

Electronic supplementary information

SYNTHESIS OF POLY(5-NORBORNENE-2,3-DICARBOXYLIC ANHYDRIDE) BY ROMP IN THE PRESENCE OF THE SECOND-GENERATION GRUBBS CATALYST AND 1-HEXENE IN DMF

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Experimental section

General remarks

All reactions were carried out under a dry argon atmosphere using standard Schlenk and vacuum-line techniques. DMF was purchased from ReaktivTorg (Russia), distilled over anhydrous CuSO_4 under low pressure and stored under argon. The second-generation Grubbs catalyst (no less than 98%, Shaanxi Dideu Medichem Co. Ltd.), inhibitor 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (Sigma Aldrich), ethyl vinyl ether (no less than 98%, Jiangsu Ambition New Materials Co., Ltd.), $\text{DMSO-}d_6$ (no less than 99.8%, SOLVEX-D (Russia)) were used as received. 1-Hexene was purchased from Komponent-Reaktiv (Russia), distilled over sodium under a dry argon atmosphere and stored under argon. 5-Norbornene-exo-2,3-dicarboxylic anhydride was synthesized by the Diels–Alder reaction at 200 °C according to the published procedure [S1]. The fraction of the *exo*-isomer was 97%.

Syntheses

Synthesis of poly(5-norbornene-2,3-dicarboxylic anhydride). 0.04 mL of a 1-hexene solution obtained by mixing 1-hexene (0.0844 g, 0.13 mL) with DMF (0.9767 g, 1.03 mL) and 0.09 mL of a solution of the second-generation Grubbs catalyst (0.01050 g) in DMF (0.83 mL) were added to a solution of NDA (0.4951 g, 3.02 mmol) in absolute DMF (2.43 mL), prepared in a 4 mL vial equipped with a septum. The reaction was carried out for 20 h, including 7 h of stirring at 35 °C, after which it was stopped by adding vinyl ethyl ether (0.2 mL). The product was precipitated with methanol with the addition of an oxidation inhibitor. The precipitated polymer was purified by double reprecipitation from acetone and subsequent drying under vacuum. Yield: 92% (0.4578 g).

For the assignments of the proton and carbon signals, see Figs. S1, S2 and Ref. [S2].

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ , ppm: 5.61, 5.44 (br. m, 2.00H, *cis*-/*trans*- $\text{C}^{6,7}$), 3.55 (br. m, 2.01H, $\text{C}^{2,3}$), 3.32 (br. m, 1.13H, $\text{C}^{5,8}$), 3.00 (br. m, 2.01H, $\text{C}^{5,8}$), 1.80 (br. m, 0.93H, C^9), 1.27 (br. m, 1.03H, C^9).

^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ , ppm: 171.69, 171.57 (br. m, $\text{C}^{1,4}$), 129.35, 128.99 (br. m, *cis*-/*trans*- $\text{C}^{6,7}$), 49.74 (br. m, $\text{C}^{2,3}$), 44.38, 44.10 (br. m, $\text{C}^{5,8}$), 39.52 (br. m, $\text{C}^{5,8}$ and $\text{DMSO-}d_6$), 37.64 (br. m, C^9).

Characterization

The ^1H and ^{13}C NMR spectra of poly(NDA) solutions in $\text{DMSO-}d_6$ were recorded with a Bruker Avance DRX 400 spectrometer operating at 400.1 MHz for ^1H and 100.6 MHz for ^{13}C . The proton chemical shifts were determined relative to the residual signal of $(\text{CD}_3)_2\text{SO}$ (2.50 ppm for ^1H , 39.51 ppm for ^{13}C). Each sample was prepared by dissolving ~40 mg of the polymer in 0.6 mL of the deuterated solvent. To obtain the ^1H NMR spectrum, 4 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 results of the ^1H – ^{13}C HSQC experiments.

