Electronic supplementary information

RING-OPENING METATHESIS POLYMERIZATION OF 5-ETHYL-2-NORBORNENE IN THE PRESENCE OF DIMETHYL MALEATE AS A CHAIN TRANSFER AGENT

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Experimental section

General remarks

Chloroform (reagent grade, OOO Komponent-Reaktiv) and dimethyl maleate (at least 98%, Jiangsu Ambition New Materials) were distilled over CaH_2 in an argon flow and stored under argon. Ethyl alcohol (reagent grade, KHIMMED), deuterochloroform (the fractions of deuterobenzene and tetramethylsilane 99.60 and 0.03%, respectively; Shandong Zhi Shang Chemical), oxidation inhibitor 2,2'-methylene-bis(6-*tert*-butyl-4-methylphenol) (at least 96%, Sigma-Aldrich), the second-generation Grubbs catalysts (at least 98%, Shaanxi Dideu Medichem), dicyclopentadiene (at least 96%, Jiangsu Juming Chemical Process Technology), and ethyl vinyl ether (at least 98%, Jiangsu Ambition New Materials) were used as received. 5-Ethyl-2-norbornene was synthesized by the Diels-Alder reaction at 180 °C according to the published procedure [S1]. The fraction of the exo-isomer was 18% [S2].

Ring-opening metathesis polymerization of 5-ethyl-2-norbornene was carried out in a 4 mL vial as a result of adding 0.1 mL of a solution of 1.1 mg (0.00129 mmol) of the second-generation Grubbs catalyst (Gr2) in chloroform to a mixture of 0.35 mL (0.31 g, 2.547 mmol) of 5-ethyl-2-norbornene (EtNB), 0.16 mL (0.18 g, 1.254 mmol) of dimethyl maleate (DMM), and 0.43 mL of chloroform. After that the vial was placed in a shaker. The reaction was carried out at 60 °C and quenched by adding vinyl ethyl ether in 6 h. The product was isolated by quadruple precipitation of the polymer solution in chloroform in ethanol filled with oxidation inhibitor and drying under vacuum at 90 °C until constant weight. Yield: 0.129 g (40%). M_n^{GPC} = 6.2 kDa, $Đ$ = 2.7; M_n^{NMR} = 3.9 kDa; T_g = 35 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.01–6.88 (br. m, 6.2H, –**CH**=CH–(C=O)–), 5.84–5.72 (br. m, 5.56H, –CH=**CH**–(C=O)–), 5.45–5.05 (br. m, 200.00H, cis/trans –**CH**=**CH**– main chain), 3.73–3.71 (br. m, 17.97H, -CH=CH(C=O)O**CH**$_3$), 3.00–2.68 (br. m, 112.94H, *cis*-CH=CH-), 2.67–2.29 (br. m, 78.55H, *trans*-CH=CH-), 2.10–1.74 (br. m, 247.80H, **CH**$_2$ and **CH**), 1.71–1.29 (br. m, 126.45H, **CH**$_2$ and **CH**), 1.23–0.96 (br. m, 265.54H, **CH**$_3$ and **CH**), 0.95–0.78 (br. m, 371.93H, **CH**$_3$ and **CH**) ppm. The molar fraction of *cis*-C=C bonds was 59%.

^{13}C NMR spectrum (101 MHz, CDCl$_3$): δ 167.46, 167.22 (C=O), 154.17, 154.06, 152.03 (–**CH**=CH–(C=O)–), 135.54, 135.27, 134.73, 134.65, 134.57, 134.45, 134.07, 133.44, 133.06, 132.86, 132.46, 131.73, 131.64, 131.17, 131.06, 130.93, 130.80, 130.44, 129.99, 129.84, 129.55, 129.46 (*cis/trans* -**CH**=**CH**– main chain), 120.02, 119.01, 118.97, 118.79, 117.65 (-CH=**CH**–(C=O)–), 51.46 (–(C=O)O**CH**$_3$), 51.06, 50.72, 50.48, 50.28, 47.85, 47.73, 47.67, 47.56, 47.04, 47.00, 46.87, 46.82, 45.79, 45.66, 45.58, 45.44, 45.26, 45.20, 45.08 (**CH**), 42.92 (**CH**$_2$), 42.50 (**CH**), 42.41, 42.14, 41.92, 41.73, 41.61, 41.29, 41.00, 40.57 (**CH**$_2$), 40.05 (**CH**$_2$ or **CH**), 39.97, 39.91, 39.84, 39.74, 39.70, 39.56, 39.42, 38.96, 38.77, 38.63, 38.30, 38.22, 38.12, 38.09 (**CH**$_2$), 37.62, 37.41, 37.37, 37.29, 37.14, 36.42, 36.16, 35.95 (**CH**), 29.80, 27.74, 27.62, 27.54, 27.38, 27.23, 24.79, 24.75, 24.68, 24.58, 24.50, 24.45 (**CH**$_2$), 13.28, 13.17, 13.13, 13.09, 12.97, 12.89, 12.84 (**CH**$_3$) ppm.

