Electronic supplementary information

PREPARATION OF POLYDIMETHYLSILOXANE COPOLYMERS BY THE AZIDE–ALKYNE HUISGEN CYCLOADDITION METHOD

K. K. Bakanov,*[a,b] K. S. Klokova,[a] K. A. Bezlepkina,[a,b,c] S. A. Milenin,[a,b,c] E. Yu. Kramarenko,[a,d] and A. M. Muzafarov[a]

[a] *Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, ul. Profsoyuznaya 70, Moscow, 117393 Russia*
[b] *Research Laboratory of New Silicone Materials and Technologies, Tula State Lev Tolstoy Pedagogical University, pr. Lenina 125, Tula, Tula Oblast, 300026 Russia*
[c] *Center of National Technological Initiative, Bauman Moscow State Technical University, 2-ya Baumanskaya ul. 5, Moscow, 105005 Russia*
[d] *Faculty of Physics, Lomonosov Moscow State University, Leninskye Gory 1, Moscow, 119991 Russia*

1. Syntheses

Synthesis of di(prop-2-yn-1-yl) adipate. Propargyl alcohol (8.77 g, 156.5 mmol) was added to a solution of adipic acid (8.80 g, 60.2 mmol) and *p*-toluenesulfonic acid monohydrate (0.572 g, 3 mmol) in benzene (20 mL). The stirred reaction mixture was heated at 110 °C for 5 h. The resulting mixture was diluted with CH_2Cl_2 and washed with aq. Na_2CO_3. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness (the solvent was removed at 1 Torr) to give the target product as a yellow powder. Yield: 8.54 g (85.4%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.64–4.63 (s, 4H, ≡C-$\underline{CH_2}$-O-), 2.46–2.44 (s, 2H, $\underline{CH}$≡C-), 2.37–2.33 (m, 4H, $\underline{CH_2}$-COO), 1.68–1.63 (m, 4H, CH_2-$\underline{C_2H_4}$-CH_2) ppm.

Synthesis of copolymer 1. Di(propynyl) adipate (0.052 g, 0.233 mmol) was added to bis(3-azidopropyl)polydimethylsiloxane (0.700 g, 0.233 mmol). The stirred reaction mixture was heated at 140 °C for 18 h. The reaction course was monitored by ^{1}H NMR spectroscopy. The target product was obtained as a yellowish transparent viscous liquid. Yield: 0.731 g (97.2%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 2H, CH triazole ring (1,5-substitution)), 7.57 (s, 2H, CH triazole ring (1,4-substitution)), 5.21–5.16 (d, 4H, O-$\underline{CH_2}$), 4.34–4.29 (t, 4H, $\underline{CH_2}$-N), 2.35–2.31 (m, 4H, $\underline{CH_2}$-COO), 1.96–1.90 (m, 4H, $\underline{CH_2}$-CH_2-Si), 1.66–1.63 (m, 4H, CH_2-$\underline{C_2H_4}$-CH_2), 0.56–0.50 (m, 4H, Si-$\underline{CH_2}$), 0.07 (m, 3H, Si-$\underline{CH_3}$) ppm.

Synthesis of copolymer 2. Di(prop-2-yn-1-yl) hexane-1,6-diyldicarbamate (0.065 g, 0.233 mmol) was added to bis(3-azidopropyl)polydimethylsiloxane (0.700 g, 0.233 mmol). The stirred reaction mixture was heated at 140 °C for 21 h. The reaction course was monitored by ^{1}H NMR spectroscopy. The target product was obtained as a yellowish semi-transparent viscous liquid. Yield: 0.743 g (97.1%).

