

Electronic supplementary information

SYNTHESIS OF POLYSILOXANE–(BUTYLENE OXIDE)– URETHANE–UREAS IN THE PRESENCE OF BISMUTH(III) NEODECANOATE

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Experimental section.

Initial reagents for synthesis

α,ω -bis-[(3-Aminopropyl)diethoxy]oligodimethylsiloxanes (DASs) were synthesized according to the published procedures [S1, S2]. The molecular mass of oligodiamines was determined by ^1H NMR spectroscopy and then refined using the results of spectrophotometric and gravimetric analysis. The absence of cyclic products in DASs was confirmed by ^{29}Si NMR spectroscopy.

Oligo(butylene oxide)s (OBOs) with the following characteristics were used: $M_n = 250$ and 650 Da (OBO-250 and OBO-650, respectively, Sigma-Aldrich), $M_n = 1060$ Da (OBO-1060, technical product). OBOs were preliminarily dried at $T = 100$ °C and $P = 1$ mmHg for 3 h. The moisture content in the oligodiols, which did not exceed 0.01%, was controlled by the Fischer method [S3, S4]. The molecular masses of OBOs were refined using the standard method [S5]. 4,4'-Dicyclohexylmethane diisocyanate (H_{12} -MDI, TCI), isophorone diisocyanate (IPDI, Acros Organics), bismuth(III) neodecanoate (Aldrich), and diethyltin dicaprylate (DETC, technical product) were used as purchased.

Methyl ethyl ketone (MEK, Komponent-Reaktiv, Russia) was distilled at atmospheric pressure; the fraction with a boiling point $T = 79$ – 80 °C was collected, dried over 3 Å molecular sieves and re-distilled.

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 [S6].

An aqueous solution of hydrochloric acid (0.1 N) was obtained from fixanals (Uralkhiminvest, Russia) according to the standard method.

A solution of diethylamine (Komponent-Reaktiv, Russia) in methyl ethyl ketone (0.2 N) was prepared according to the standard procedure.

To determine the glass transition temperatures of the organic and siloxane phases, as well as to study the occurrence of urethane formation and cross-linking reactions for simpler systems, model polybutylene oxide–urethanes (PBOUs) and polysiloxane–ureas (PSUs) were synthesized.

Synthesis of model polybutylene oxide–urethanes

Short-chain model polybutylene oxide–urethanes (PBOU-1 and PBOU-2) were obtained in CHCl_3 solutions by reacting H_{12} -MDI with OBO-250 and OBO-650, respectively. In the case of PBOU-3 and PBOU-4, OBO-1060 and diisocyanate (DI) were dissolved in MEK. The concentrations of the starting components in solutions in all syntheses were $c = 0.2 \text{ M}$; the molar ratio of the starting components was OBO: DI = 1:1.1. The catalyst (bismuth(III) neodecanoate) loading was 2 wt %.

The syntheses were carried out in an argon flow. The diisocyanate solutions were added to the stirred solutions of the OBO and catalyst upon reflux. The resulting mixtures were heated for 14 (PBOU-1 and PBOU-2) or 11 (PBOU-3 and PBOU-4) h. After the reaction completion, the solutions were cooled and filtered; the polymers were reprecipitated from solutions into hexane, then dried to constant weight at room temperature first in air and then under vacuum.

Table S1. Chemical compositions of the polybutylene oxide–urethanes

PBOU	$\frac{C_{calc.}}{C_{found}}$	$\frac{H_{calc.}}{H_{found}}$	$\frac{N_{calc.}}{N_{found}}$
PBOU-1	65.50	9.72	5.70
	65.58	9.69	5.75
PBOU -2	65.98	10.34	3.28
	66.08	10.34	3.16
PBOU -3	66.17	10.60	2.29
	64.29	10.25	2.10
PBOU -4	65.37	10.62	2.37
	65.31	10.61	2.43