The molar ratio of the initial reagents was calculated based on the Mayo equation:

$$\overline{P} = \frac{[EtNB]}{[Gr2] + [DMM]}, \tag{1}$$

where $\overline{P}$ is the average degree of polymerization, $[EtNB]$ is the concentration of 5-ethyl-2-norbornene, $[Gr2]$ is the concentration of the second-generation Grubbs catalyst, $[DMM]$ is the concentration of dimethyl maleate. The initial concentration ratio of the reactants is equal to the molar one.

If $\overline{P} = 2$, then

$$\frac{[EtNB]}{[Gr2] + [DMM]} = 2, \tag{2}$$

$$[EtNB] = 2[Gr2] + 2[DMM], \tag{3}$$

$$[Gr2] = \frac{[EtNB] - 2[DMM]}{2}, \tag{4}$$

$$\text{Примем, что } \frac{[EtNB]+[DMM]}{[Gr2]} = 3000, \tag{5}$$

$$\frac{2([EtNB] + [DMM])}{[EtNB] - 2[DMM]} = 3000 \tag{6}$$

$$\frac{[EtNB]}{[DMM]} = \frac{3001}{1499} \approx 2 \tag{7}$$

Consequently, $[EtNB] \,/\, [DMM] \,/\, [Gr2] = 2000 \,/\, 1000 \,/\, 1$ mol / mol / mol $\qquad$ (8).

Characterization

The ^{1}H and ^{13}C NMR spectra of poly(EtNB) solutions in deuterated CDCl$_3$ were recorded with a Bruker Avance DRX 400 spectrometer operating at 400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C. The chemical shifts were determined relative to the signals of residual or deuterated chloroform (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C). Each sample was prepared by dissolving ~40 mg of the copolymer in 0.6 mL of the deuterated solvent. About 100 mg of poly(EtNB) in 0.5 mL CDCl$_3$ was required for ^{13}C NMR and two-dimensional ^{1}H–^{13}C HSQC (pulse sequence hsqcedetgpsisp2.3), ^{1}H–^{13}C H2BC (pulse sequence h2bcetgpl3), ^{1}H–^{13}C HMBC (pulse sequence hmbcetgpl3nd), and ^{1}H–^{1}H COSY (pulse sequence cosygpmfqf) NMR spectra. To obtain the ^{1}H NMR spectrum, four scans of the dissolved sample with the relaxation delay of 10 s were recorded. To obtain the ^{13}C NMR spectrum, 2048 scans of the dissolved sample with the relaxation delay of 2 s were recorded. The signal assignments were made based on the ^{1}H–^{13}C HSQC, ^{1}H–^{13}C H2BC, ^{1}H–^{13}C HMBC, and ^{1}H–^{1}H COSY 2D experiments.

Gel permeation chromatography of the copolymers was performed with an Agilent 1280 Infinity II installation with three series-connected 250×4.6 mm PLgel 10 µm MiniMIX-B columns using a refractometer detector. Tetrahydrofuran (no less than 99.9%, Panreac Química SLU) was used as an eluent; the flow rate was 0.3 mL·min^{-1}, the sample volume was 50 µL, and the sample concentration was 1 mg·mL^{-1}. The molecular mass and polydispersity were calculated from the calibration dependence of the molecular mass on the retention time, constructed using monodisperse polystyrene standards (Sigma–Aldrich): $M_w = 1.1$ kDa (catalog no. 81402), $M_w = 2.8$ kDa (catalog no. 327719), $M_w = 9.8$ kDa (catalog no. 81406), $M_w = 27.1$ kDa (catalog no. 81408), $M_w = 67.6$ kDa (catalog no. 81409), $M_w = 269.5$ kDa (catalog no. 81413), $M_w = 482$ kDa (catalog no. 327794), $M_w = 729.5$ kDa (catalog no. 327808), $M_w = 1074$ kDa (catalog no. 81416), $M_w = 1956$ kDa (catalog no. 327816), and $M_w = 9260$ kDa (catalog no. 81419). The dependence was linear in the range of 0.001–9 MDa. The chromatograms were processed using the Agilent GPC/SEC software.