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

Gel permeation chromatography (GPC) was performed on a STAYER chromatographic system (Aquilon, Russia) consisting of a high-pressure pump, column thermostat, UVV 104M spectrophotometric detector (wavelength 268 nm), and a refractometric detector (Gilson RI 133, France). Thermostat temperature was 60 °C (± 0.1 °C). An eluent was DMF, the flow rate was 1.0 mL/min, the sample volume was 20 μL . Columns were 300 \times 7.8 mm, Phenogel sorbent (Phenomenex, USA), 5 μm , pore size from 50 Å to 105 Å. Columns were calibrated relative to Agilent polystyrene standards (USA). The chromatograms were processed and the molecular weight parameters were calculated using the MultiChrom program for Windows, version 1.6. (Ampersend, Russia).

Differential scanning calorimetry (DSC) was performed using a 2920 MDSC calorimeter (TA Instruments, USA) at a constant heating rate of 10 °C/min in the range from 25 to 400 °C in an argon atmosphere. The sample weight ranged from 6 to 14 mg. The glass transition temperature T_g was determined from the data obtained after repeated heating of the sample.

The thermogravimetric analysis (TGA) of the polymers was performed under argon or in the air with a TGA 7 thermogravimetric analyzer (Perkin Elmer) at a heating rate of 10 °C/min in the temperature interval from 30 to 1000 °C; the gas flow rate was 10 mL/min. The samples (10 mg) were preliminarily thermostated at 30 °C.

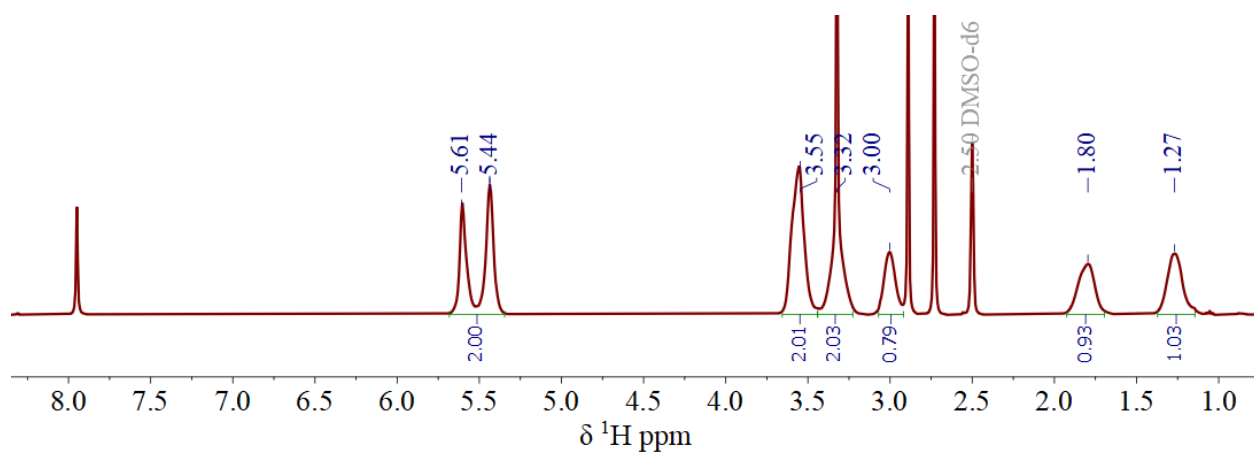


Figure S1. ^1H NMR spectrum of poly(NDA). $M_n^{\text{GPC}} = 46$ kDa, $\bar{D} = 1.3$.

