

*Appendix B*POLYMER SYNTHESIS OF END-FUNCTIONAL
POLYCYCLOOCTADIENE

All methods contained within written and performed by Hojin Kim.

B.1 Experimental Methods**Materials**

All chemical reagents were obtained at 98-99% purity from Sigma-Aldrich or Alfa Aesar, unless specified otherwise. Magnesol®XL was purchased from The Dallas Group of America, Inc. ZSM-5 used was NH₄-ZSM-5, SiO₂:Al₂O₃ = 50:1 (Alfa Aesar). ¹H-NMR spectra were recorded in CDCl₃ or DMSO-d₆ (Cambridge Isotope Laboratories) using a Varian Inova 500 spectrometer (500 MHz) with 128 scans. The molecular weights and dispersity index of the polymers were determined on a GPC system with a Wyatt DAWN EOS multi-angle laser light scattering detector ($\lambda=690\text{nm}$), a Waters 410 differential refractometer (RI) ($\lambda=930\text{nm}$), and four Agilent PLgel columns (pore size 103, 104, 105, and 106 Å) connected in series. THF was used as the eluent at the flow rate of 0.9mL/min with a temperature of 35°C. The data were analyzed using Wyatt Astra Software (version 5.3.4) using the Zimm fitting formula with $dn/dc = 0.125 \text{ mL/g}$ for PCOD in THF to obtain weight-average molecular weight (M_w) for each polymer reported.

**Purification of Cyclooctadiene Monomer by Hydroboration with
BH₃·THF**

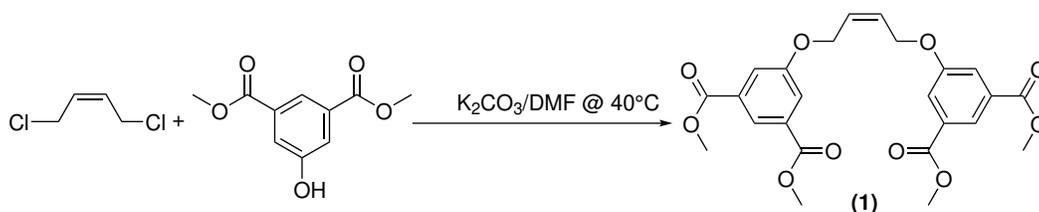
Representative procedure adapted from Ji and coworkers,¹ with the Magnesol®XL treatment of Wei and coworkers' procedure.² Instead of drying

Magnesol®XL with CaH_2 as in Wei and coworkers' procedure, Magnesol®XL was heated and vacuum-dried to remove moisture in this work.

Redistilled-grade cis-1,4-COD (66.7 g, 0.62 mol) was syringe transferred to a Schlenk flask in an ice bath under argon. 1M $\text{BH}_3 \cdot \text{THF}$ complex (108 ml, 0.11 mol) was slowly added into the flask. The flask was left to stir under argon at room temperature overnight. THF was evaporated under reduced pressure at room temperature until the concentration of residual THF in the mixture was below 300 ppm (verified by $^1\text{H-NMR}$ analysis). The COD was vacuum distilled from the mixture at 40°C . In a separate Schlenk flask, 9 g of Magnesol®XL (pre-dried under vacuum at 100°C) was added with a stir bar, and the air in the flask was removed via vacuum and the flask filled with argon. The distilled COD was syringe transferred into the Magnesol®XL and stirred under argon at room temperature overnight. After stirring with Magnesol®XL, the COD was vacuum distilled again from the Magnesol®XL mixture to a Schlenk flask in a dry-ice tub. After distillation, the flask was sealed with a Suba-Seal rubber septum under continuous argon flow, and stored in a freezer at -30°C . The purified COD was weighed to determine yield (35.3 g, 0.33 mol, 53.4% yield) and vacuum distilled again prior to use.

Purification of COD Monomer by ZSM-5

In a Schlenk flask, 2.5 g of Magnesol®XL, and 3.6 g of ZSM-5 were added without a stir bar. To remove water, the mixture of particles was dried overnight under vacuum at 100°C . After cooling the flask to room temperature, a stir bar was added and the flask was sealed with a Suba-Seal rubber septum, evacuated, and filled with argon. To the sealed flask, as-received redistilled-grade COD (26.5 g, 0.24 mol) was syringe transferred, and stirred at room temperature overnight. The COD was then vacuum distilled from the mixture to a