The IR spectra were measured with an IFS-66 v/s Fourier spectrometer (Bruker) using attenuated total reflection technique. The spectra were recorded on a ZnSe crystal in the range from 4000 to 600 cm^{-1} with 2 cm^{-1} resolution, 15 IR absorption scans were taken.

Differential scanning calorimetry (DSC) was performed with a Mettler TA 4000 device at the temperature variation rate of 20 deg/min in the range from -5 to 160 °C under argon (99.99%, Argon, Russia; gas flow rate 70 mL/min). The glass transition temperature (T_g) was determined from the data obtained after the repeated heating of the sample. The measurement results were processed using the STARe service program supplied with the device. The measurement accuracy was as follows: $\Delta T = \pm 0.3$ °C and $\Delta H = \pm 1$ J/g.
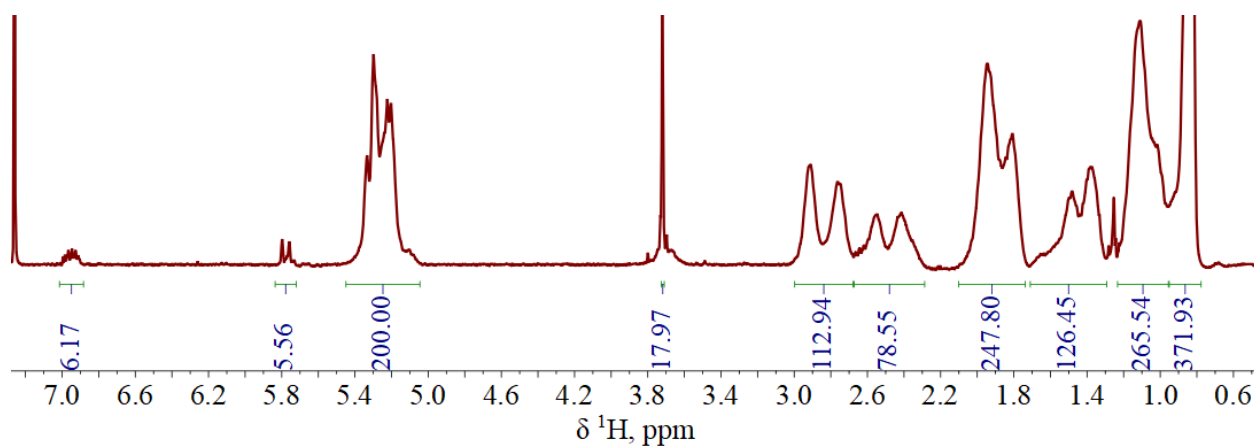
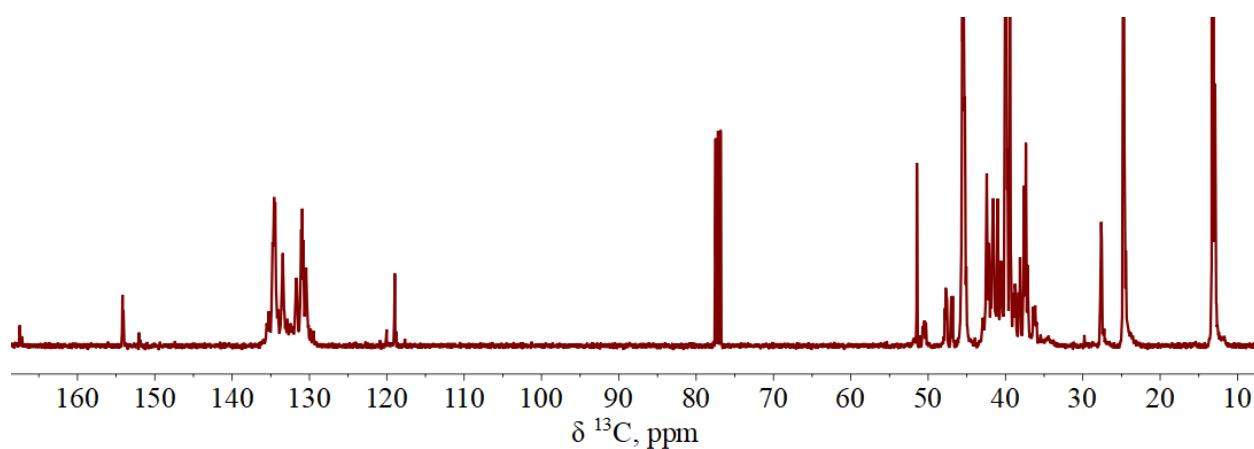**Figure S1**. ^{1}H NMR spectrum of telechelic poly(EtNB) characterized by M_n^{GPC} = 6.2 kDa, $Đ$ = 2.7.