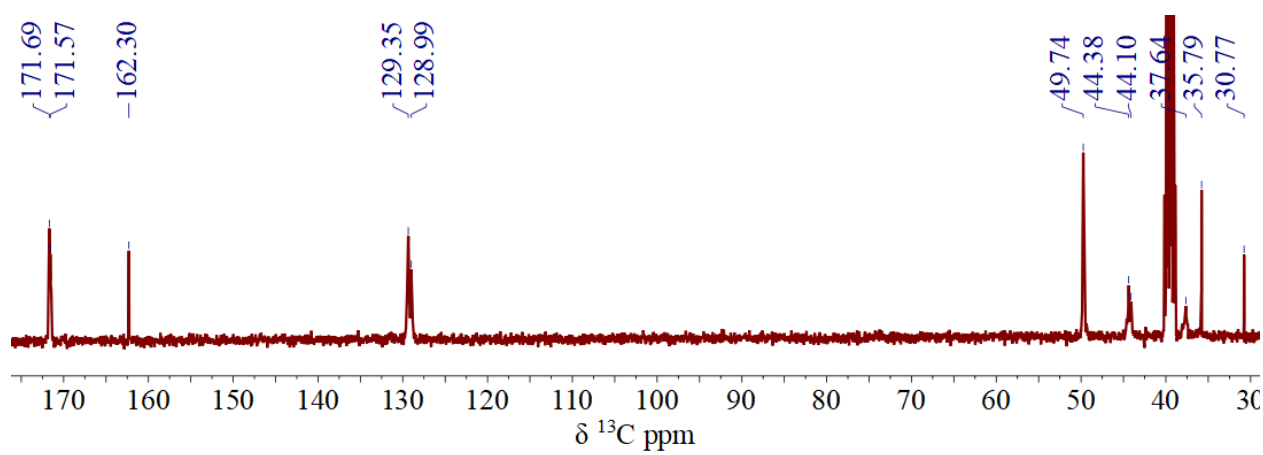


Figure S2. ^{13}C NMR spectrum of poly(NDA). $M_n^{\text{GPC}} = 46$ kDa, $\bar{D} = 1.3$.