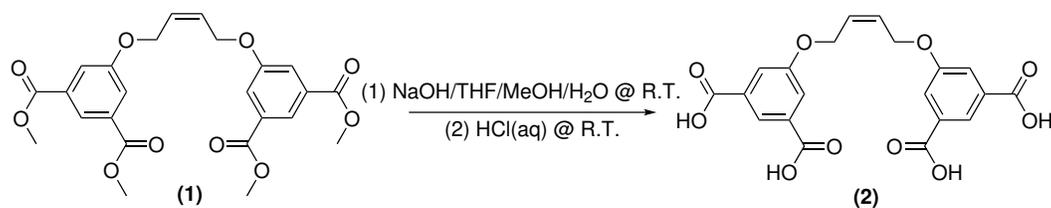
Scheme B.1: Reaction of dimethyl 5-hydroxyisophthalate and *cis*-1,4-dichloro-2-butene to form a tetra methyl ester intermediate, product (1).

Schlenk flask in a dry-ice tub. After distillation, the flask was sealed with a Suba-Seal rubber septum under continuous argon flow, and stored in a freezer at $-30^\circ C$. The purified COD was weighed to determine yield (25.2 g, 0.23 mol, 96.0% yield) and vacuum distilled again prior to use.

Synthesis of Tetra Methyl Ester Intermediate (1)

Dimethyl 5-hydroxyisophthalate (7.28 g, 34 mmol) and dry K_2CO_3 (7.06 g, 51 mmol) were weighed and loaded into a round-bottom flask (RBF). DMF (60 ml) was added into the flask, followed by *cis*-1,4-dichloro-2-butene (2.00 g, 15.3 mmol). The RBF was placed in an oil bath at $40^\circ C$ and stirred overnight (Scheme B.1). The reaction mixture was poured into a separatory funnel, diluted with DCM (120 ml), washed with water (120 ml), and then 4 times with 1M HCl(aq) (120 ml each wash). The resultant organic phase was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum at room temperature. The crude product was purified by recrystallization in ethanol (40 ml) in the refrigerator overnight to yield analytically pure product (6.0 g, 12.7 mmol, 83.0% yield) as white crystals after filtration and solvent removal.

Tetra Methyl Ester Intermediate (1): 1H -NMR ($CDCl_3$, 500 MHz) 3.94 (s, 12H), 4.78 (d, 4H), 5.99 (t, 2H), 7.76 (d, 4H), 8.30 (t, 2H).



Scheme B.2: Hydrolysis of product (1) to produce product (2), di-acid chain transfer agent (DA-CTA).

Synthesis of Di-Acid ended CTA, (DA-CTA) (2)

NaOH pellets (1.18 g, 0.030 mol) were dissolved in DI-water (6 ml) in a RBF, and methanol (12 ml) was added. The tetra methyl ester intermediate (1) (1 g, 2.1 mmol) was dissolved in THF (18 ml) in a separate container, and added slowly to the RBF. The mixture was stirred at room temperature overnight. Next, 1M HCl(aq) (40 ml) was added slowly into the RBF (Scheme B.2). The reaction mixture was poured into a separatory funnel, diluted with ethyl acetate (125 ml), and then washed twice with water (120 ml each wash). The resultant organic phase was dried over MgSO₄ and filtered, and the solvent was removed under vacuum at room temperature to yield analytically pure product (0.76 g, 1.8 mmol, 86.0% yield).

DA-CTA (2): ¹H-NMR (DMSO-d₆, 500 MHz) 4.89 (d, 4H) 5.91 (t, 2H), 7.68 (d, 4H), 8.06 (t, 2H), 13.28 (br, 2H, OH).

Synthesis of macro CTAs (mCTAs)

DA-CTA (2) (415.5 mg, 0.99 mmol) and 2,6-di-tert-butyl-4-methylphenol (BHT, 0.1 g, 0.45 mmol) were dissolved in THF (10 ml) in a Schlenk flask. The dissolved solution was degassed by 3 freeze-pump-thaw cycles and filled with argon. To the degassed mixture, 1 ml of degassed THF solution of second generation Grubbs Catalyst (G2, 8.4 mg, 9.89 μmol) was syringe transferred, immediately followed by addition of degassed, freshly vacuum distilled puri-

fied COD (5.0 g, 45.8 mmol). The mixture was stirred at 40°C overnight. The reaction was stopped by exposure to the air, and diluted with THF (40 ml). The polymers were precipitated by adding the THF solution drop-wise to a large excess of methanol. Methanol was decanted, and the polymers were collected in a vial with a silicone/PTFE septum cap, and dried under high vacuum. The vial was degassed by 3 cycles of evacuating/filling argon, and stored at -30°C. An mCTA for non-associative end groups was synthesized similarly using cis-2-hexene in place of DA-CTA, with same monomer:CTA molar ratio.

