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Supporting Information

Synthesis of norbornene - cyclooctene copolymers by cross-metathesis of polynorbornene and polyoctenamer

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Experimental Section

Instrumentation

Nuclear magnetic resonance measurements were carried out at room temperature using a Bruker Avance™ 600 NMR spectrometer operating at 600.22 MHz (¹H NMR), 150.93 MHz (¹³C NMR); CDCl₃ (Aldrich) was used as solvent. Chemical shifts δ are reported in parts per million relative to the residual CHCl₃ signal as an internal reference standard.

Differential scanning calorimetry (DSC) was performed on Mettler TA 4000 system. The heating and cooling of samples was performed at a rate of 10 K/min under a flow of argon (70 mL/min) in the range of -100°C to 100°C.

Molecular weight of PNB and copolymers was determined by GPC technique on a Waters high pressure chromatograph equipped with a refractometric detector (Microgel mix (1–5 μ m) column of 300 mm \times 7.8 mm Waters Styragel HR 5E), with toluene as a solvent, the flow rate of 1 ml/min, sample volume of 100 μ L, and sample concentration of 1 mg/mL. The molecular weight and polydispersity index were calculated by a standard procedure relative to monodisperse polystyrene standards. Molecular weight of PCOE was determined by the similar technique with THF as a solvent (Microgel mix (1–5 μ m) column of 300 mm \times 7.8 mm Waters Styragel HR 5).

Chemicals

All manipulations involving air- and moisture-sensitive compounds were carried out in oven-dried glassware using dry solvents and standard Schlenk and vacuum-line techniques under argon atmosphere. Monomers, norbornene (Acros Organics) and cis-cyclooctene (Aldrich), were dried over sodium, distilled, and stored under argon. The 1st generation Grubbs catalyst

$\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$ (Aldrich) was used without further purification as 0.007–0.077M solutions in toluene or CHCl_3 . All other reagents and solvents were purchased from Aldrich and used as received or purified according to standard procedures.

Polymer Synthesis

Polyoctenamer (PCOE). *Cis*-cyclooctene (3.58 g, 32.6 mmol) was added to the 1st generation Grubbs catalyst (38.3 mg, 0.0465 mmol) solution in CH_2Cl_2 (12.2ml) prepared in a round-bottomed glass flask (50ml) equipped with a magnetic stirrer under an inert atmosphere at 20 °C. The polymerization was stopped by the addition of 0.3ml of ethyl vinyl ether after 2 h. The polymers were precipitated in a 0.1% acetone solution of an antioxidant 2,2'-methylenebis(6-tert-butyl-4-methylphenol) (**I**), decanted, washed with several portions of the same solution, and dried under reduced pressure at room temperature until constant weight. The yield was 2.72 g (76%). Polymer (1 g) was dissolved in 0.4% THF solution of HCl (30 ml), stirred for 4 h and precipitated in a 0.1% ethanol solution of an antioxidant **I**, decanted, washed with several portions of the same solution, and dried under reduced pressure at room temperature until constant weight. Just before the cross-metathesis, 0.9M polymer solution in CHCl_3 was passed through column with SiO_2 (SiO_2 :PCOE=8:1, wt) and precipitated in ethanol, decanted, washed with several portions of the ethanol, and dried under reduced pressure at room temperature until constant weight.