Figure S2. ^{13}C NMR spectrum of telechelic poly(EtNB) characterized by M_n^{GPC} = 6.2 kDa, $Đ$ = 2.7.

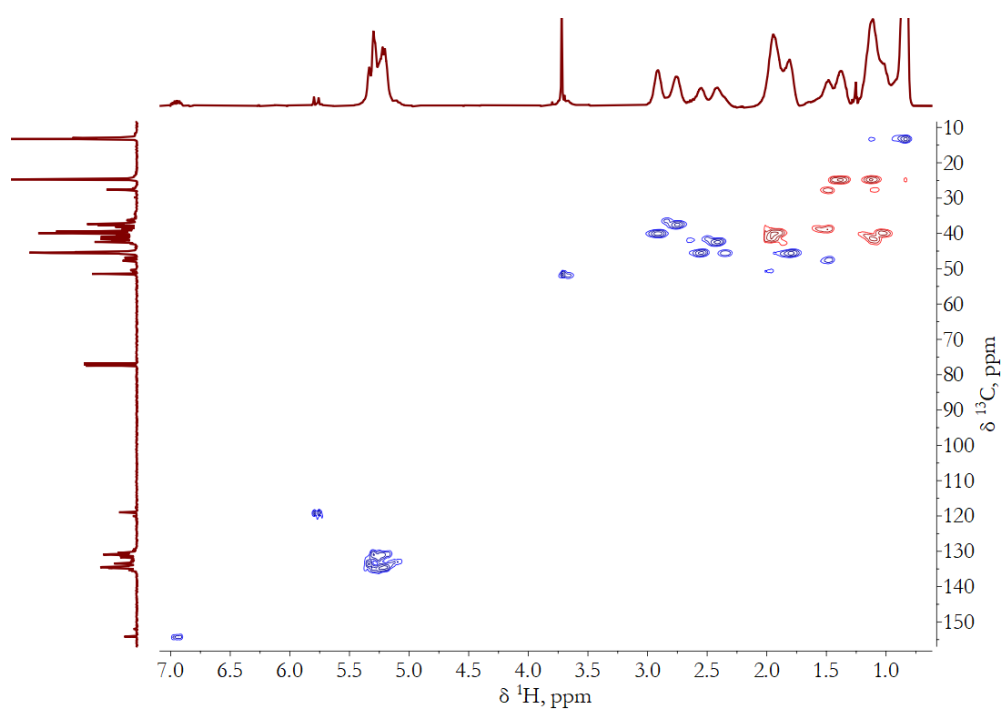**Figure S3**. ^{1}H–^{13}C HSQC (DEPT-135) spectrum of telechelic poly(EtNB) characterized