTIES OF POLYSILOXANE–(PROPYLENE OXIDE)–URETHANE–UREAS BASED ON H₁₂-MDI

L. V. Filimonova,^a G. G. Nikiforova,^a I. O. Volkov,^a M. I. Buzin,^a
E. S. Afanasyev,^a K. L. Boldyrev,^a Z. S. Klemenkova,^a and E. A. Cherkas^b

^a Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, str. 1, Moscow, 119334 Russia

^b MIREA—Russian Technological University,
pr. Vernadskogo 78, Moscow, 119454 Russia

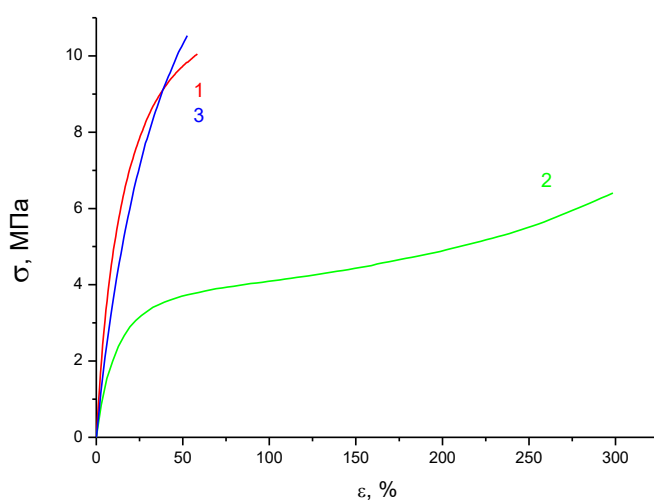


Figure S1. Stress–strain curves for PSPOUUr **1** (1), PSPOUUr **2** (2), and PSPOUUr **3** (3).

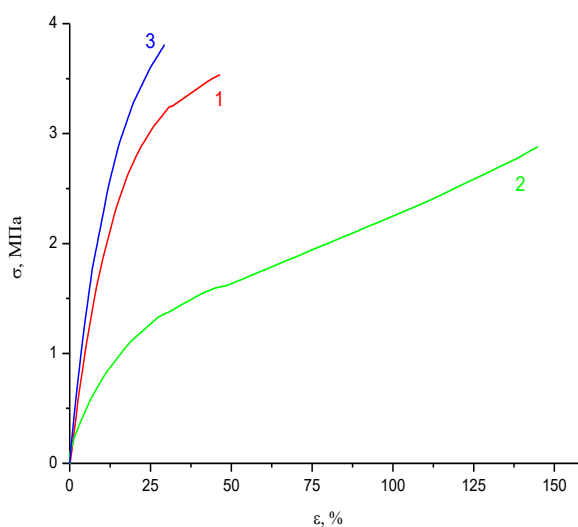


Figure S2. Stress–strain curves for PSUr **1** (1), PSUr **2** (2), and PSUr **3** (3).

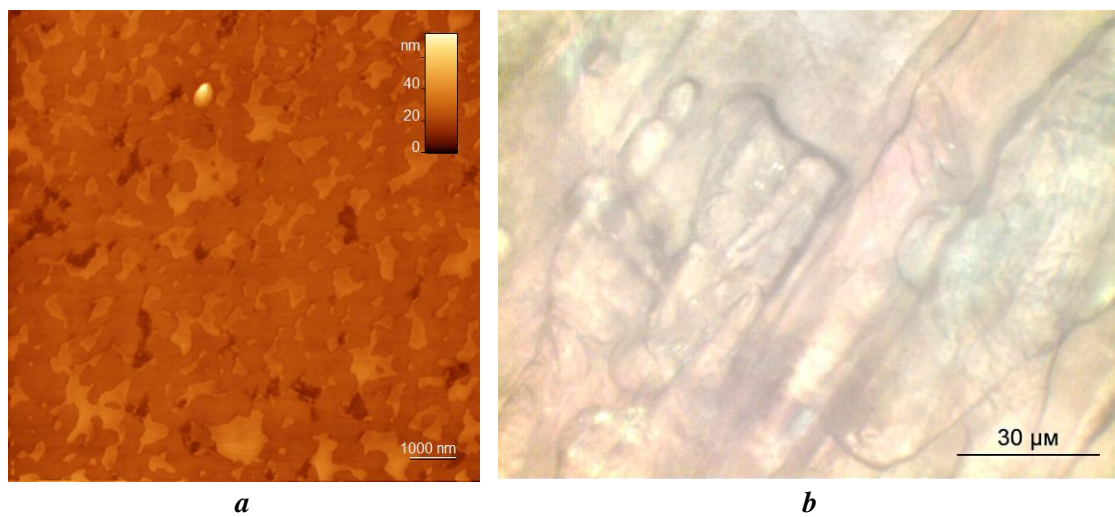


Figure S3. AFM image of PSPOUUr 1 (*a*) and optical micrograph of PSPOUUr 2 (*b*).