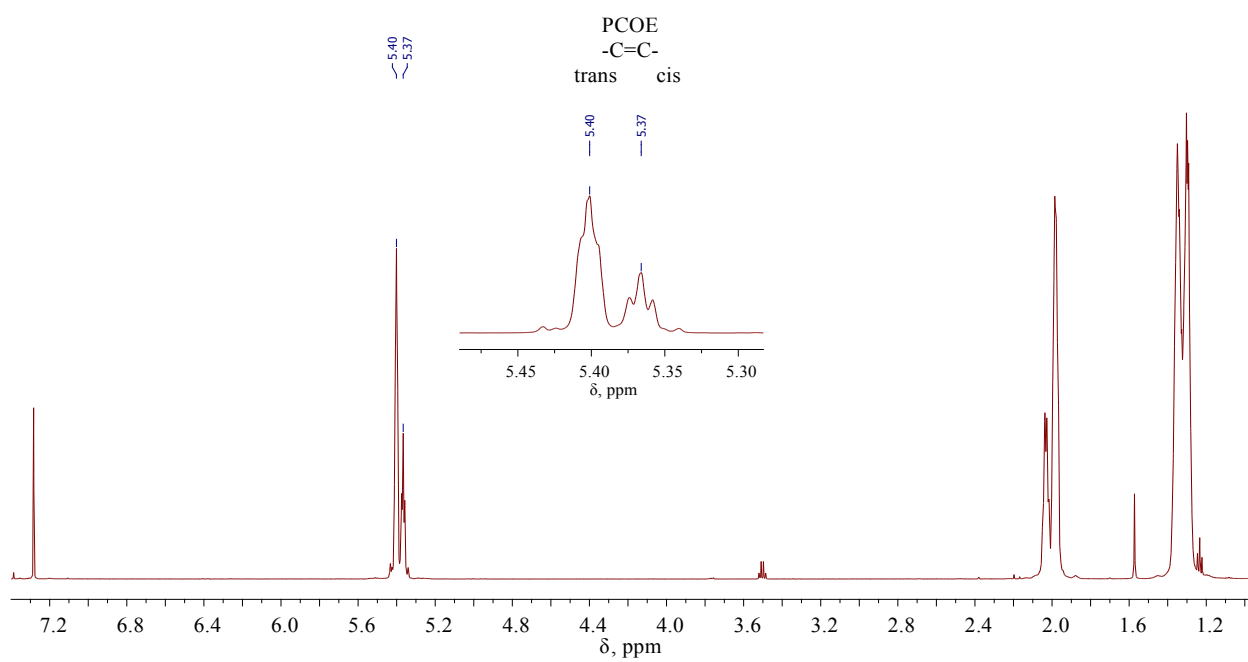
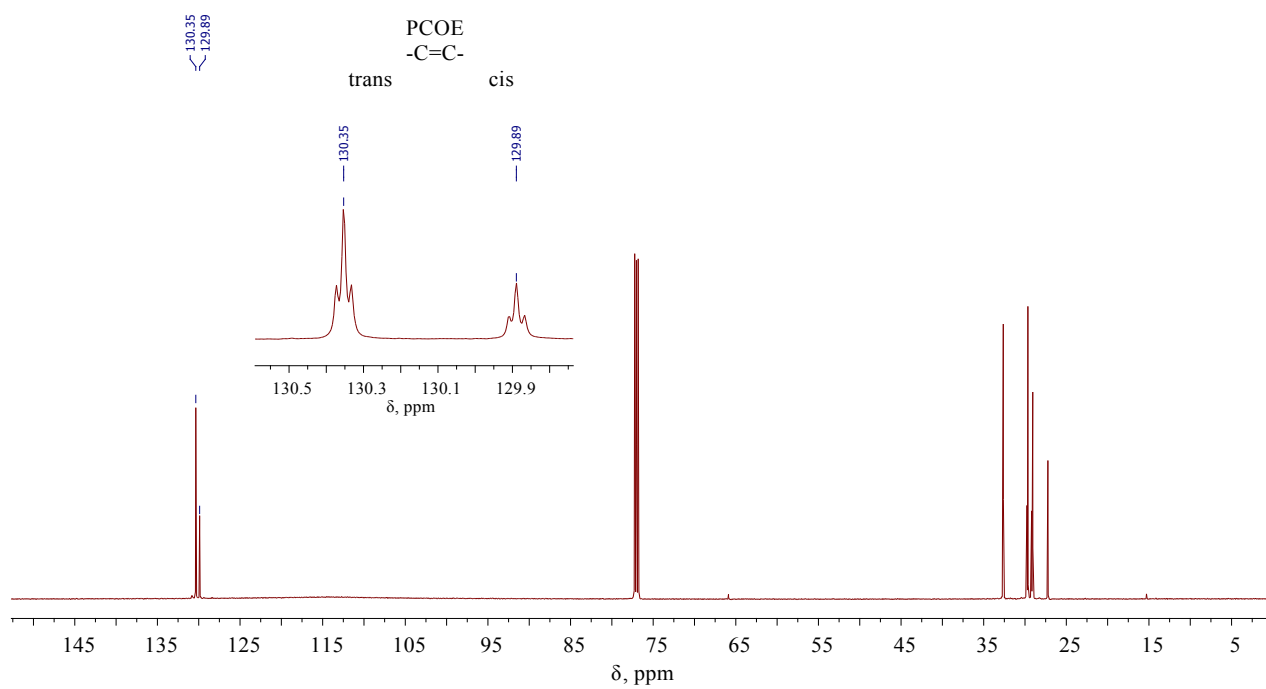
$M_n = 144000 \text{ g mol}^{-1}$, $M_w/M_n = 1.8$.

