

Electronic supplementary information

SYNTHESIS AND PROPERTIES OF POLYSILOXANE COPOLYMERS WITH UREA FRAGMENTS FOR 3D PRINTING

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Experimental section

Analysis and general methodology

The ¹H NMR spectra were recorded on a Bruker WP 250 SY spectrometer (Germany). The ¹³C and ²⁹Si NMR spectra were recorded on a Bruker AVANCE II 300 spectrometer (Germany). The solvent was CDCl₃. The spectra were processed using the MestRenova program.

The GPC analysis was conducted on a chromatographic system consisting of a STAIER c.2 high-pressure pump (Akvilon, Russia), a Smartline RI 2300 refractometer (KNAUER, Germany), and a JETSTREAM 2 PLUS thermostat (KNAUER, Germany) at 40 ± 0.1 °C using a toluene–THF (2%) system as an eluent and a flow rate of 1.0 mL/min. Columns with the sizes of 300×7.8 mm and sorbent Phenogel (5 μm, pore sizes from 10³ to 10⁵ Å) (Phenomenex, USA) were used. The column calibration was performed against Agilent polystyrene standards (USA). The processing of chromatograms and calculation of molecular weight parameters was carried out using the MultiChrom program for Windows version 1.6. (Ampersend, Russia).

The rheological properties of the resulting materials were studied on an MCR 302 rotation rheometer (Anton Paar, Austria). The dynamic mechanical tests were carried out in the dynamic mode of shear oscillations in the range of linear viscoelastic behavior (strain amplitude 0.1%) at an angular frequency ω = 10 rad/s.

Syntheses

Synthesis of the aminopropyl polydimethylsiloxane telechelic. Octamethylcyclotetrasiloxane (D4) (100 g, 0.33 mol), α,ω-aminopropyltetramethyldisiloxane (6.7 g, 0.03 mol) and tetramethylammonium hydroxide (0.005 g) were loaded into a 250 mL one-neck round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and a calcium chloride tube. The reaction mixture was heated at 80 °C under vigorous stirring for 16 h. After the molecular weight equilibrium was established, which was determined by GPC analysis of the samples of the reaction mixture in 12 and 16 h, the reaction mixture was heated at 100 °C for 2 h to decompose the catalyst. The product was isolated by vacuum distillation at 1 mbar at 130 °C. Yield: 97%. The molecular weight characteristics were determined by GPC ($M_n = 4600$, $M_w/M_n = 2.37$) and ¹H NMR spectroscopy ($M_n = 3800$). ¹H NMR (CDCl₃): δ 0.30–(–0.20) (s, SiMe₂, NH₂–CH₂–CH₂–CH₂–SiMe₂), 0.46–0.56 (t, 4H, NH₂–CH₂–CH₂–CH₂–SiMe₂), 0.46–0.56 (t, 4H, NH₂–CH₂–CH₂–CH₂–SiMe₂), 1.16–1.57 (m, 8H, NH₂–CH₂–CH₂–CH₂–SiMe₂), 2.60–2.70 (t, 4H, NH₂–CH₂–CH₂–CH₂–SiMe₂) ppm.

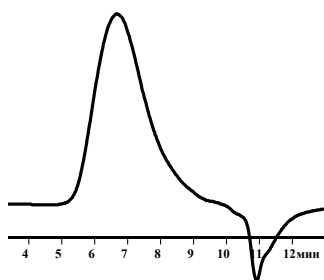


Figure 1. GPC curve of α,ω -aminopropyltetramethyldisloxane.

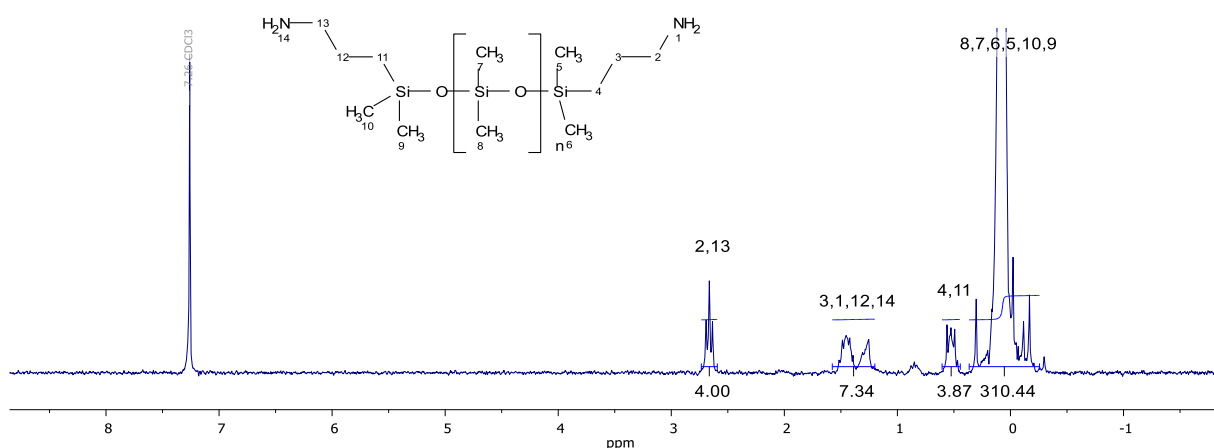


Figure 2. ^1H NMR spectrum of α,ω -aminopropyltetramethyldisloxane.