by M_n^{GPC} = 6.2 kDa, $Đ$ = 2.7.
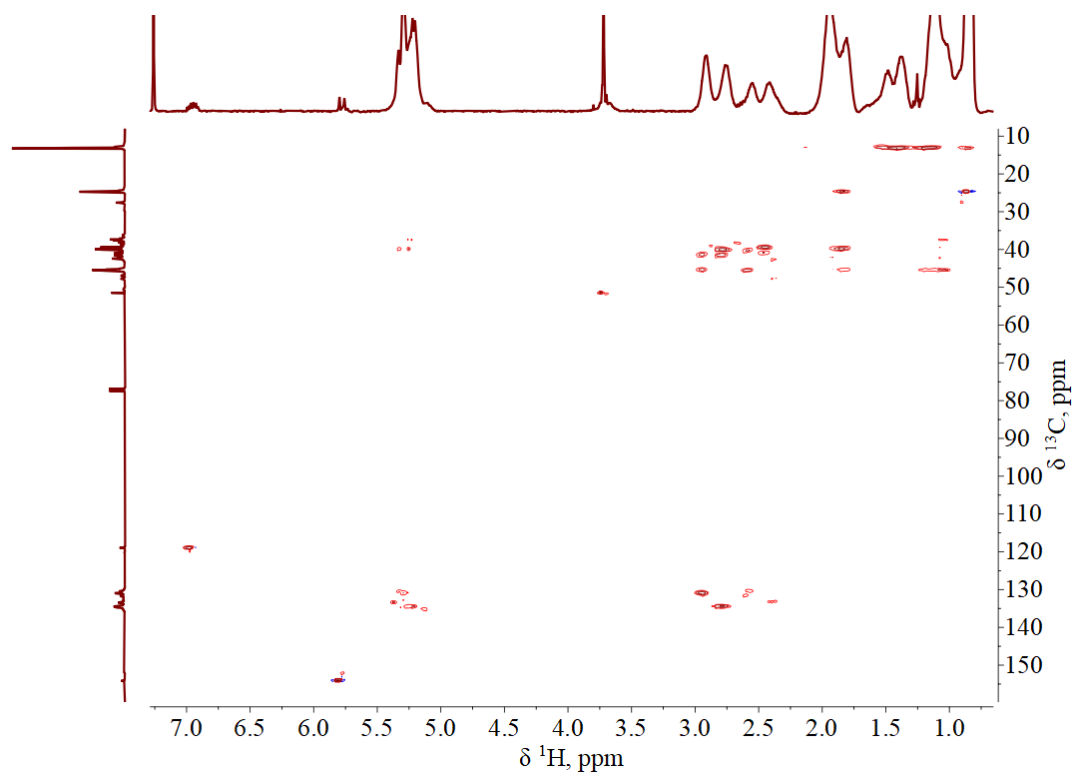
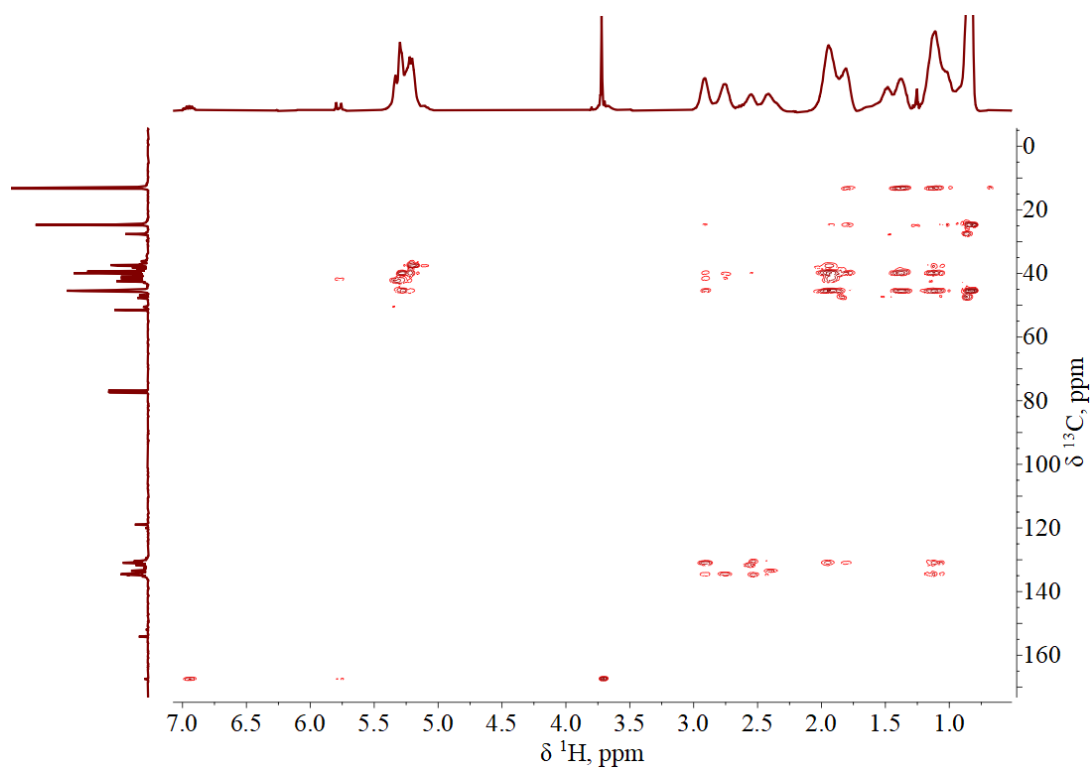**Figure S4**. ^1H–^{13}C H2BC spectrum of telechelic poly(EtNB) characterized by M_n^{GPC} = 6.2 kDa, Đ = 2.7.