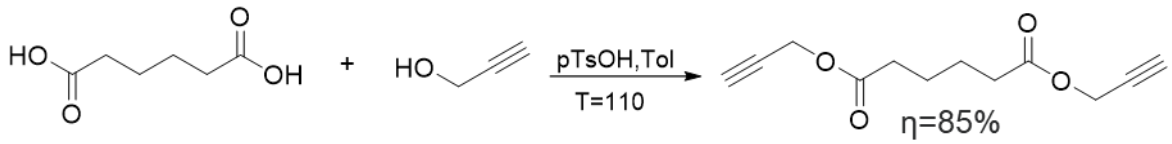
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (s, 2H, CH triazole ring (1,5-substitution)), 7.59 (s, 2H, CH triazole ring (1,4-substitution)), 5.15–5.13 (d, 4H, O-$\underline{CH_2}$), 4.31–4.29 (m, 4H, $\underline{CH_2}$-N), 3.14–3.12 (m, 8H, $\underline{C_4H_8}$), 1.93–1.88 (m, 4H, $\underline{CH_2}$-CH_2-Si), 1.46–1.29 (d, 4H, C_4H_8-$\underline{CH_2}$-N), 0.54–0.48 (m, 4H, Si-$\underline{CH_2}$), 0.07 (m, 3H, Si-$\underline{CH_3}$) ppm.

Synthesis of copolymer 3. Di(propynyl) adipate (0.089 g, 0.247 mmol) was added to di(prop-2-yn-1-yl) [methylenebis(4,1-phenylene)]dicarbamate (0.741 g, 0.247 mmol). The stirred reaction mixture was heated at 140 °C for 12 h. The reaction course was monitored by ^{1}H NMR

spectroscopy. The target product was obtained as a yellowish semi-transparent viscous liquid. Yield: 0.802 g (96.6%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 2H, CH triazole ring (1,5-substitution)), 7.64 (s, 2H, CH triazole ring (1,4-substitution)), 7.10–7.07 (m, 4H, $\underline{C_6H_4}$), 5.28–5.24 (m, 4H, O-$\underline{CH_2}$), 4.36–4.28 (m, 4H, $\underline{CH_2}$-N), 3.87 (s, 4H, $\underline{CH_2}$-C_6H_4), 1.95–1.89 (m, 4H, $\underline{CH_2}$-CH_2-Si), 0.55–0.48 (m, 4H, Si-$\underline{CH_2}$), 0.07 (m, 3H, Si-$\underline{CH_3}$) ppm.

2. Structures, ^{1}H NMR spectra, and GPC curves



Scheme S1. Synthesis of di(propynyl) adipate.