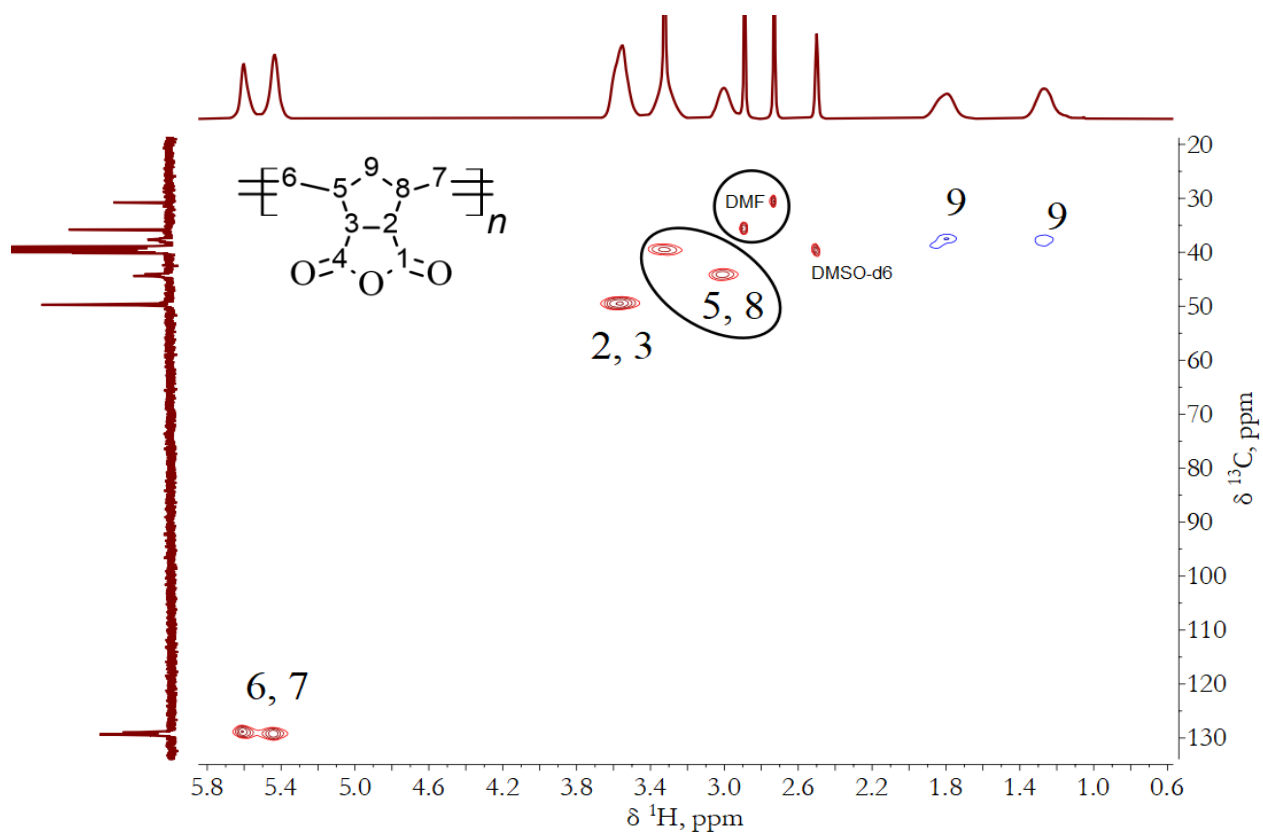


Figure S3. ^1H - ^{13}C HSQC (DEPT-135) spectrum of poly(NDA). $M_n^{\text{GPC}} = 46\text{ kDa}$, $D = 1.3$.

