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New multiblock copolymers of norbornene and 5-hydroxycyclooctene

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Instruments

Nuclear magnetic resonance measurements were carried out at room temperature using a Bruker Avance™ 600 NMR spectrometer operating at 600.22 MHz (^{1}H NMR), 150.93 MHz (^{13}C NMR); $CDCl_3$ (Aldrich) was used as solvent. Chemical shifts δ were reported in parts per million relative to the residual $CHCl_3$ signal as an internal reference standard.

Molecular mass distribution of the polymers was determined by GPC on a Waters high pressure chromatograph equipped with a refractometric detector and Microgel mix 1–5 μm 300x7.8 mm Waters Styragel HR 5E column, with toluene for PNB and NB-HCO copolymers and tetrahydrofuran for PCO as a solvent, the flow rate of 1 ml min^{-1}, sample volume of 100 μl, and sample concentration of 1 mg ml^{-3}. Molecular mass M_w and dispersity $Đ$ were calculated by a standard procedure relative to monodisperse polystyrene standards.

ROMP of HCO

Polyhydroxyoctenamer (poly(5-hydroxy-1-octenylene), PHCO) was synthesized by ring-opening metathesis polymerization (ROMP) of 5-hydroxycyclooctene in the presence of the 1st generation Grubbs' catalyst **$Cl_2(PCy_3)_2Ru{=}CHPh$** (Gr-1, Aldrich). Bulk polymerization gives a good result, but it is necessary to add a few drops of dry chloroform to the catalyst to make it soluble in the monomer. The catalyst (5.3 mg, 0.0064 mmol) was placed into the reactor and 5-hydroxy-cyclooctene (1.16 g, 9 mmol) was added under argon. The reaction was carried out for 24 h and stopped by adding dry ethyl vinyl ether (2 ml) to the reaction mixture and stirring for 30 min. Then an oxidation inhibitor 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (Sigma-Aldrich) (0.1 wt% per polymer) was added. Polymer was precipitated from chloroform/methanol solution to dry hexane, and dried under reduced pressure at room temperature until constant mass. The yield of PHCO was 0.6 g (52%). Structure of the obtained homopolymer corresponds to the literature data [19]:

^{1}H NMR (600 MHz, $CD_3OD/CDCl_3$) δ 5.45 – 5.33 (m, 2H), 3.53 (br s, 1H), 2.07 (br m, 4H), 1.55 – 1.31 (m, 6H).

^{13}C NMR (151 MHz, $CD_3OD/CDCl_3$) δ 130.18 – 128.77 (m), 70.63 – 69.88 (m), 48.47 – 47.38 (m), 37.06 – 35.90 (m), 32.10 (s), 28.27 (s), 26.94 – 26.36 (m), 25.48 – 24.81 (m), 23.24 – 22.63 (m).