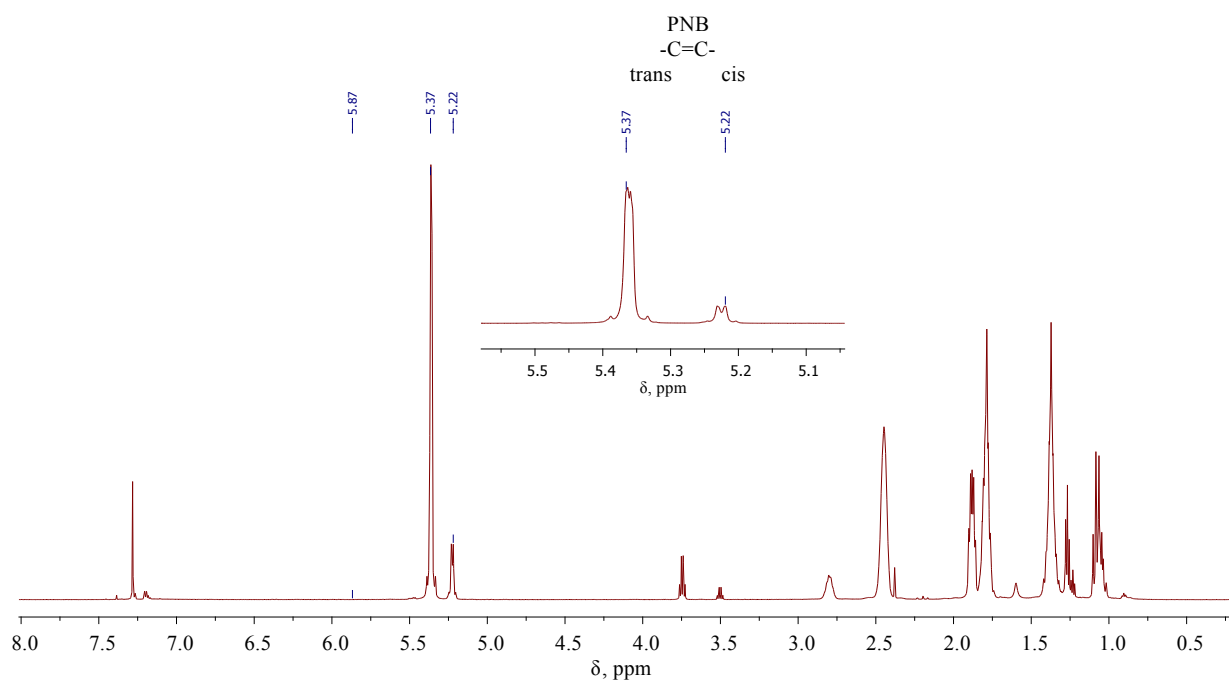
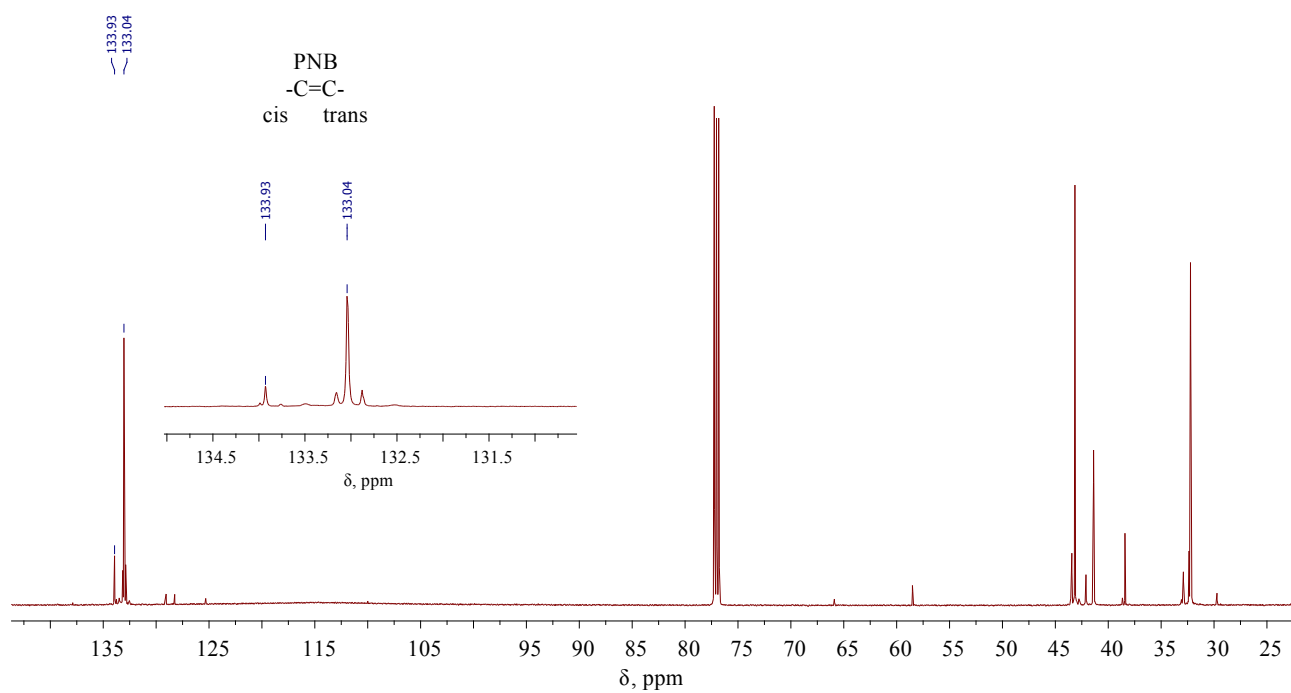
Polynorbornene (PNB). 8.1 mL of 3.2M solution of norbornene (2.44 g, 26 mmol) in toluene was added to the 1st generation Grubbs catalyst (42.8 mg, 0.052 mmol) solution in toluene (24.5 ml) prepared as described above. The polymerization was stopped by the addition of 0.4 ml of ethyl vinyl ether after 1 h. The polymers were precipitated in a 0.1% ethanol solution of an antioxidant **I**, decanted, washed with several portions of the same solution, and dried under reduced pressure. The polymer was twice reprecipitated in ethanol from toluene solution and dried under reduced pressure at room temperature until constant weight. The yield was 2.4 g (98%). PNB was purified with HCl solution in THF and column chromatography (SiO_2) as described above. $M_n = 100000 \text{ g mol}^{-1}$, $M_w/M_n = 3.1$. The polymerization of NB mediated by Gr-1 proceeds very rapidly and inevitably involves back-biting and chain-transfer reactions. For instance, Grubbs et al. [S1] reported the formation of PNB with PDI=2.5-2.6 in just a few seconds.