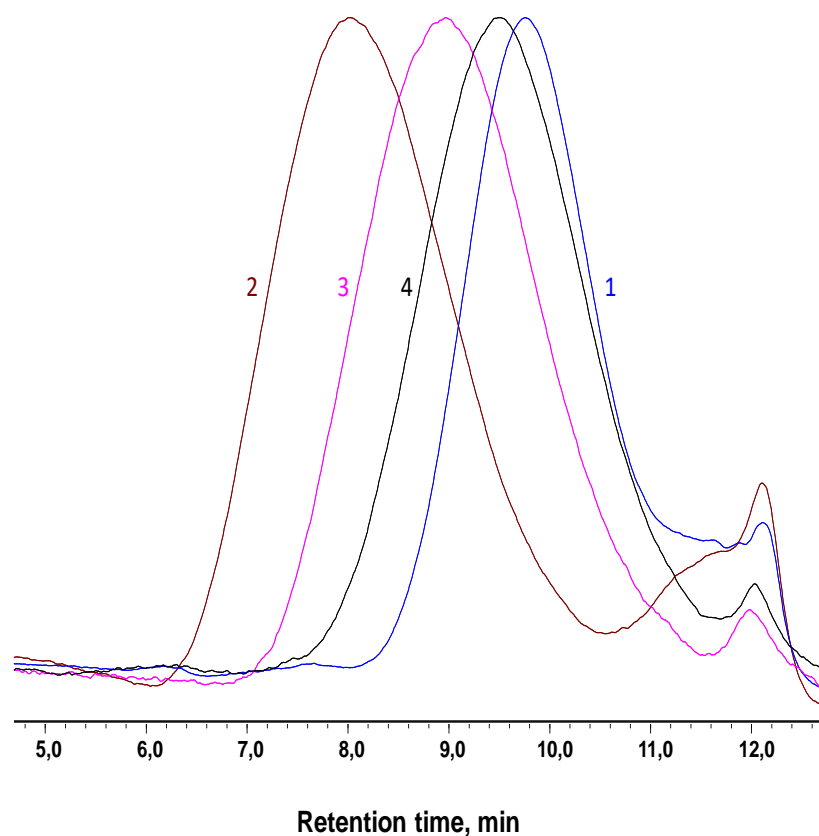


Figure S1. Gel chromatograms of PBOU-1 (1), PBOU-2 (2), PBOU-3 (3), PBOU-4 (4).

Table S2. Molecular-weight characteristics of the polybutylene oxide–urethanes

PBOU	OBO, M_n	DI	M_n , kDa	M_w , kDa	M_w/M_n
PBOU-1	250	H ₁₂ -MDI	14.4	36.3	2.52
PBOU-2	650	H ₁₂ -MDI	107.9	217.0	2.01
PBOU-3	1060	H ₁₂ -MDI	36.0	93.0	2.58
PBOU-4	1060	IPDI	23.4	57.0	2.45

Table S3. Main characteristics of the polybutylene oxide–urethanes

PBOU	Solvent	Yield, %	T_g	ε_p , %	σ_p , MPa
PBOU-1	CHCl ₃	57	34	850	1
PBOU-2	CHCl ₃	66	−50	980	7
PBOU-3	MEK	68	−57	—	—
PBOU-4	MEK	67	−62	—	—

Synthesis of the model polysiloxane–ureas

The model polysiloxane–ureas (PSUrS) were synthesized by the reaction of H₁₂-MDI with α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane in MEK solutions (concentrations of the resulting PSUrS in the solutions were $c = 10$ g/dL; the molar ratio of the starting components was DAS:DI = 1:1). The solutions with the samples of diisocyanate and α,ω -bis-[(3-aminopropyl)diethoxy]oligodimethylsiloxane were loaded into a flask, stirred, filtered and poured onto a Teflon substrate. To obtain PSUr-2, vinyltrimethoxysilane was added to the oligodiamine solution in an amount of 4 wt %. In the case of PSUr-1, DETC was used as a catalyst in an amount of 2 wt %, which allowed for increasing the gel fraction content and improving the mechanical characteristics. The formation of the cross-linked polymers occurred at room temperature and atmospheric pressure as the solvent evaporated. The resulting films were dried to constant weight at room temperature and atmospheric pressure and then under vacuum.

Table S4. Main characteristics of the polysiloxane–ureas

PSUr	DAS $\frac{n}{M_n}$	DI	Cat.	W_{sil} , wt %	Solvent	Gel fraction, %	T_g	ε_p , %	σ_p , MPa
PSUr-1	$\frac{14}{1380}$	H ₁₂ -MDI	DETC	75	MEK	80	–114 ^a	17	8
PSUr-2	$\frac{25}{2230}$	H ₁₂ -MDI	–	83	MEK	65	–116	125	2

^a glass transition temperature determined by TMA.