Experimental section

Initial reagents for synthesis

α,ω -bis[(3-Aminopropyl)diethoxy]oligodimethylsiloxane (DAS, $M_n = 2110$ Da) was synthesized according to the published procedure [S1, S2]. The molecular weight of the intermediate oligosiloxanediol was determined by GPC. The molecular mass of the oligodiamine was determined by ^1H NMR spectroscopy and then refined using the results of spectrophotometric and gravimetric analysis. The absence of cyclic products in DAS was confirmed by ^{29}Si NMR spectroscopy.

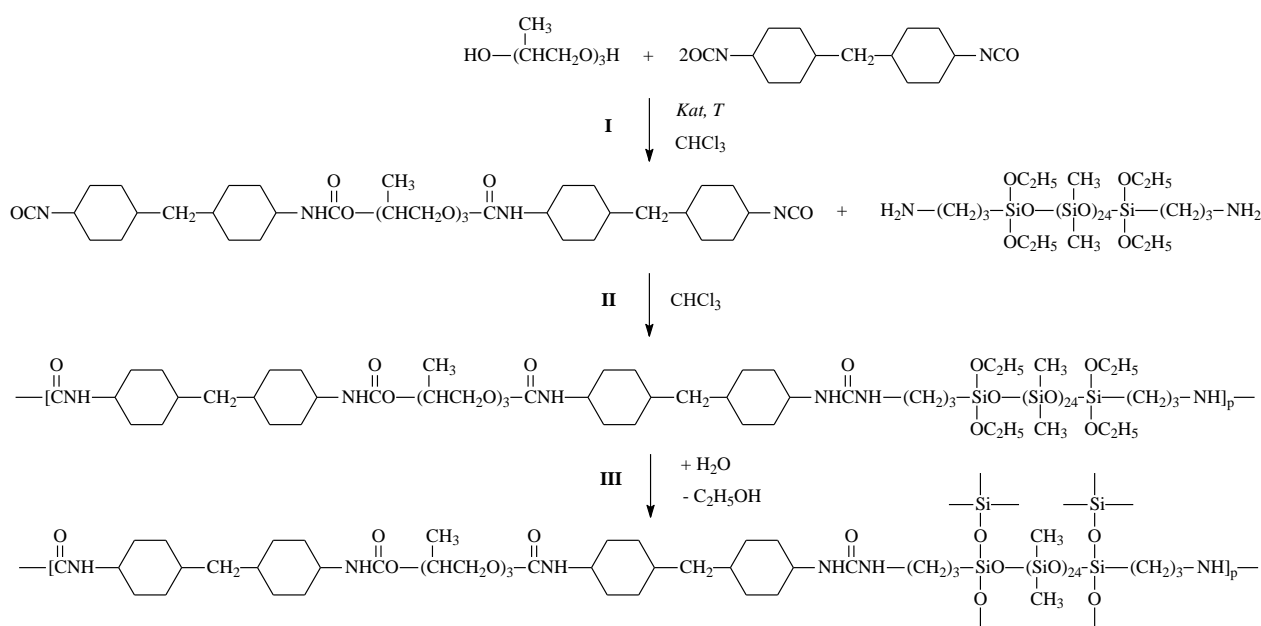
Oligo(propylene oxide) (OPO, $M_n = 200$ Da) (Merck) was pre-dried at $T = 100$ °C and $P = 1$ mmHg for 4 h. The water content in the oligodiol, which did not exceed 0.01%, was controlled by the Fischer titration [S3, S4].

4,4'-Dicyclohexylmethane diisocyanate (H_{12} -MDI) (TCI), bismuth(III) neodecanoate (Bi-ND) (Aldrich), diethyltin dicaprylate (DETDC) (technical product) and dibutyl tin dilaurate (DBTL) (Merck) were purchased from commercial sources and used without purification.

Chloroform (Ekos-1, Russia) was washed with water to remove the stabilizer (ethanol), dried over CaCl_2 , and distilled at atmospheric pressure. The fraction with a boiling point $T = 61$ – 62 °C was collected [S5].

Synthesis of the polysiloxane–(propylene oxide)–urethane–ureas (PSPOUUs)

The synthesis of PSPOUUs were carried out in two stages (Scheme S1). At the first stage, the prepolymers were obtained by reacting 1.05 g (0.004 mol) of H_{12} -MDI with 0.4 g (0.002 mol) of OPO. The reaction was carried out in chloroform upon refluxing in an inert atmosphere (Ar) for 1 h. The concentrations of the initial reagents were 0.2 mol/L. The catalysts were added at the beginning of the first stage with the oligo(propylene oxide) solution and were taken in such an amount that their concentrations in the resulting films were 2 wt % for DBTL and DETDC and 4 wt % for Bi-ND. The reaction course was monitored by IR spectroscopy.