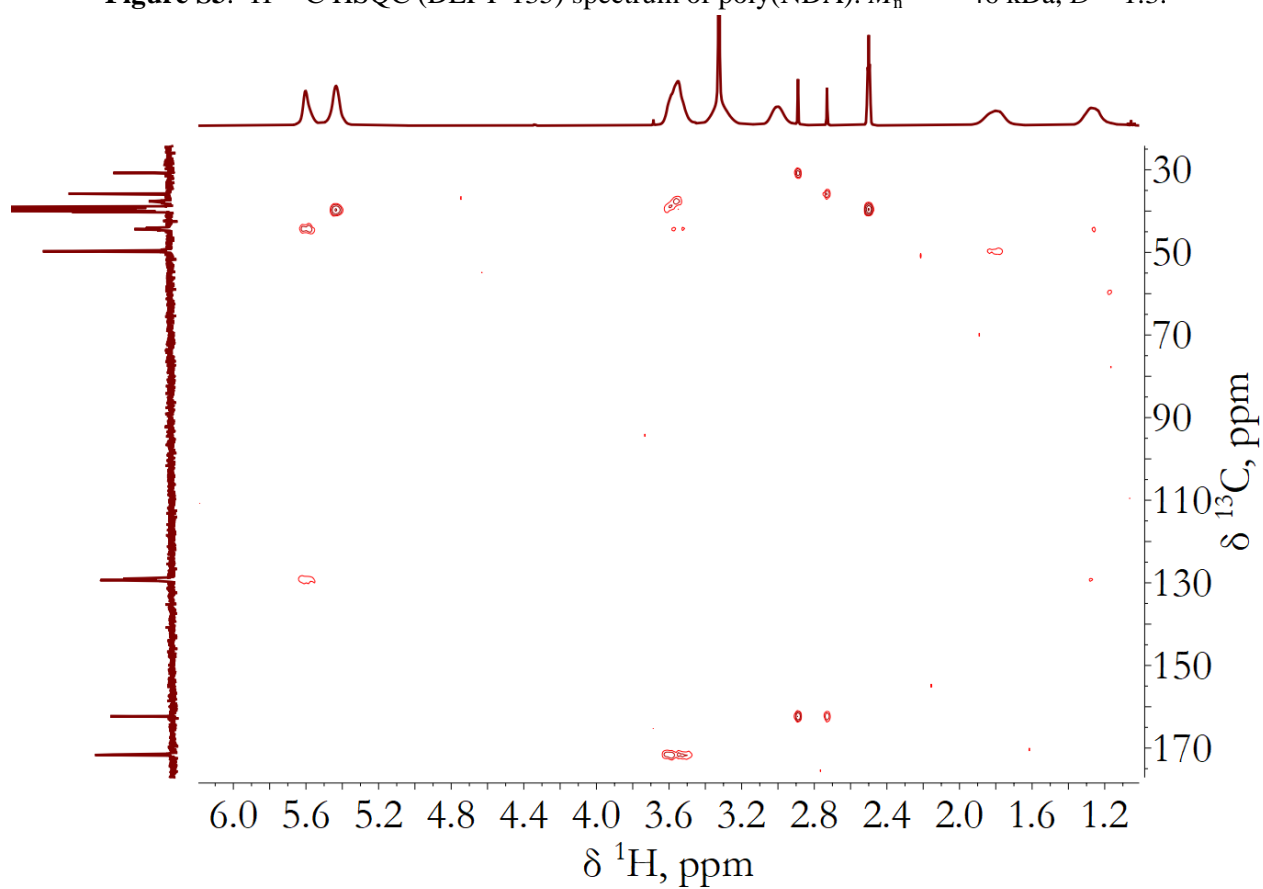


Figure S4. ^1H - ^{13}C HMBC spectrum of poly(NDA). $M_n^{\text{GPC}} = 46\text{ kDa}$, $D = 1.3$.