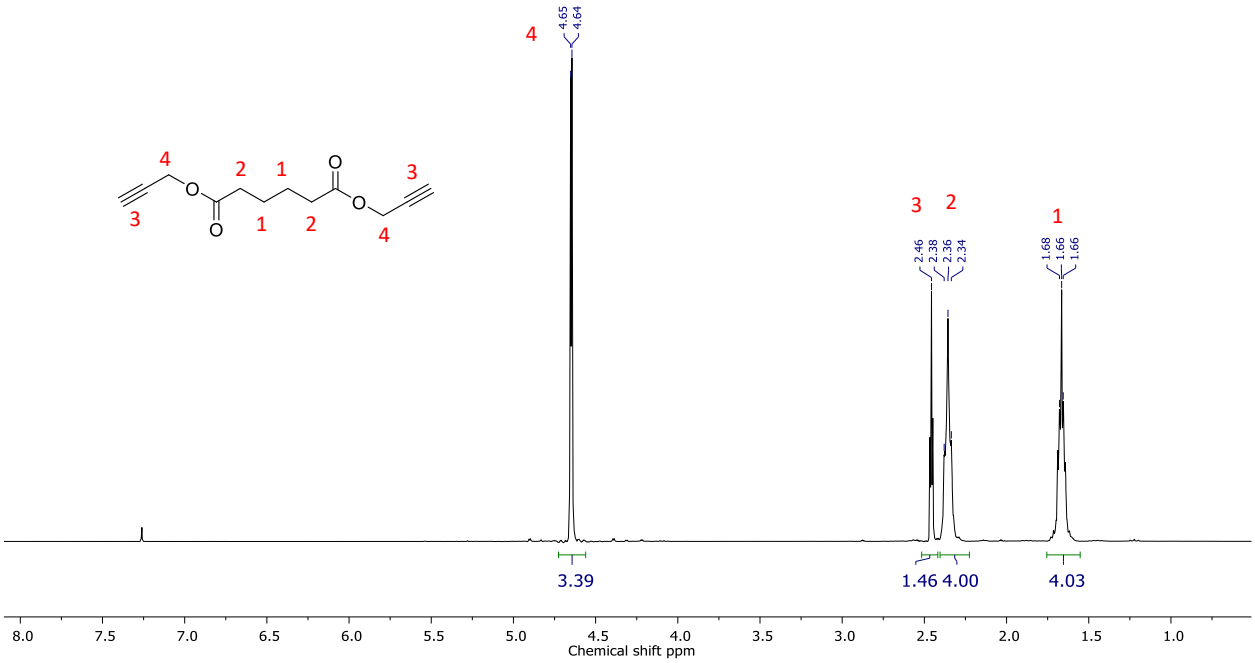


Figure S1. ^{1}H NMR spectrum of di(propynyl) adipate.