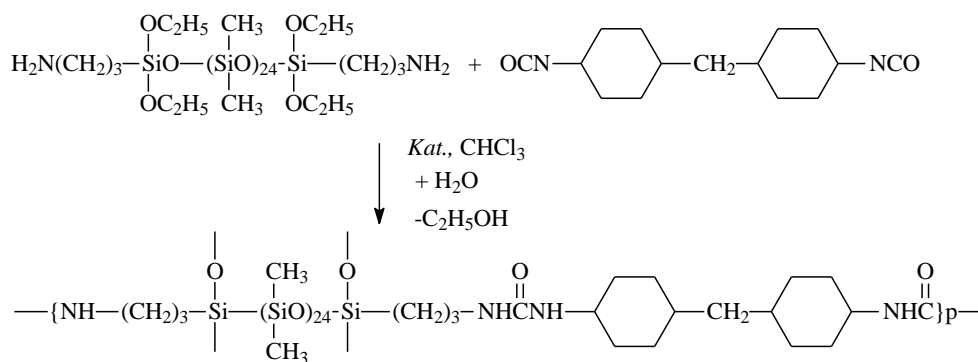


Scheme S1. Synthesis of the polysiloxane–(propylene oxide)–urethane–ureas.

At the second stage, a solution of DAS (4.22 g, 0.002 mol) was added to the prepolymer

solution at room temperature. The reaction mixture was stirred and then filtered. The films were cast on a cellophane substrate. The concentrations of the resulting polymers in the solvents were 10 g/dL. The PSPOUUr films were dried to constant weight at room temperature and, first, at atmospheric pressure and then under vacuum. The resulting samples were colorless and transparent, with a thickness of about 180–200 μm .

Synthesis of the model polysiloxane–ureas (PSUrs)



Scheme S2. Synthesis of the polysiloxane–ureas.

The solutions of H₁₂-MDI (0.26 g, 0.001 mol) and DAS (2.11 g, 0.001 mol) in chloroform were combined, stirred at room temperature, and filtered. The films were cast onto a cellophane backing. The concentrations of the resulting polymers in the solutions were $c = 10$ g/dL.

The catalyst was added to the DAS solution in an amount of 2 wt % in the case of DBTL and DETDC and 4 wt % in the case of Bi-ND. The formation of the cross-linked polymers occurred at room temperature and atmospheric pressure during solvent evaporation. The resulting films were dried to constant weight at room temperature and, first, at atmospheric pressure and then under vacuum. The resulting samples were colorless and transparent, with a thickness of about 180–200 μm .

Physicochemical methods

The ¹H and ²⁹Si NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. The solutions in CDCl₃ were used. The spectra were recorded at $T = 298$ K, the chemical shifts were measured relative to TMS.

The GPC analysis was performed on a Shimadzu device (Japan, Germany) using a RID-20A refractometer, an SPD M20A photodiode matrix, SSSDV 5 μm 10E5A column (300 \times 7.8 mm), tetrahydrofuran as a n eluent at a temperature of 40 $^{\circ}\text{C}$ and a flow rate of 1 mL/min.

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

The content of a gel fraction in the samples was determined by the standard method in a Soxhlet extractor in methyl ethyl ketone.

The deformation and strength characteristics of the polymer films were determined on a LLOYD Instruments LR5K Plus universal testing machine at a stretching speed of 100 mm/min. The measurement error was 7%.

The TMA studies were carried out on a TMA Q400 device (TA Instruments) with a probe diameter 2.5 mm, $F = 1$ N (load), and a heating rate of 5 $^{\circ}\text{C}/\text{min}$.

The atomic force microscopic studies were carried out on a FemtoScan device (Advanced Technologies Center, Russia) in tapping mode using the FemtoScan Online software and HA_HR cantilevers (TipsNano).

The microscopic studies were performed with a MET-5S microscope (Altami, Russia) in reflected light according to the standard method using a plan achromatic lens for bright field PL L 100X/0.85 $\infty/0$ (working distance 0.40 mm) and the Altami Studio software.

References

- S1. A. Kalinina, N. Strizhiver, N. Vasilenko, N. Perov, N. Demchenko, A. Muzafarov, *Silicon*, **2015**, 7, 95–106. DOI: 10.1007/s12633-014-9233-z
- S2. I. B. Meshkov, A. A. Kalinina, V. V. Gorodov, A. V. Bakirov, S. V. Krashennnikov, S. N. Chvalun, A. M. Muzafarov, *Polymers*, **2021**, 13, 2848. DOI: 10.3390/polym13172848
- S3. E. Scholz, Karl–Fisher–Titration. Methoden zur Wasserbestimmung, Springer, Berlin, **1984**. DOI: 10.1007/978-3-642-69368-7
- S4. G. Wieland, Water Determination by Karl Fisher Titration. Theory and Applications, GIT Verlag, Darmstadt, **1987**.
- S5. A. J. Gordon, R. A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley, **1972**.