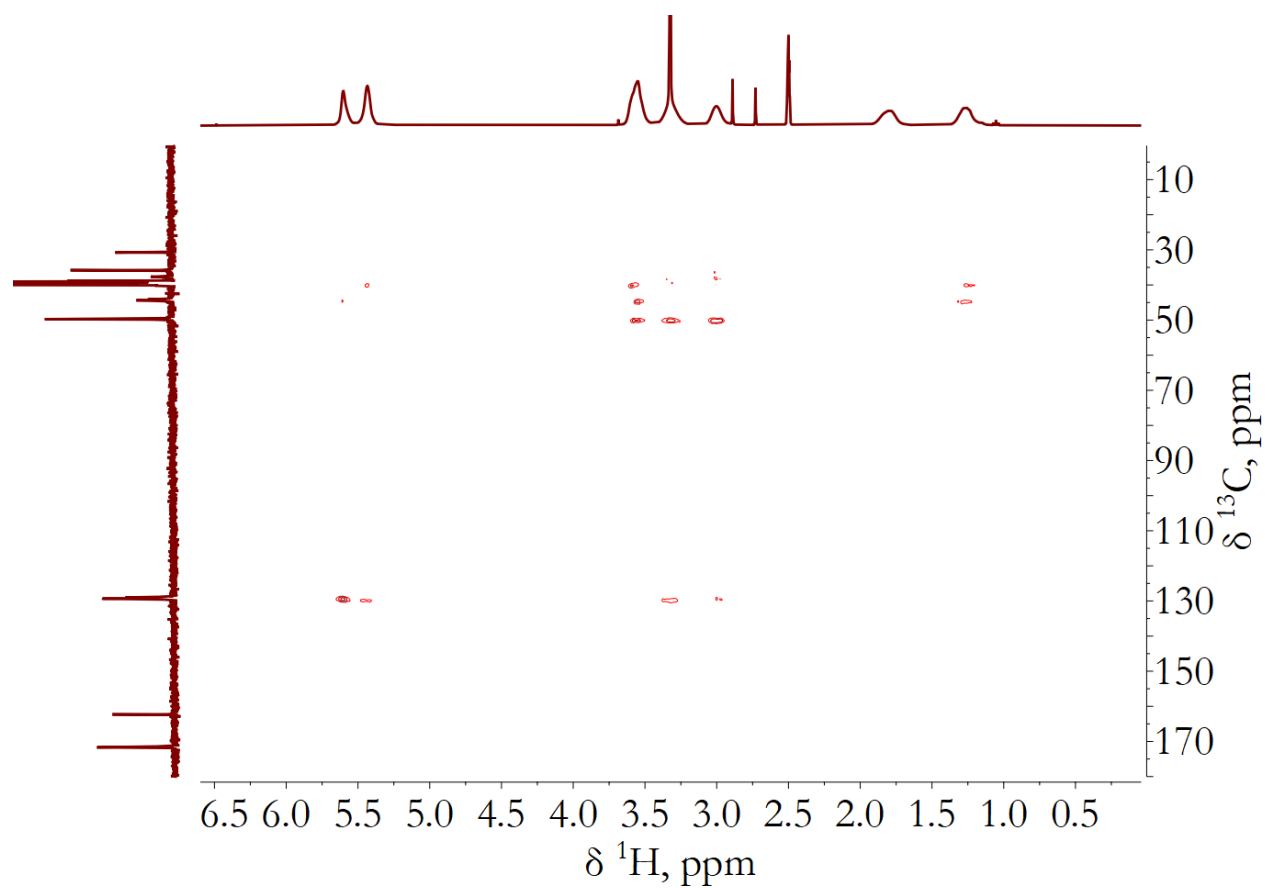


Figure S5. ^1H - ^{13}C HMBC spectrum of poly(NDA). $M_n^{\text{GPC}} = 46$ kDa, $\bar{D} = 1.3$.