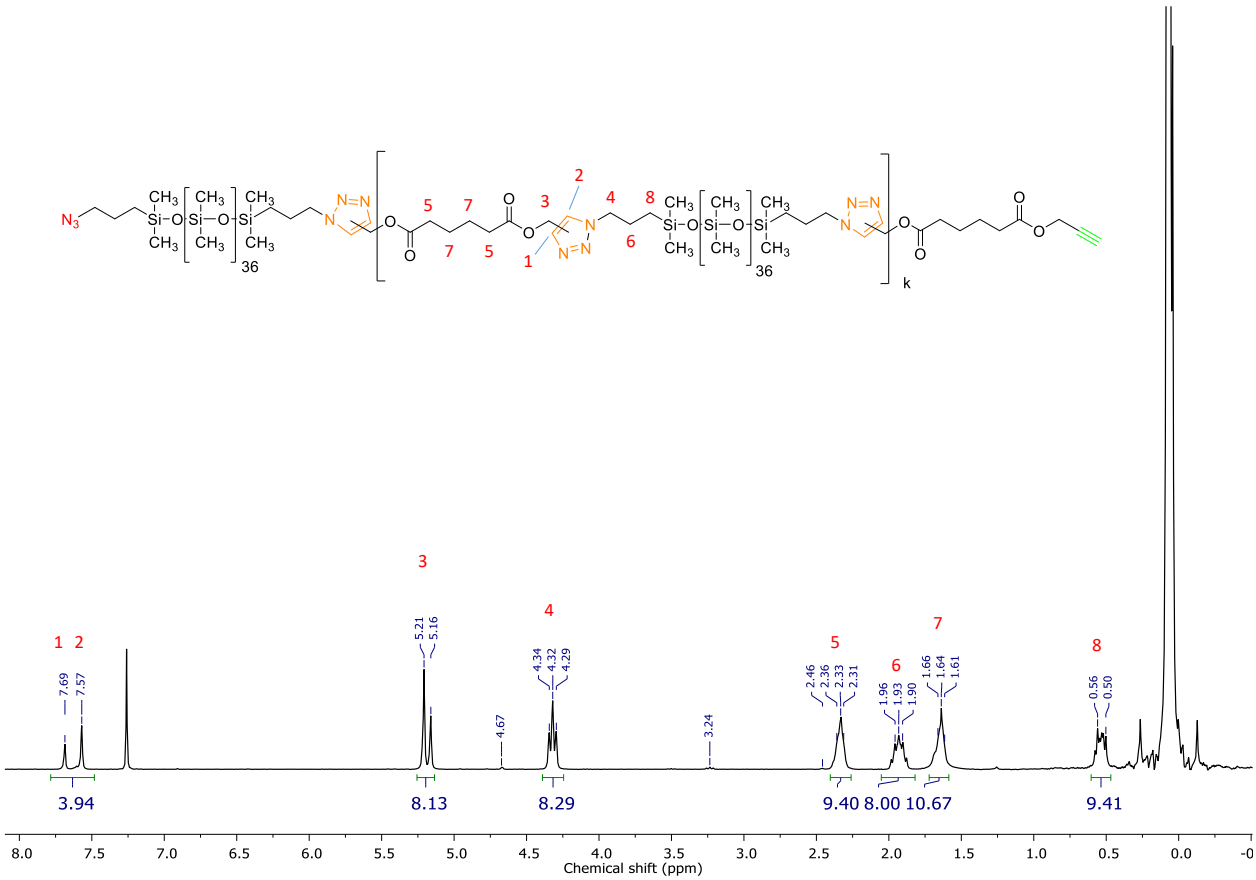


Figure S2. ^{1}H NMR spectrum of copolymer **1**.

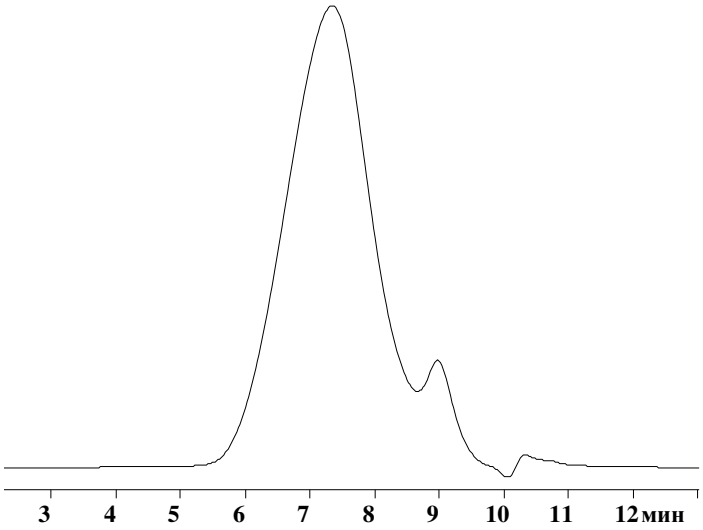


Figure S3. GPC curve of copolymer **1**.