Polymerization Procedure without a CTA

A representative procedure for polymerization without a CTA is presented here. Additional polymerizations were also conducted with catalyst loadings of 0.5, 2, and 3 times the amount presented below at full conversion (and 0.5 times at partial conversion), while keeping the concentrations of all other components constant. BHT (0.1 g, 0.45 mmol) was added to a Schlenk flask, and dissolved in THF (10 ml). THF solution was degassed by 3 freeze-pump-thaw cycles and filled with argon. In a separate vial, a degassed THF solution of **G2** (1 mg/ml) was prepared, and 0.19 ml (0.224 μ mol) of this solution was syringe transferred into the Schlenk flask, immediately followed by addition of degassed, freshly vacuum-distilled COD (5.0g, 45.8 mmol). For full conversion, the mixture was stirred at 40°C overnight. For partial conversion, the reaction was stopped either at 8 minutes for 400,000 COD/**G2** molar ratio or 16 minutes for 200,000 COD/**G2** by opening the Schlenk flask to expose the reaction mixture to air and diluting it in non-degassed solvent. A small aliquot was diluted with a large excess of deuterated chloroform for ^1H NMR analysis. The remainder (approximately 15ml) was diluted with 50ml non-degassed THF.

The polymer was recovered by pouring the THF solution into acetone (600 mL) for precipitation. The resulting polymers were stored as described previously.

Telechelic PCOD

Telechelic PCOD was synthesized following same procedure for the synthesis of mCTA, using mCTA instead of CTA. All telechelic polymers used in this study were synthesized using 5 g of COD, 0.16 ml of 1 mg/ml **G2** THF solution, 0.1 g of BHT, and 10 ml of THF, with COD/mCTA molar ratios of 390, 950, 2000, 3200, 6500, 8400, and 14000.

B.2 Characterization of Materials

Purification of Cyclooctadiene

To demonstrate removal of VCH by both hydroboration and zeolite treatment methods, NMR spectra were acquired before and after purification (Figure B.1). VCH peaks appeared in the untreated COD (Figure B.1a), while residual VCH after purification (Figure B.1b and c) was below the detection limit of 100 ppm.¹ After purification, the yield of COD was less than 55% for hydroboration and greater than 95% for the zeolite treatment.

Control and Accessible Range of Polycyclooctadiene Molecular Weight

Using hydroboration-purified COD, in polymerizations spanning a broad range of COD/catalyst and COD/CTA ratios, the highest PCOD weight average molecular weight (M_w) synthesized was 240 kg/mol (degree of polymerization, $DP \sim 2500$, number average molecular weight, M_n , of 145 kg/mol) at full conversion with no CTA. Under the same conditions, zeolite-purified COD provided M_w greater than 2 Mg/mol ($M_n > 1.3$ Mg/mol). Access to even higher molecular weight non-associative PCOD was achieved with zeolite-purified COD by stopping the reactions at low conversions, reaching M_w in