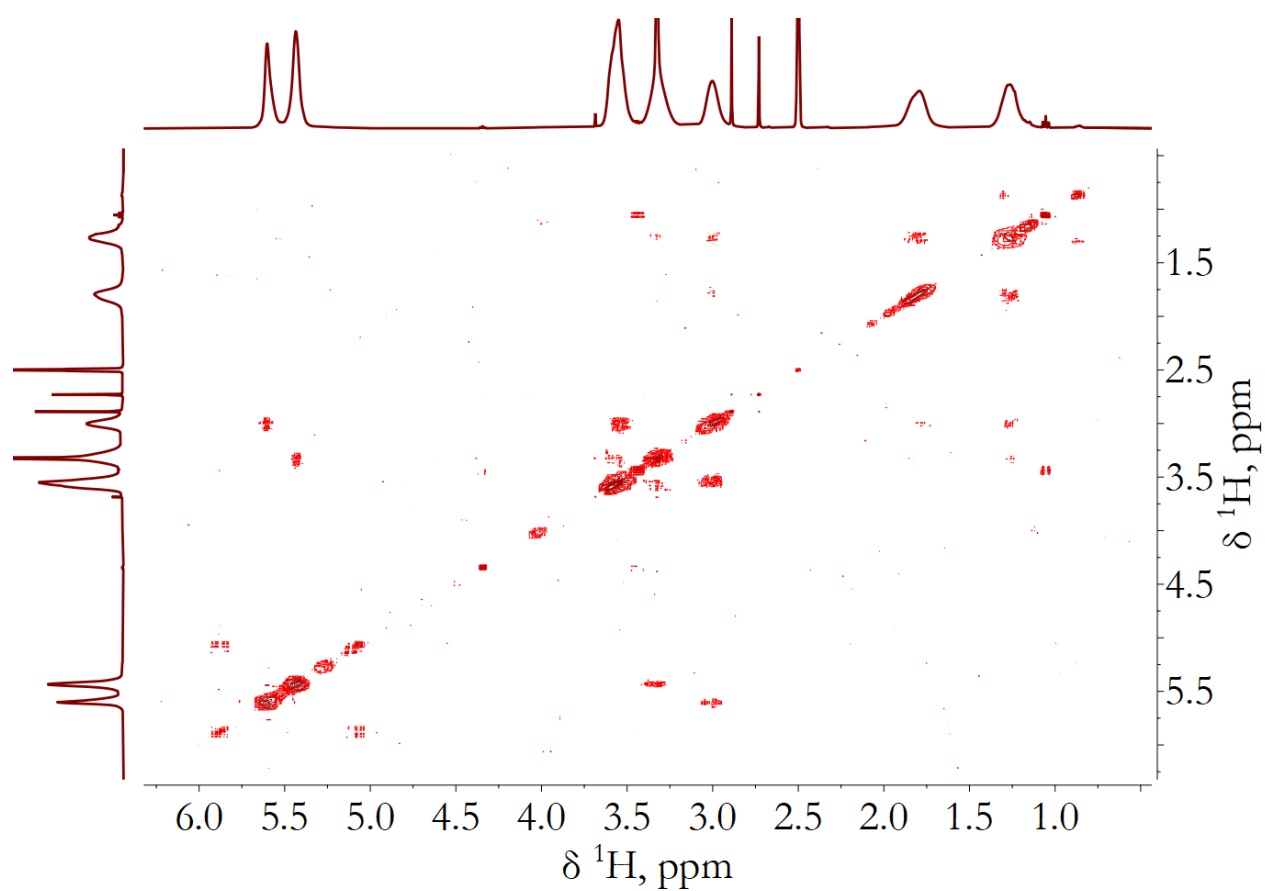


Figure S6. ^1H - ^1H COSY spectrum of poly(NDA). $M_n^{\text{GPC}} = 46$ kDa, $\bar{D} = 1.3$.