Figure S5. ^1H–^{13}C HMBC spectrum of telechelic poly(EtNB) characterized by M_n^{GPC} = 6.2 kDa, Đ = 2.7.
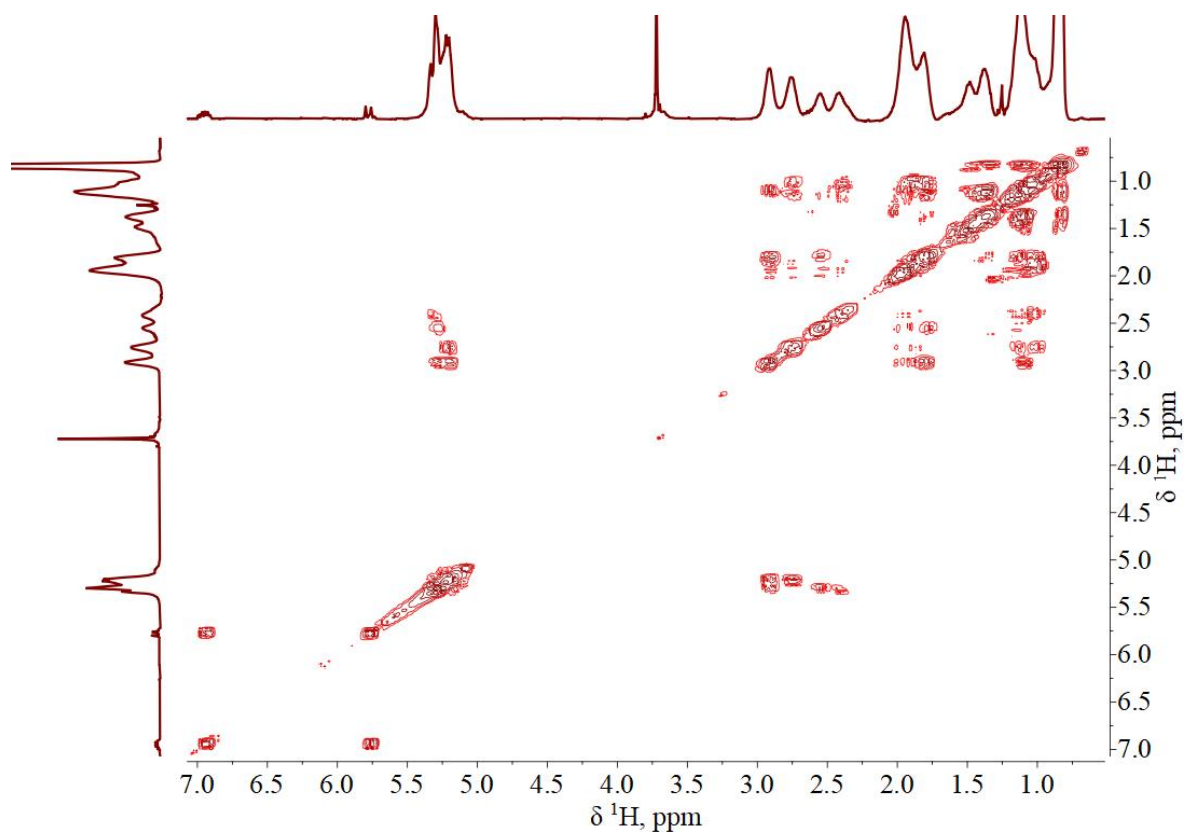
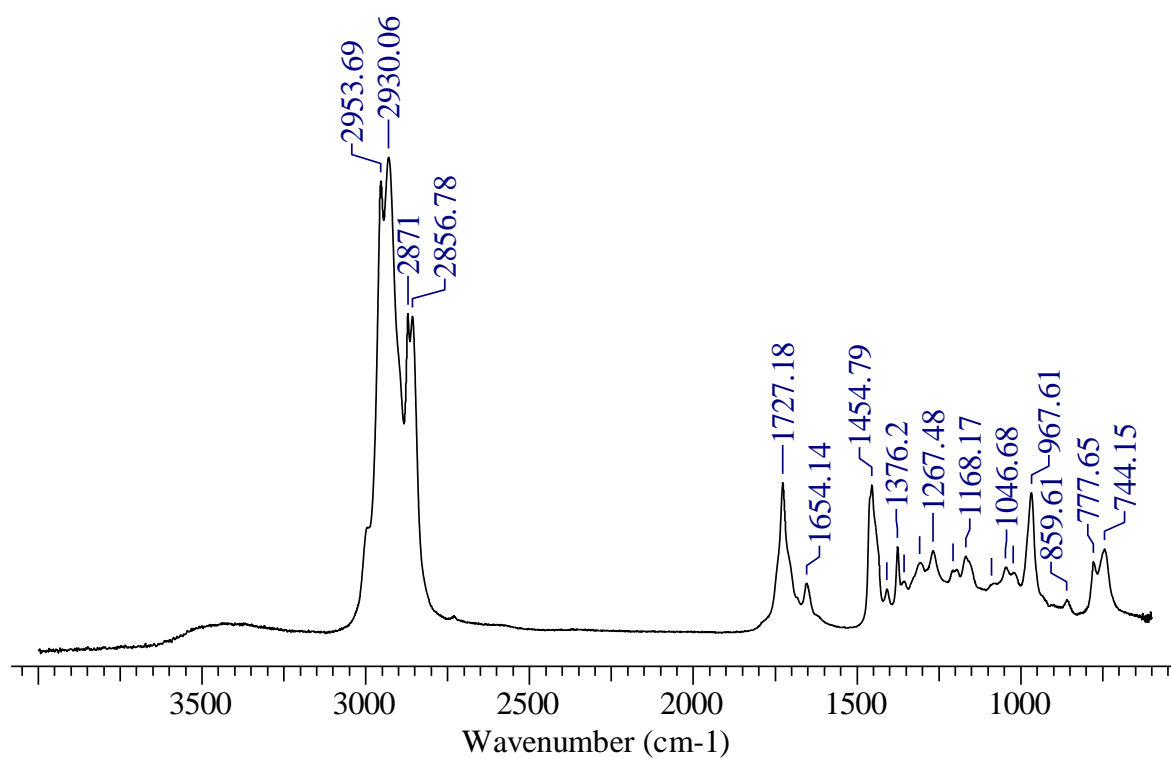**Figure S6**. ^{1}H–^{1}H COSY spectrum of telechelic poly(EtNB) characterized by $M_n^{GPC} = 6.2$ kDa, $Đ = 2.7$.