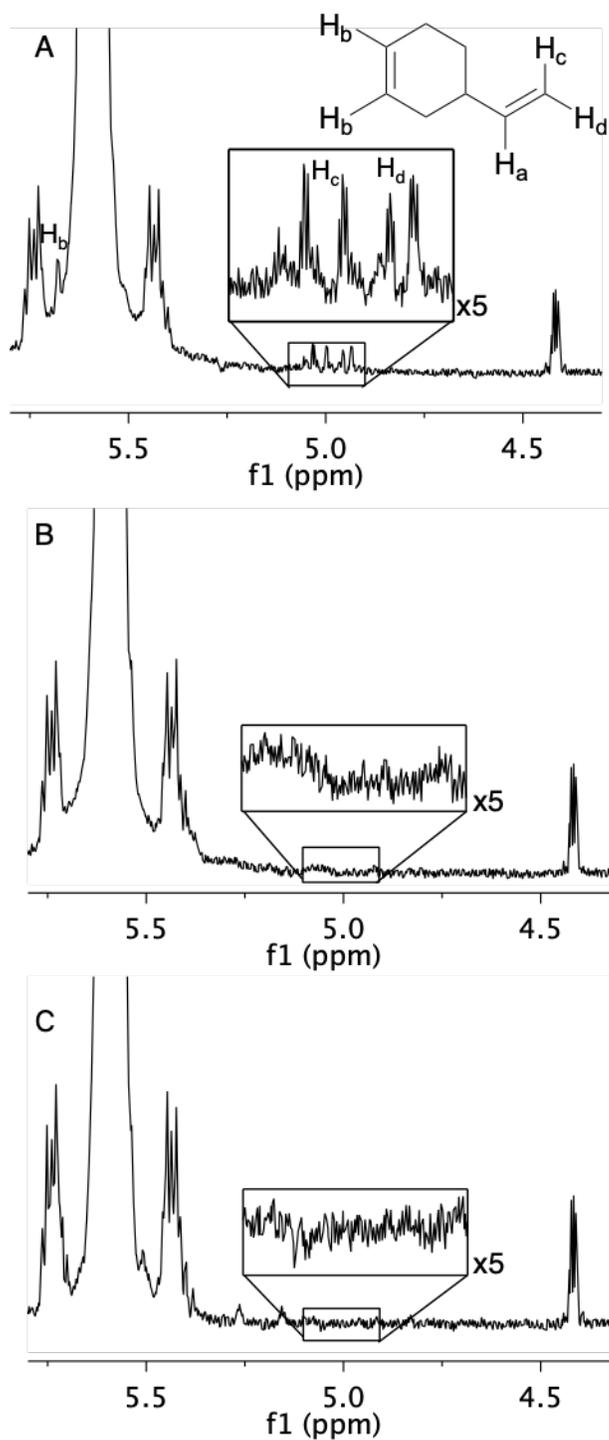


Figure B.1: (A) $^1\text{H-NMR}$ spectrum of untreated cyclooctadiene (COD) with VCH peaks at 5.67, 5.03, 5.00, 4.95, and 4.93 ppm, with labeled structure of VCH.¹ (B) $^1\text{H-NMR}$ spectrum of COD following treatment by hydroboration. (C) $^1\text{H-NMR}$ spectrum of COD following treatment by zeolite. Insets show 5x magnification of 5.1-4.9 ppm region.

Table B.1: Low Reaction Time Polymerizations

Catalyst (molar ppm)	Reaction Time (min)	Conversion (%)	Trans/Cis Ratio	M_n (Mg/mol)	M_w (Mg/mol)	\bar{D}
2.5	8	7	20/80	2.48	3.53	1.43
2.5	8	7	19/81	2.47	3.49	1.41
2.5	32	99	60/40	0.93	1.38	1.48
5	16	33	25/75	1.73	2.94	1.70
15	4	99	70/30	0.47	0.69	1.47

excess of 3 Mg/mol (M_n 2.5 Mg/mol) at the highest COD/catalyst ratio (Figure B.2).

With hydroboration-purified COD, control of molecular weight using COD/CTA ratio only extended to a COD/CTA ratio of ~ 3000 (Figures B.2 and B.3). In contrast, using zeolite-purified COD, control of telechelic polymers extended to M_w over 1 Mg/mol (M_n over 740 kg/mol). The weight-average molecular weights produced from zeolite-purified COD were well fit by a logarithmic regression, with an equation $M_w[g/mol] = 390(COD/CTA)^{0.83}$ (Figure B.2), where the 95% confidence interval for the exponent was [0.80,0.87] and for the prefactor was [280, 530] (g/mol). In ROMP of COD, in addition to elongation of linear chains, there is also competing intramolecular secondary metathesis that generates small cyclic oligomers (backbiting) resulting in approximately 15% loss of COD to form small cyclic species.³

Reactions stopped at short time² to look for molecular weights achievable at low conversion are summarized in Table B.1.