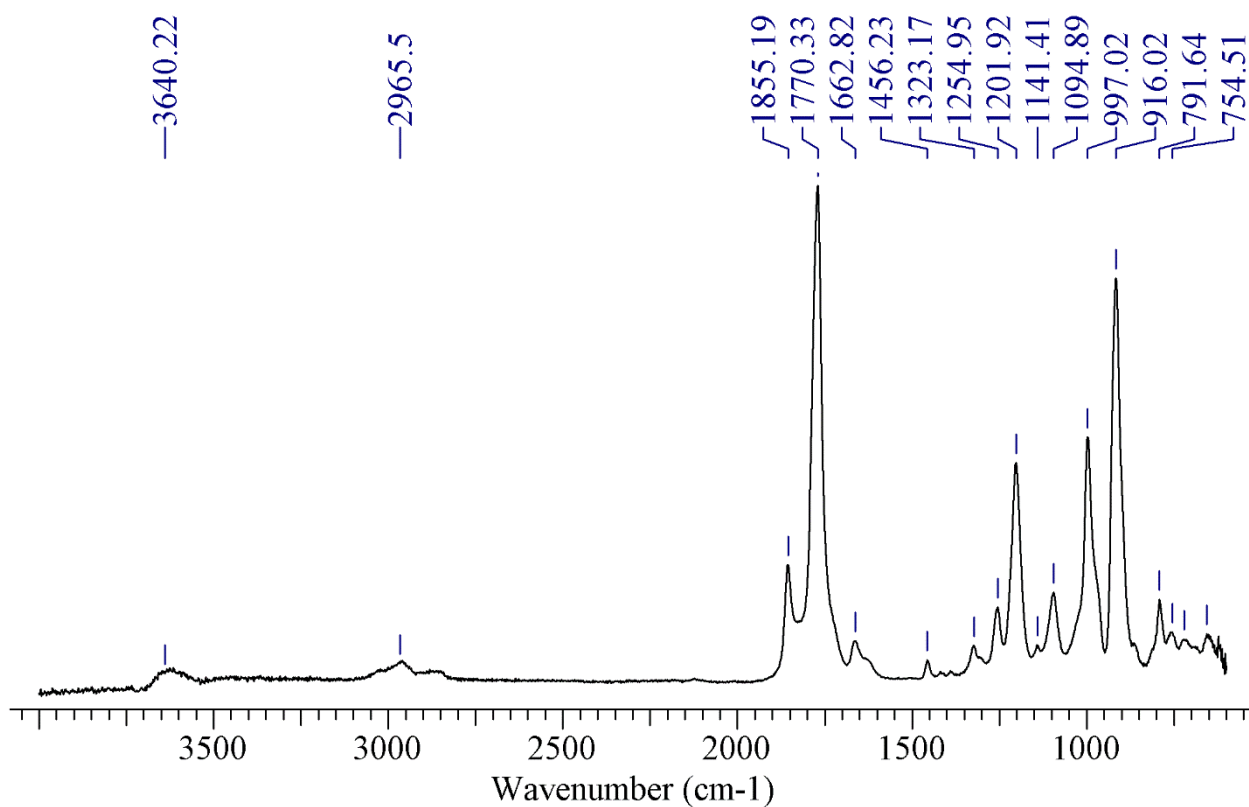


Figure S7. IR spectrum of poly(NDA). $M_n^{\text{GPC}} = 46$ kDa, $\bar{D} = 1.3$.

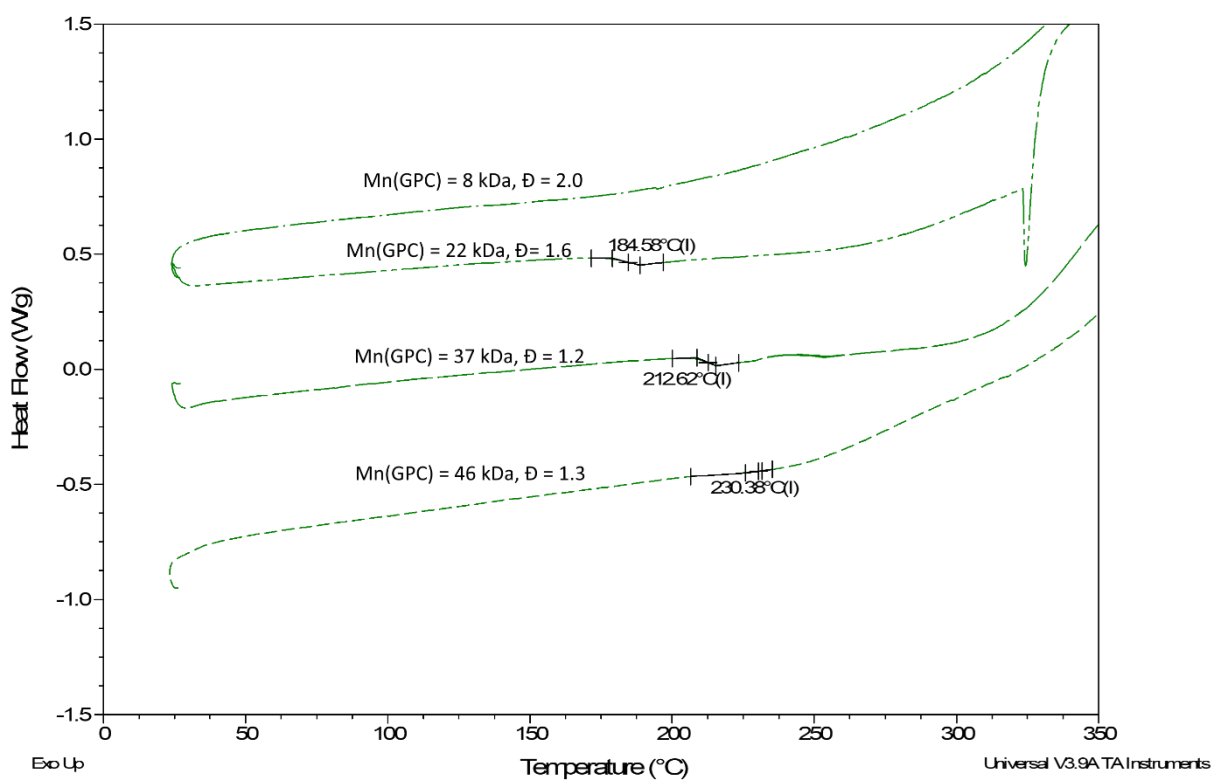


Figure S8. DSC curves of poly(NDA) characterized by different molecular weights.

References

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