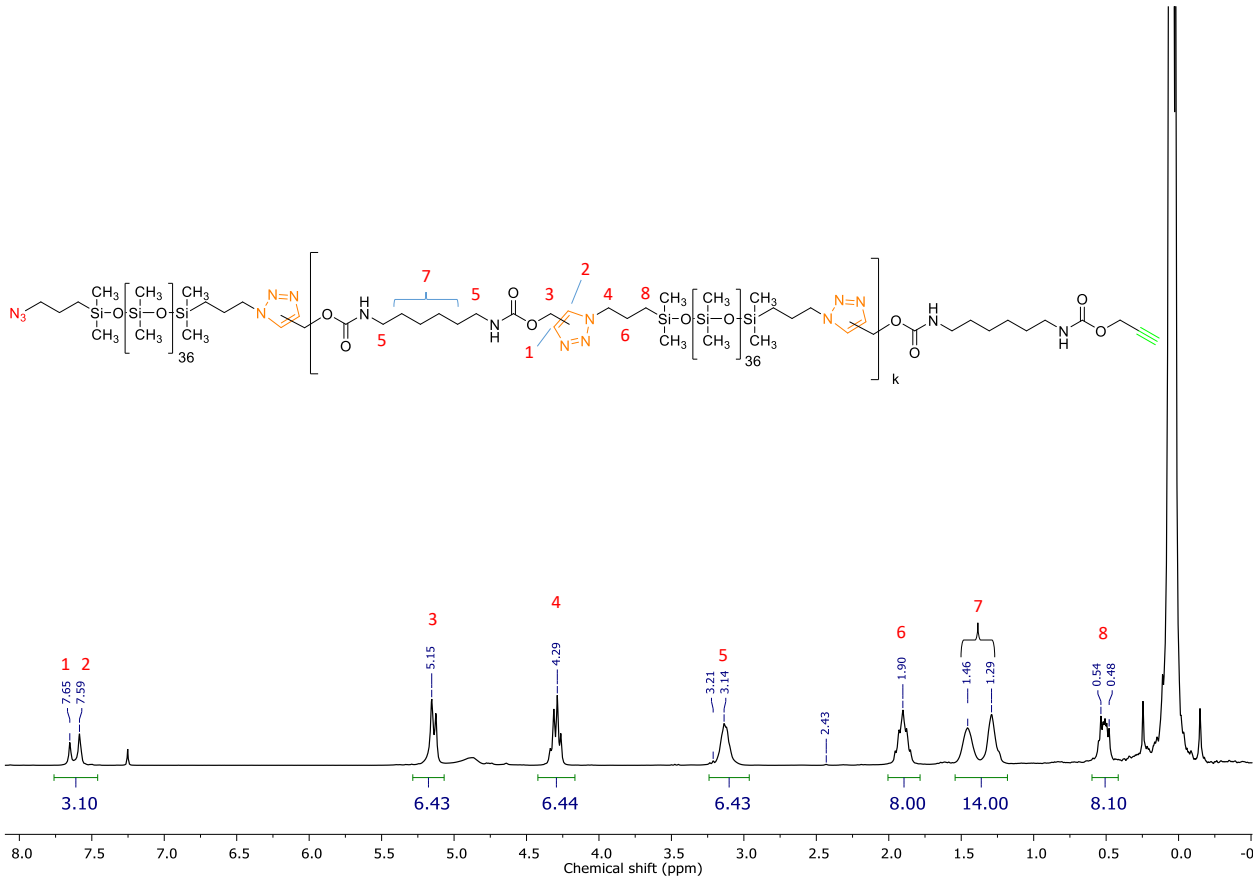


Figure S4. ^{1}H NMR spectrum of copolymer **2**.

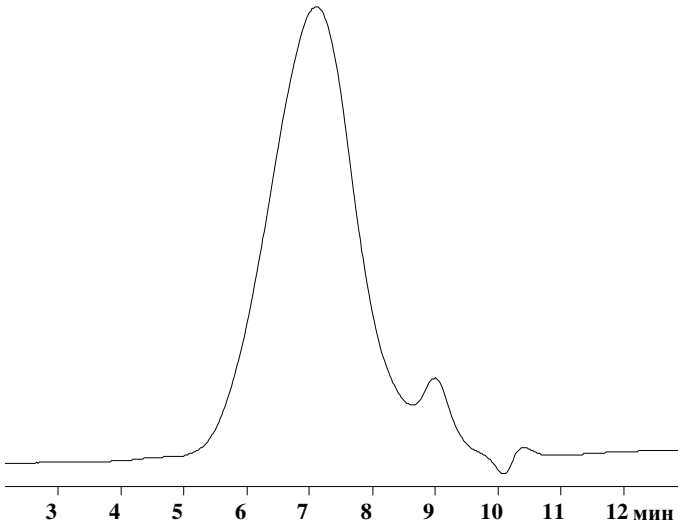


Figure S5. GPC curve of copolymer **2**.