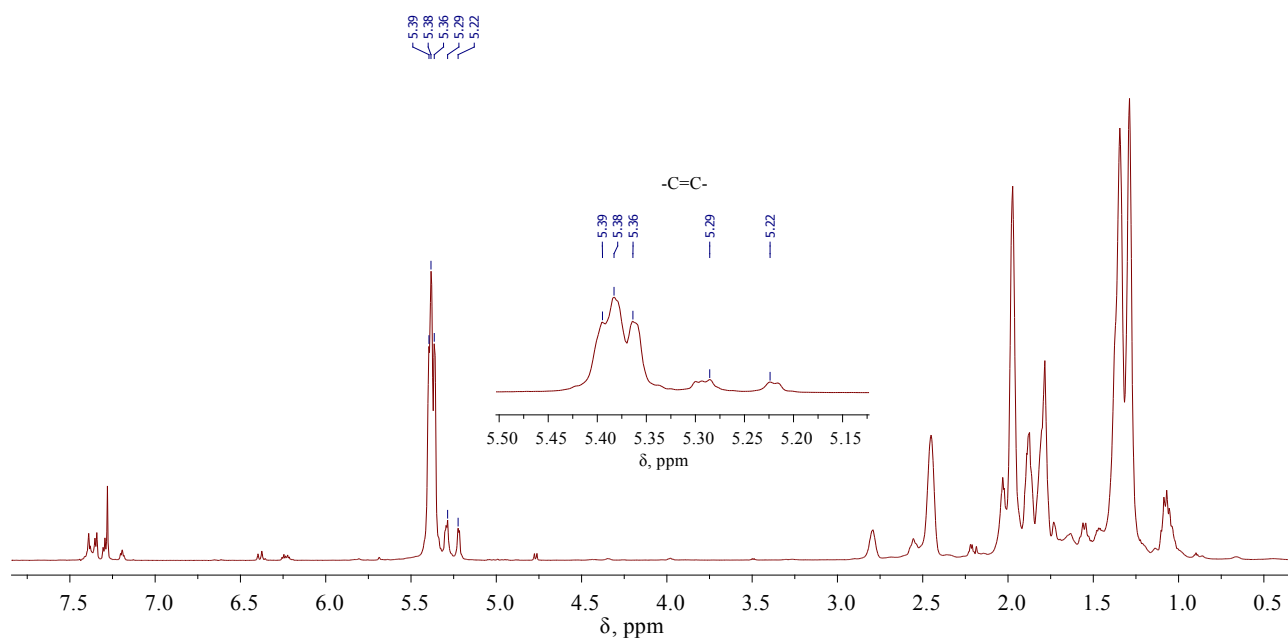
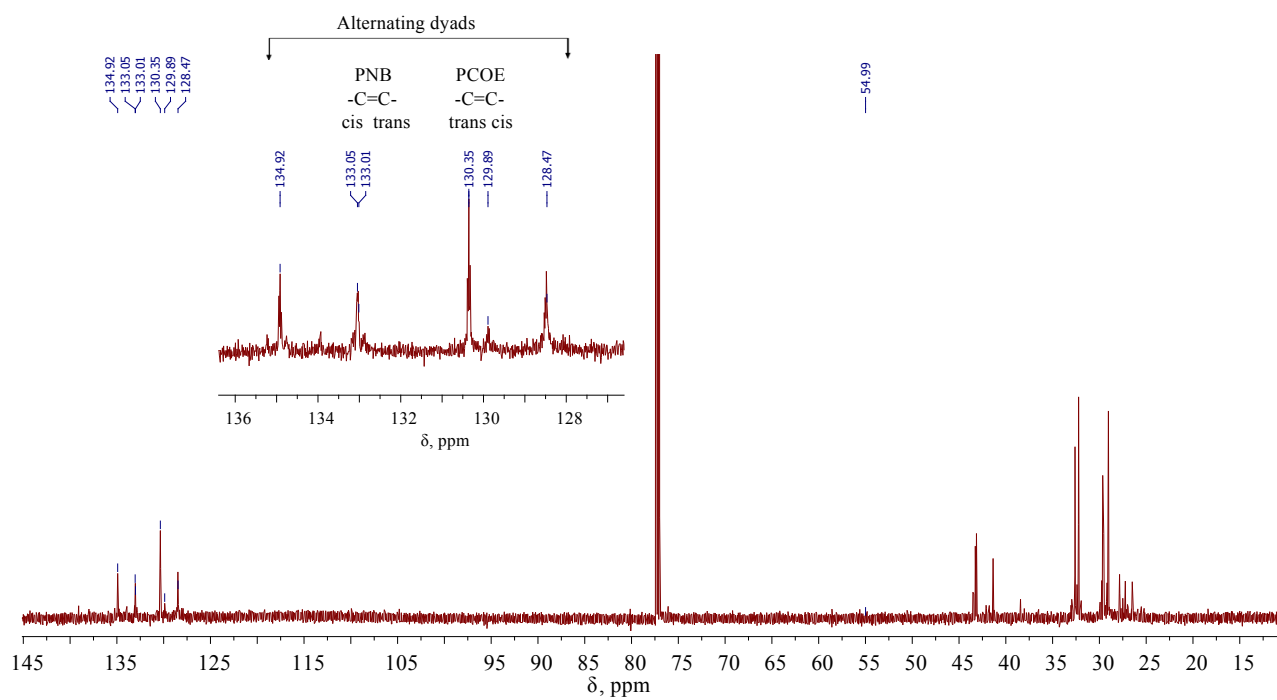
Cross-metathesis of PNB and PCOE. In a typical procedure (the example given is for the ratio [Pm]:[cat] = 100:1 mol/mol), PNB (163 mg, 1.74 mmol) and PCOE (192 mg, 1.74 mmol) were dissolved in CHCl₃ (3.5 ml) in a round-bottomed glass flask (25ml) equipped with a magnetic stirrer under an inert atmosphere at 20 °C. Then 0.007M solution of the 1st generation Grubbs catalyst (1.85 ml, 3.1·10⁻² mmol) in CHCl₃ was added under vigorous stirring. Samples for NMR analyses were obtained by adding the aliquot (0.5 ml) of reaction mixture to 0.2 ml of ethyl vinyl ether, stirred for 30-40 min at ambient temperature, and concentrated in vacuum, after that CDCl₃ was added. For DSC and GPC measurements, the polymers were precipitated in ethanol and dried as described above.

References:

S1. P. Schwab, R. H. Grubbs, and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100.

Sup. 1. ^1H NMR spectrum of PCOESup. 2. ^{13}C NMR spectra of PCOE

Sup. 3. ¹H NMR spectrum of PNBSup. 4. ¹³C NMR spectrum of PNB

Sup. 5. ^1H NMR spectrum of NB-COE copolymerSup. 6. ^{13}C NMR spectrum of NB-COE copolymer