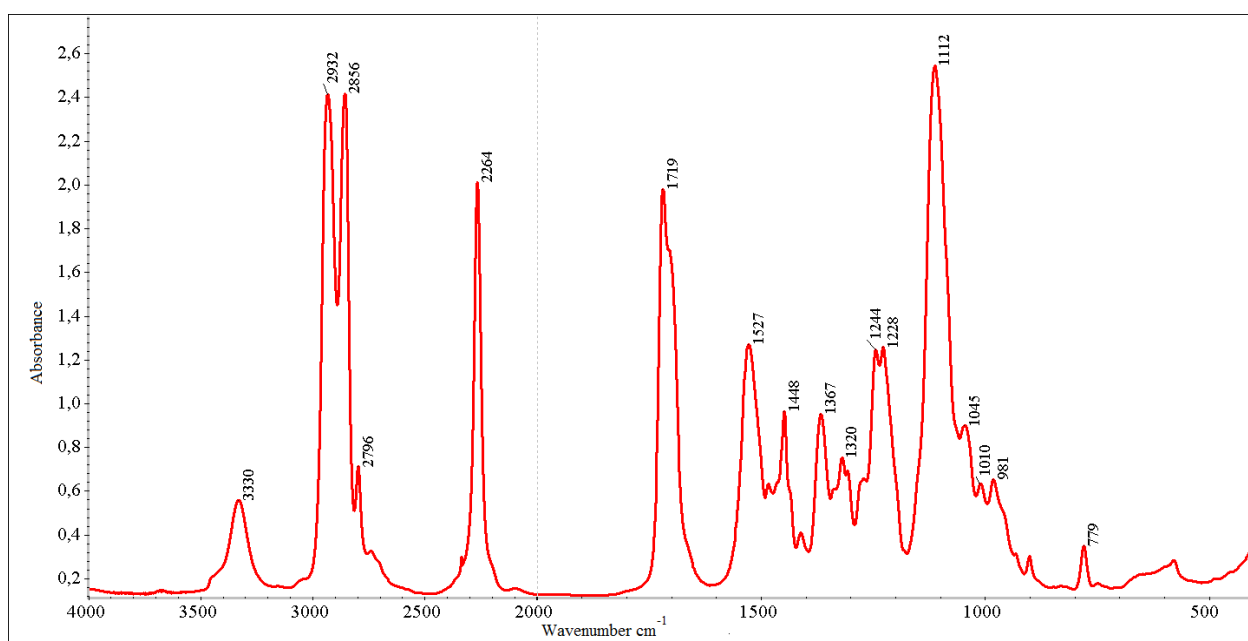
Synthesis of the prepolymers

The prepolymers (PBs) were synthesized in bulk by introducing the OBO and catalyst (2 wt %) into the diisocyanate at room temperature upon vigorous stirring in an inert atmosphere (Ar). The molar ratio of the starting components was OBO:DI = 1:2.2 ($X = 1$) or OBO:DI = 2:3.3 ($X = 2$). The diisocyanates and oligodiols are liquids, except for OBO-1060, which was heated until it became liquid. The reaction completion was monitored by titration of free isocyanate groups [S7] and IR spectroscopy [S6, S8]. The IR spectra of the prepolymers (Fig. S2) almost lack a broad band in the region of 3400–3600 cm^{–1}, corresponding to the stretching vibrations of hydroxy groups of the initial oligobutylene oxide. At the same time, a characteristic absorption band of the stretching vibrations of the carbonyl groups at 1719 cm^{–1}, a band of the stretching vibrations of the urethane NH moiety at 3330 cm^{–1} and a sharp band at 2264 cm^{–1}, corresponding to the carbonyl group of the unreacted isocyanate units, are observed. The prepolymers were stored in an inert atmosphere in a sealed container at a low temperature.

Table S5. Prepolymers based on oligobutylene oxides

Prepolymer	DI	OBO:DI	$\frac{NCO_{calc.}}{NCO_{found}}$	$\frac{Mn_{calc.}}{Mn_{found}}$
PB-1060 ^a	H ₁₂ -MDI	1:2.2	$\frac{5.90}{3.68}$	$\frac{1430}{2110}$
PB-1060 IP ^a	IPDI	1:2.2	$\frac{6.30}{4.86}$	$\frac{1330}{1730}$
PB-250 ^b	H ₁₂ -MDI	2:3.3	$\frac{6.51}{6.53}$	$\frac{1290}{1290}$

^a X = 1; ^b X = 2.