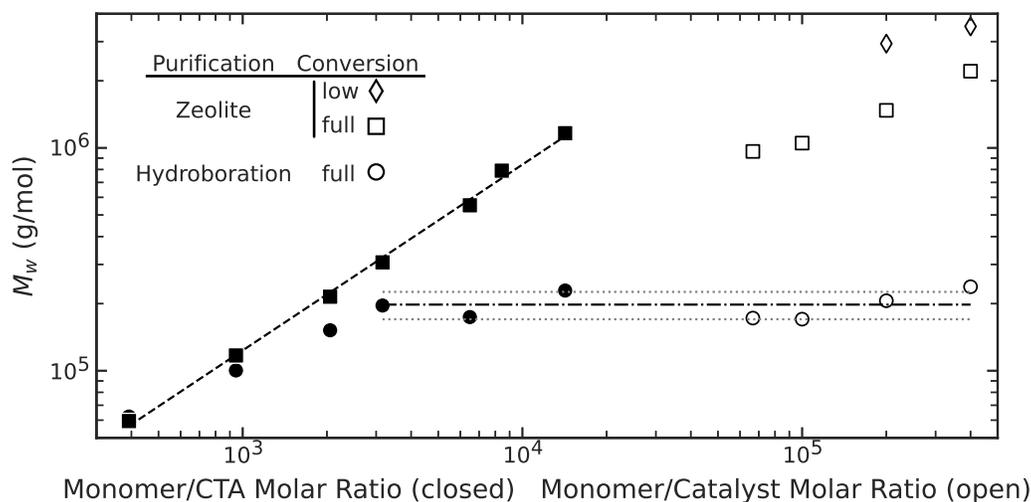


Figure B.2: Weight-average molecular weight (M_w) of polymers produced with (closed symbols) and without (open symbols) chain transfer agent (CTA) plotted as a function of monomer/catalyst molar ratio and a function of monomer/CTA molar ratio, respectively. Squares and circles indicate polymers produced from zeolite-purified and hydroboration-purified cyclooctadiene (COD), respectively, at full monomer conversion. Diamonds indicate polymers produced from zeolite-purified COD terminated at low conversion. Dashed line represents the power law regression of the molecular weights produced from zeolite-purified COD, $M_w[g/mol] = 390(COD/CTA)^{0.83}$, where COD/CTA is the monomer-to-CTA molar ratio. Dash-dotted line represents the average of the seven highest M_w obtained using hydroboration-purified COD (dotted lines above and below represent one standard deviation from this average, our best estimate of the uncertainty of the molecular weights represented in this figure).

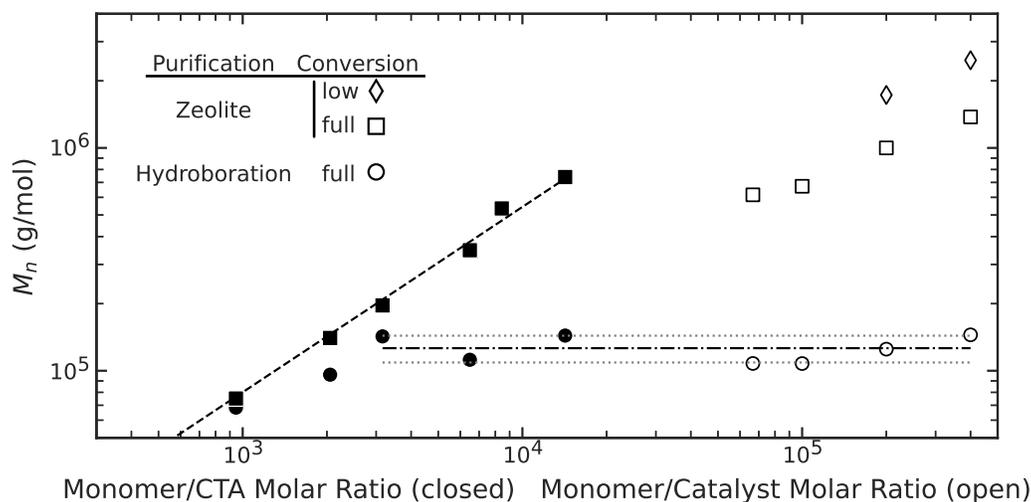


Figure B.3: Number-average molecular weight (M_n) of polymers produced with (closed symbols) and without (open symbols) chain transfer agent (CTA) plotted as a function of monomer/catalyst molar ratio and a function of monomer/CTA molar ratio, respectively. Squares and circles indicate polymers produced from zeolite-purified and hydroboration-purified cyclooctadiene (COD), respectively, at full monomer conversion. Diamonds indicate polymers produced from zeolite-purified COD terminated at low conversion. Dashed line represents the power law regression of the molecular weights produced from zeolite-purified COD, $M_n(g/mol) = 260(COD/CTA)^{0.83}$, where COD/CTA is the monomer-to-chain transfer agent molar ratio. Dash-dotted line represents the average of the seven highest M_n obtained using hydroboration-purified COD (dotted lines above and below represent one standard deviation from this average representing our best estimate of the uncertainty of the molecular weights represented in this figure).

References

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- [3] H. Martinez et al. “Ring-Opening Metathesis Polymerization of 8-Membered Cyclic Olefins”. In: *Polymer Chemistry* 5.11 (2014), p. 3507. ISSN: 1759-9954, 1759-9962. DOI: 10.1039/c3py01787g. URL: <http://xlink.rsc.org/?DOI=c3py01787g> (visited on 03/25/2019).