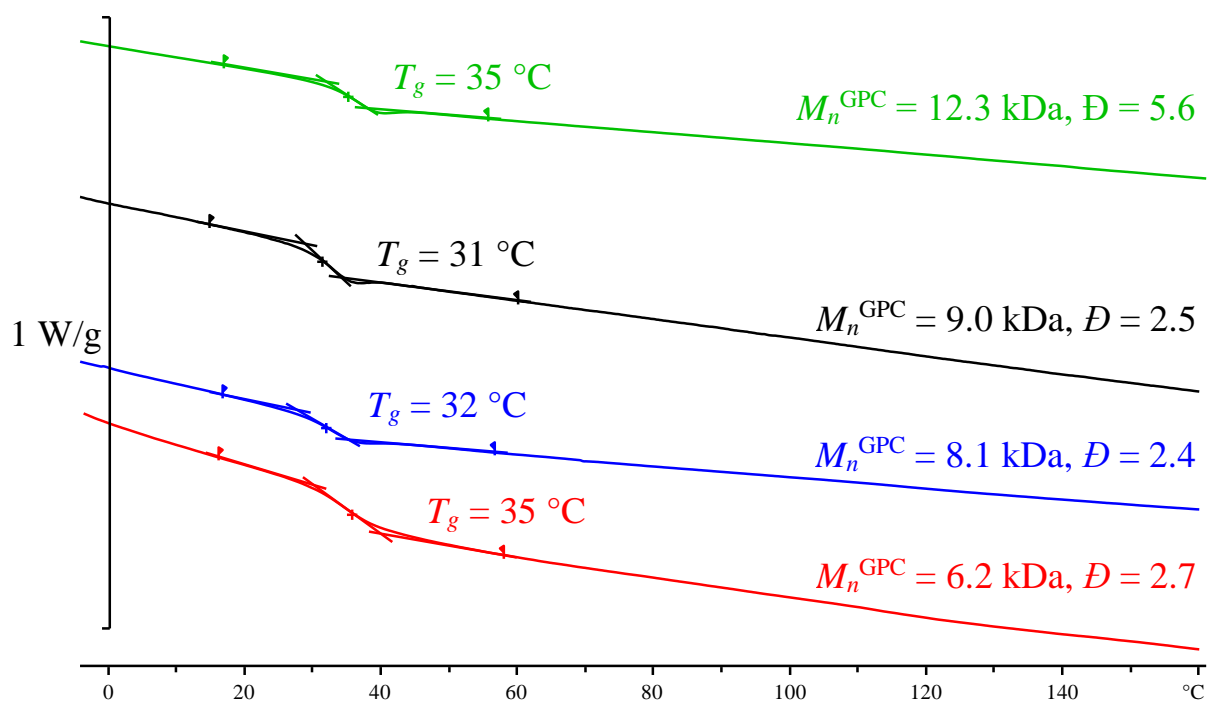**Figure S7**. IR spectrum of telechelic poly(EtNB) characterized by $M_n^{GPC} = 6.2$ kDa, $Đ = 2.7$.