Preparation of the copolymer of polydimethylsiloxane with urea fragments. The aminopropyl polydimethylsiloxane telechelic (21 g, 8 mmol) and dry THF (200 mL) were loaded into a three-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel under an argon atmosphere. The reaction mixture was cooled to 0 °C, and then triethylamine (1.18 mL) was added. The mixture was stirred at 0 °C for 1 h, adding slowly dropwise a mixture of toluene diisocyanate (1.29 g, 7 mmol) and methylene diphenyl diisocyanate (0.47 g, 2 mmol) in dry THF (20 mL). After the addition was completed, the reaction mixture was stirred at 0 °C for another 1 h. After cooling to room temperature, the resulting mixture was stirred at room temperature for 24 h, after which methanol (1 mL) was added to block unreacted isocyanates. The solvents were evaporated on a rotary evaporator, the low molecular weight products were distilled off under vacuum at 1 mm Hg and 120 °C for 2 h. The copolymer of polydimethylsiloxane with urea fragments was obtained in quantitative yield. It was characterized by GPC: $M_n = 21200$, $M_w/M_n = 2.5$.

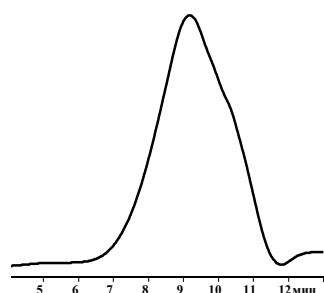


Figure 3. GPC curve of the resulting copolymer of polydimethylsiloxane with urea fragments.

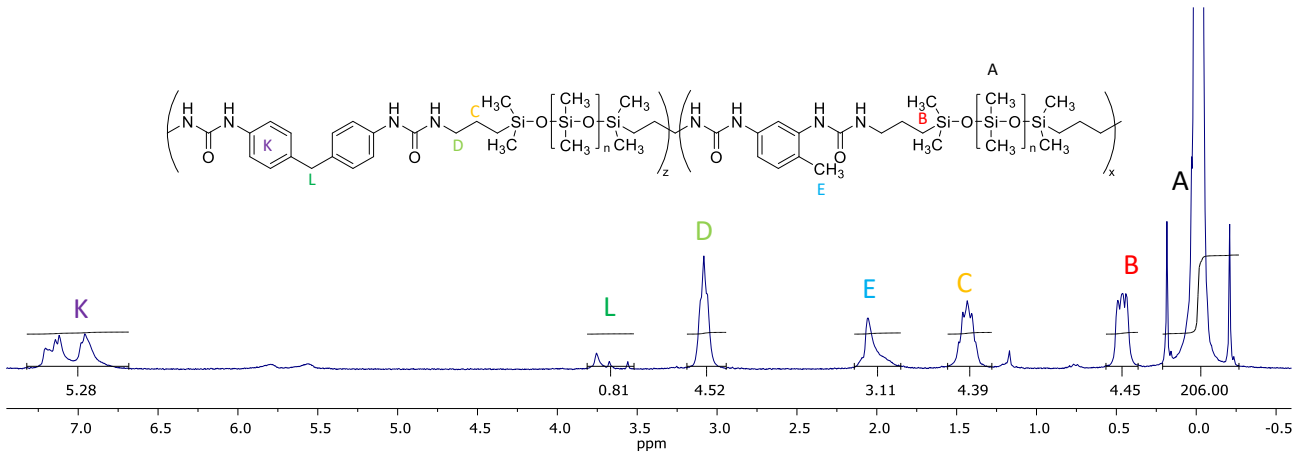


Figure 4. ^1H NMR spectrum of the resulting copolymer of polydimethylsiloxane with urea fragments.

Rheological properties

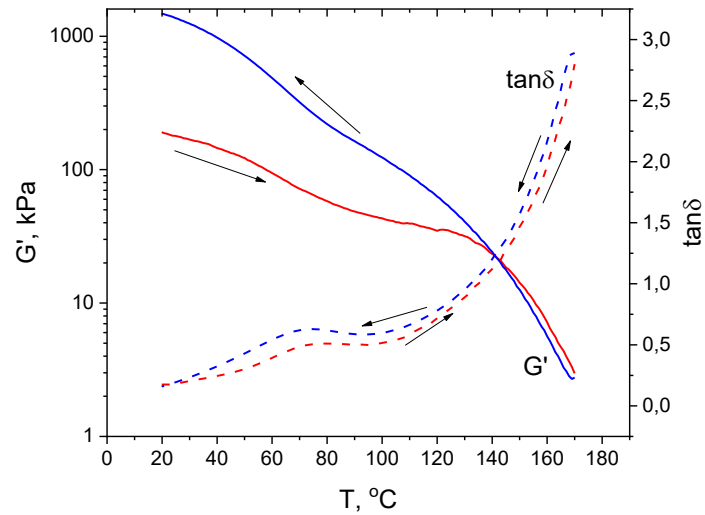


Figure 5. Dependence of shear storage modulus (solid line) and damping factor (dash line) of polysiloxane–urea on temperature during heating (red line) and cooling (blue line). Damping factor overcoming unity indicates melting point of the material (130–140 °C).