**Figure S2.** IR spectrum of prepolymer PB-250.

Synthesis of the cross-linked polysiloxane–(butylene oxide)–urethane–ureas.

Solutions of the prepolymers (PBs) and α,ω -bis[(3-aminopropyl)diethoxy]oligodimethylsiloxane in an appropriate solvent ($c = 10$ g/dL) were loaded into a flask, stirred, filtered and poured onto a Teflon substrate. The molar ratio of the initial components was PB:DAS = 1:1. During the preparation of all samples, vinyltrimethoxysilane was added to the oligodiamine solution in an amount of 4 wt %, which facilitated the formation of the samples with a smoother surface and stabilized the solution upon storage. The cross-linked polymer was formed at room temperature and atmospheric pressure as the solvent was evaporated. The resulting films were dried to constant weight at room temperature and atmospheric pressure and then under vacuum.

Physicochemical methods

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

The GPC analysis was performed on a Shimadzu device (Japan, Germany) equipped with RID-20A refractometer and SPD M20A photodiode matrix detectors, column PSSSDV 5 μ m 10E5A (Size 300 \times 7.8 mm), eluent tetrahydrofuran, temperature 40 $^{\circ}$ C, flow rate 1 mL/min.

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

The ^1H and ^{29}Si NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Solutions in CDCl_3 were used, the spectra were recorded at $T = 298$ K, the chemical shifts were measured relative to TMS.

The content of the gel fraction of 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 10%.

The glass transition temperatures of the films were determined using a DSC-3 device (Mettler-Toledo, Switzerland) at a heating rate of 10 $^{\circ}$ C/min in argon.

The TMA study was carried out on a TMA Q400 device (TA Instruments), probe diameter 2.5 mm, $F = 1$ H (load), heating rate 5 $^{\circ}$ C/min.

The atomic force microscopy studies were carried out on a FemtoScan device (Advanced Technologies Center, Russia) in tapping mode using the FemtoScan Online software and HA_HR, HA_NC and NSG01 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.

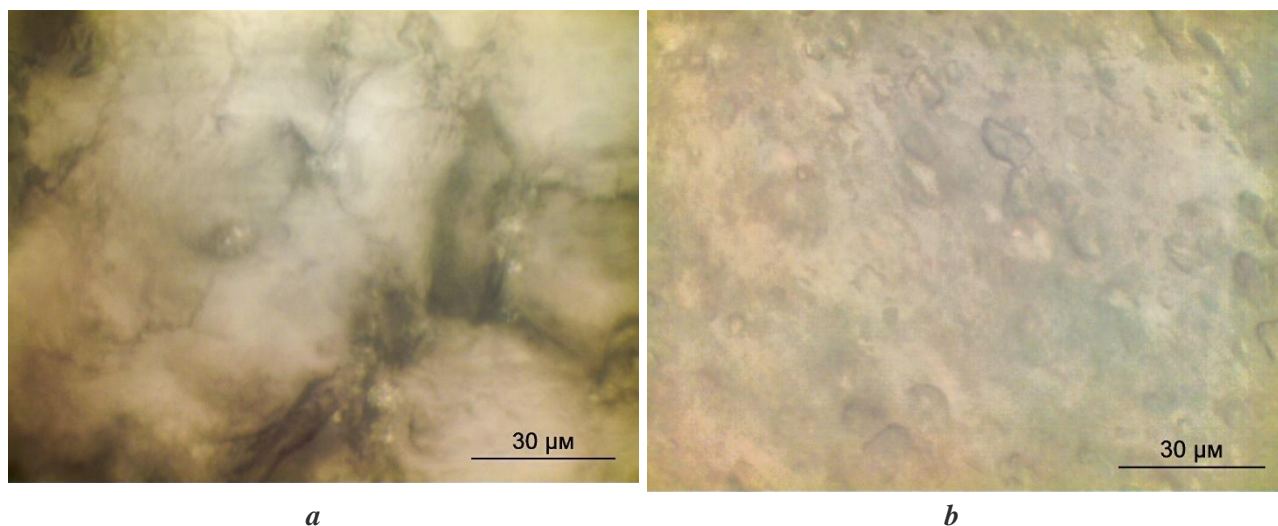


Figure S3. Optical micrographs of PSBOUUr 1 (*a*) and 2 (*b*).

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