Figure S8. DSC curves of telechelic poly(EtNB) characterized by different molar masses.
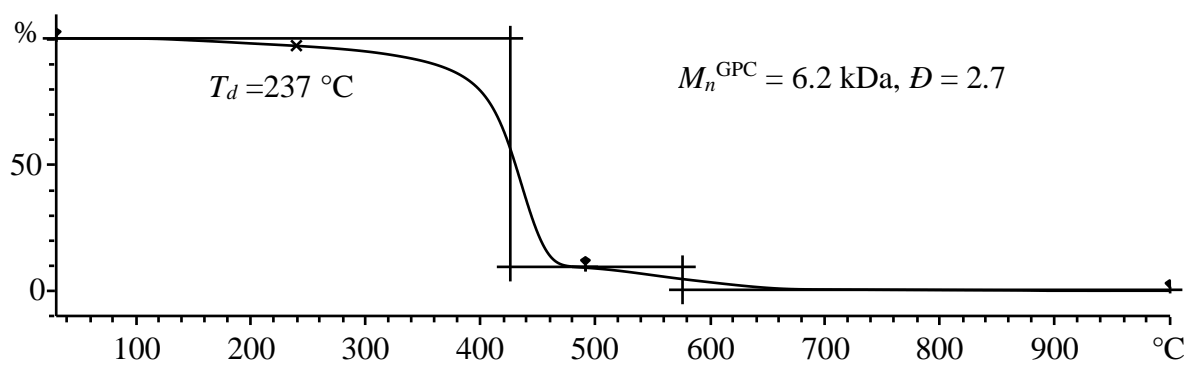

Figure S9. TGA curve of telechelic poly(EtNB) (in Ar).

References

S1.   A. I. Wozniak, E. V. Bermesheva, I. L. Borisov, A. V. Volkov, D. I. Petukhov, N. N. Gavrilova, V. P. Shantarovich, A. F. Asachenko, M. A. Topchiy, E. S. Finkelshtein, M. V. Bermeshev, *J. Membr. Sci.*, **2022**, *641*, 119848. DOI: 10.1016/j.memsci.2021.119848

S2.   J. D. Hatjopoulos, R. A. Register, *Macromolecules*, **2005**, *38*, 10320–10322. DOI: 10.1021/ma0515331