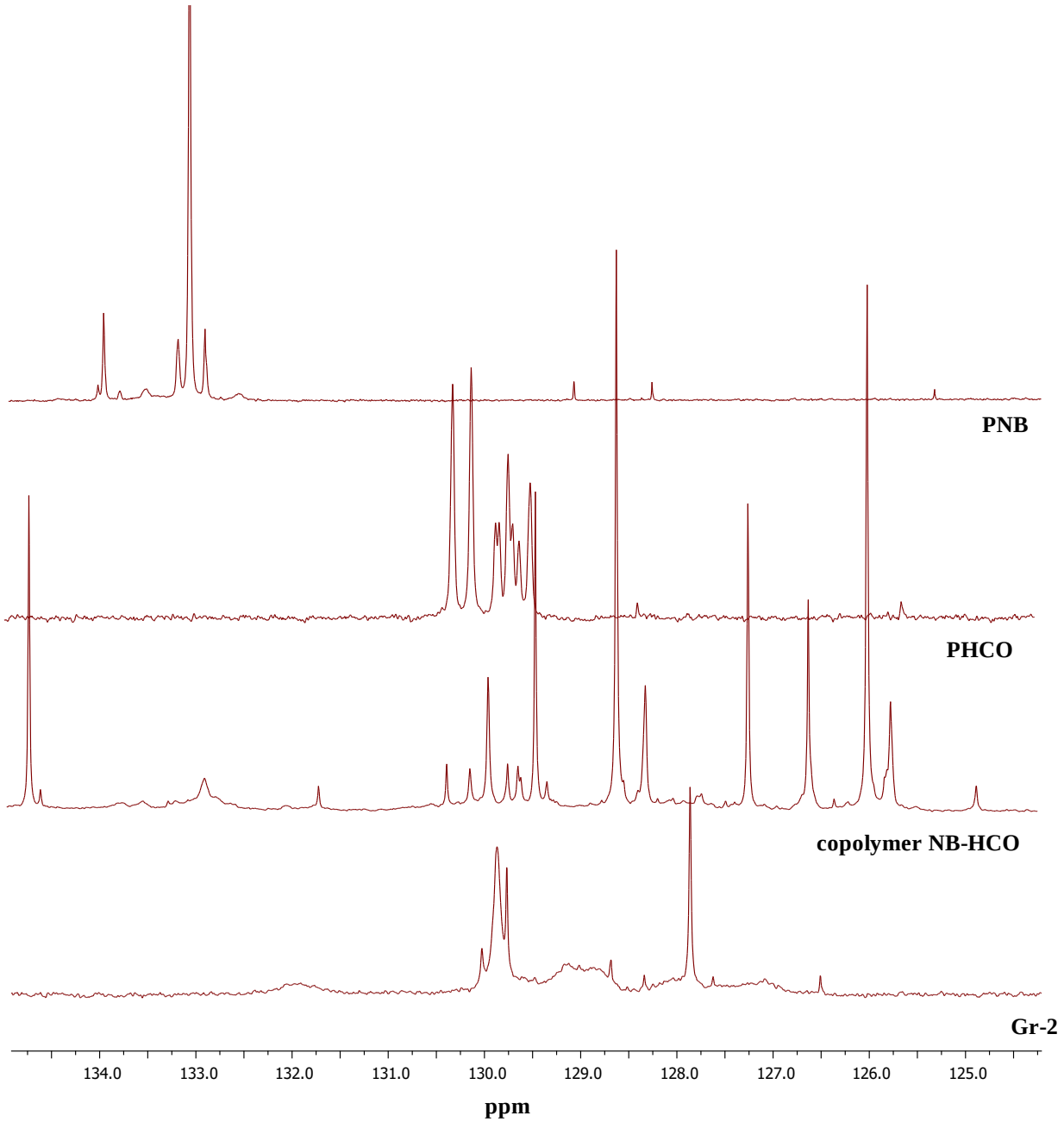

Figure S1 ^{13}C NMR spectra of PNB, PHCO, NB-HCO copolymer, and Gr-2 (C=C double bond region).