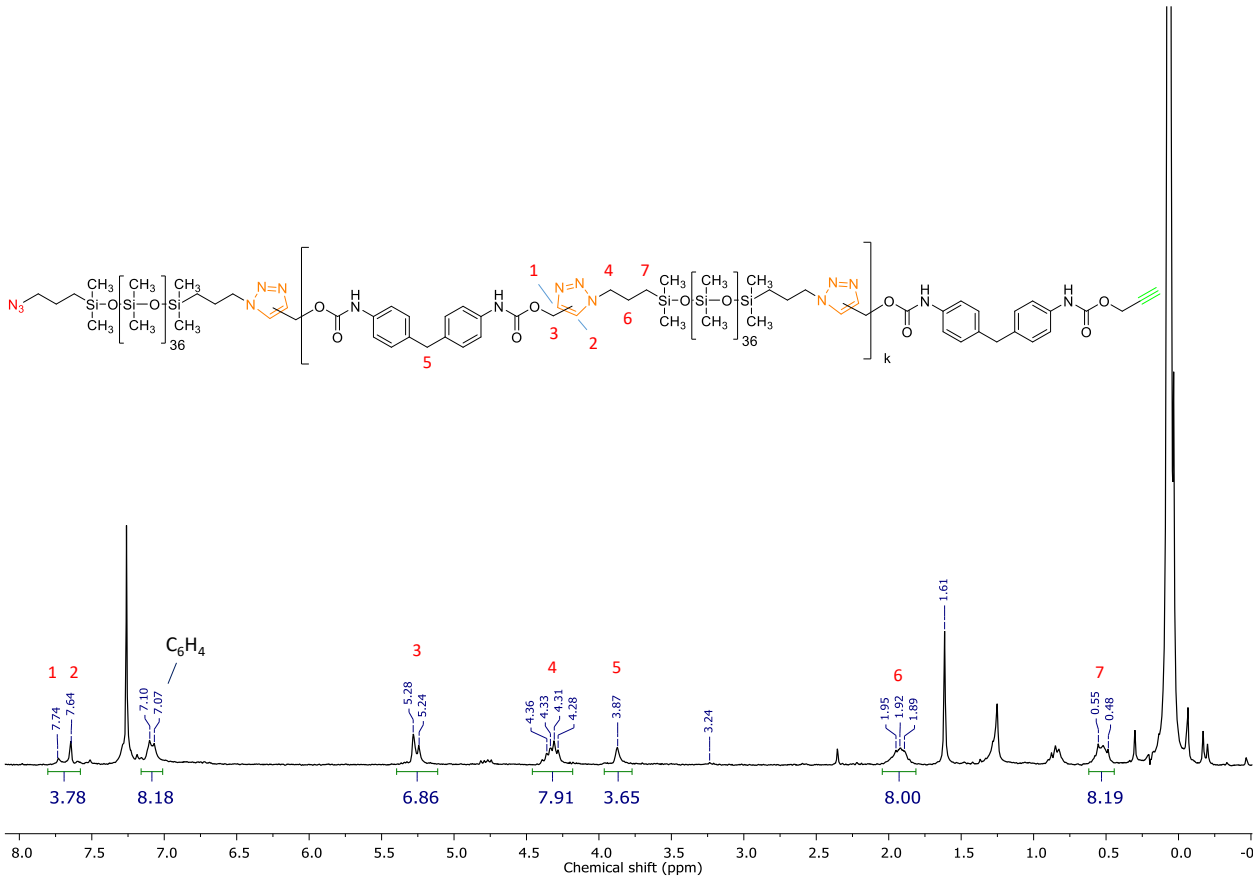


Figure S6. ^{1}H NMR spectrum of copolymer **3**.

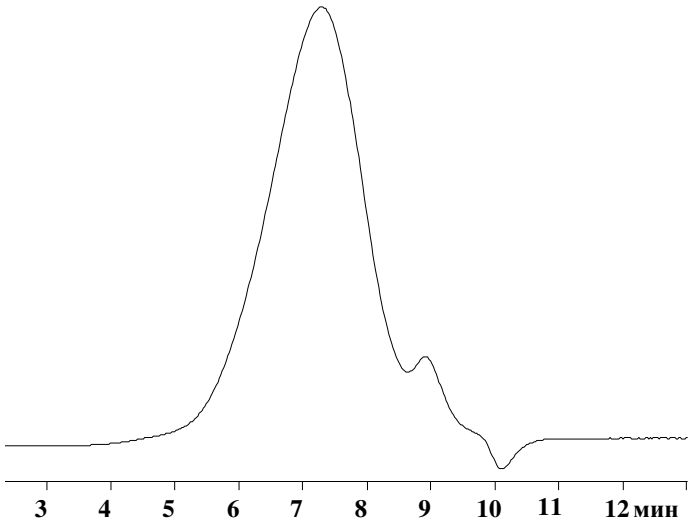


Figure S7. GPC curve of copolymer **3**.