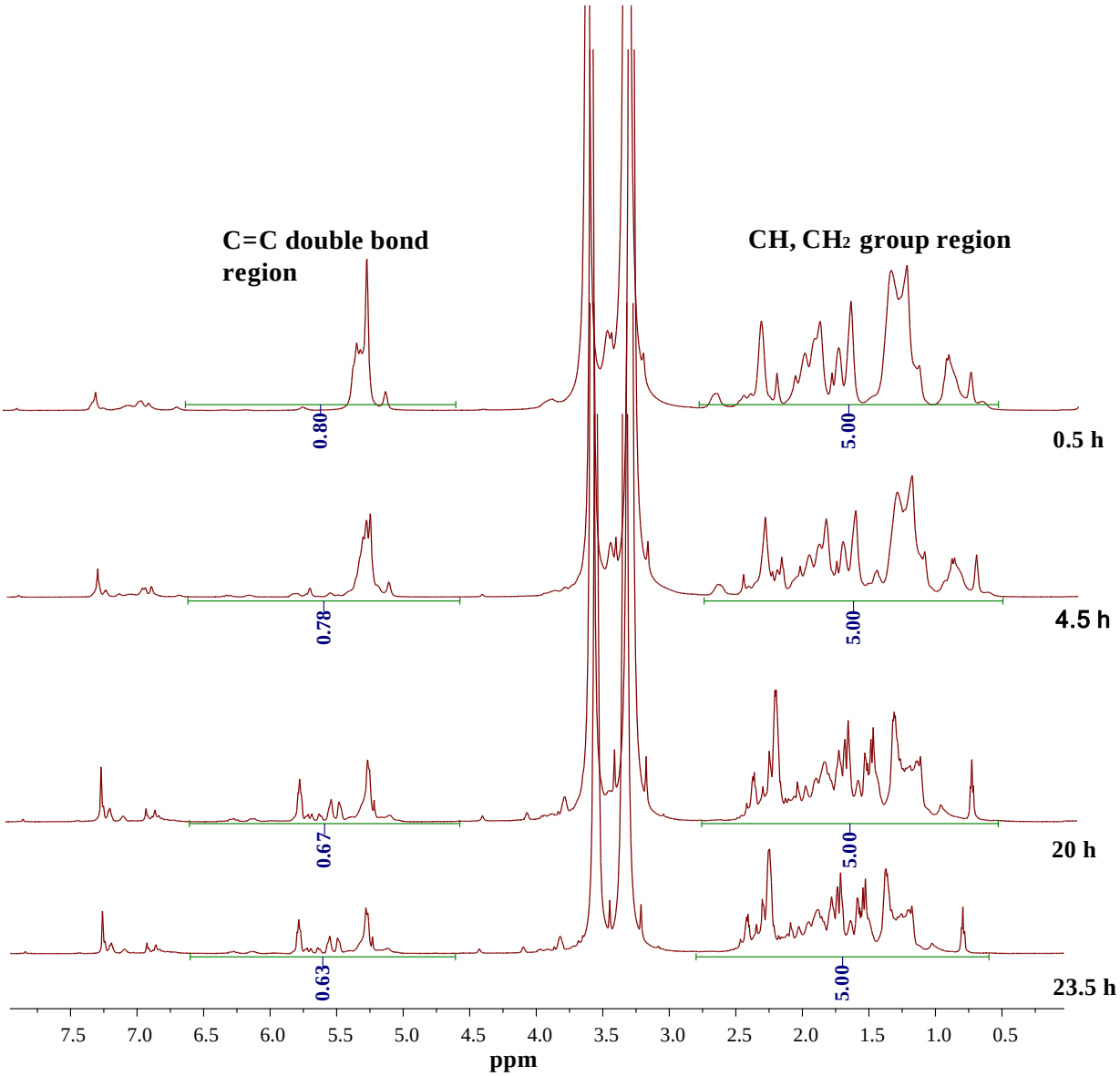

Figure S2 *In situ* ^{1}H NMR monitoring of the cross-metathesis between PNB and PHCO in the presence of Gr-2.

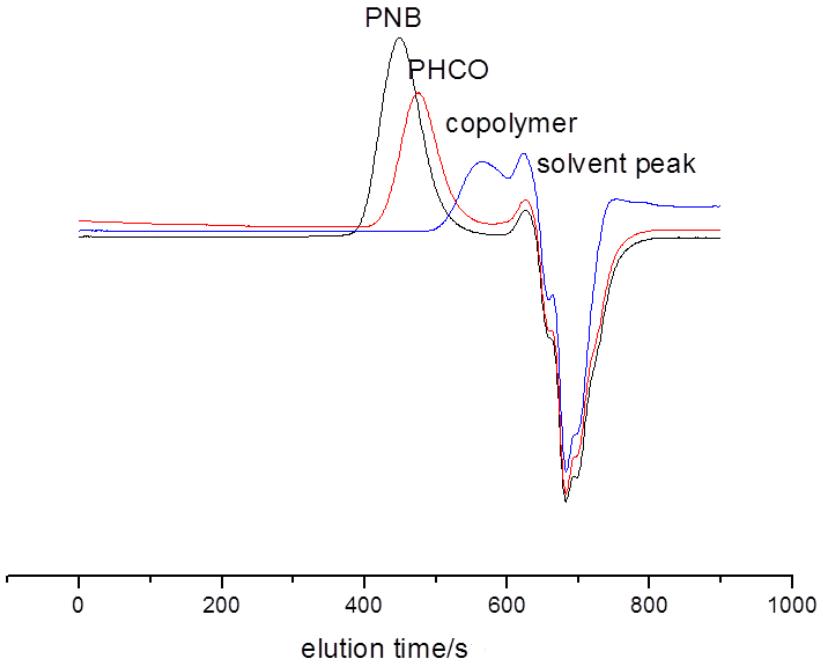

Figure S3 GPC traces of the initial homopolymers and copolymer obtained after 24 h of their cross-metathesis mediated by Gr-2 (1 mol%).