Appendix C

END-GROUP FIDELITY: SUPPLEMENTAL SAMPLE AND RHEOLOGY INFORMATION

C.1 Samples for Solution Rheology

High Concentration Samples

Table C.1 characterizes the polymers dissolved in decahydronaphthalene with measured viscosities shown in Figures 5.2-5.6.

Low Concentration Samples

Table C.2 characterizes the polymers dissolved in decahydronaphthalene with measured viscosities shown in Figures 5.7 and 5.8.

C.2 Viscosity of Similar Molecular Weight Polymers from Hydroboration-treated COD

In Figures 5.7 and 5.8, we compared the specific viscosities of the highest molecular weight samples produced from hydroboration- and zeolite-treated

Table C.1: Polymer Samples for High Concentration Solution Rheology

purification method	M	end-group	trans/cis ratio	M_n (Mg/mol)	M_w (Mg/mol)	\mathfrak{D}
ZSM-5	60k	DA	45/55	0.039	0.59	1.53
		NA	40/60	0.043	0.063	1.47
	200k	DA	33/66	0.14	0.21	1.53
		NA	42/58	0.13	0.20	1.52
hydroboration	60k	DA	46/54	0.043	0.062	1.43
		NA	43/57	0.042	0.059	1.41
	200k	DA	46/54	0.14	0.23	1.59
		NA	36/64	0.13	0.20	1.52

M : Molecular weight label,

DA: Diacid end group,

NA: Non-associative (cis-2-hexene).

Table C.2: Polymer Samples for Low Concentration Solution Rheology (COD/CTA of 14000)

purification method	end-group	trans/cis ratio	M_n (Mg/mol)	M_w (Mg/mol)	\bar{D}
ZSM-5	DA	37/63	0.74	1.16	1.57
	NA	29/71	0.65	0.95	1.45
hydroboration	DA	46/54	0.14	0.23	1.59
	NA	36/64	0.13	0.20	1.52

DA: Diacid end group,
 NA: Non-associative (cis-2-hexene).

Table C.3: DA PCOD from Hydroboration Purified COD

monomer/CTA ratio	trans/cis ratio	M_n (Mg/mol)	M_w (Mg/mol)	\bar{D}
3200	63/37	0.14	0.2	1.38
6500	53/47	0.11	0.17	1.55
14000	46/54	0.14	0.23	1.59

COD. Here, in Figure C.1, we compared the specific viscosities of three self-associative polymers from hydroboration-purified COD at a concentration of 2.5 wt%, demonstrating that the sample shown in Figure 4 (monomer/CTA of 14,000) has the highest specific viscosity of these three samples, despite having a smaller number of CTA-controlled chain ends per polymer than the samples at lower monomer/CTA. The molecular weights corresponding to each monomer/CTA ratio are displayed in Table C.3.

C.3 Intrinsic Viscosity

Intrinsic viscosity data for polycyclooctadiene in decalin were fit to the Kuhn-Mark-Houwink-Sakurada (KMHS) equation (Figure C.2).

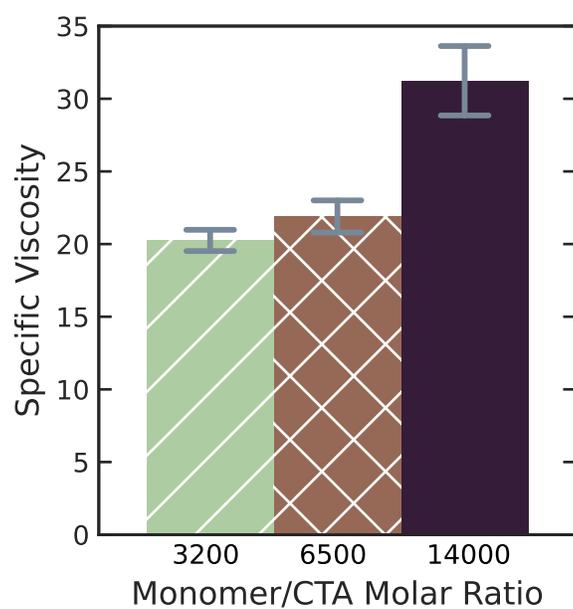


Figure C.1: Specific viscosities of solutions of three monomer/CTA molar ratios of self-associative (DA) polymers made from hydroboration-purified COD (hb) in decalin at a concentration of 2.5 wt %. Error bars represent 95% confidence interval.

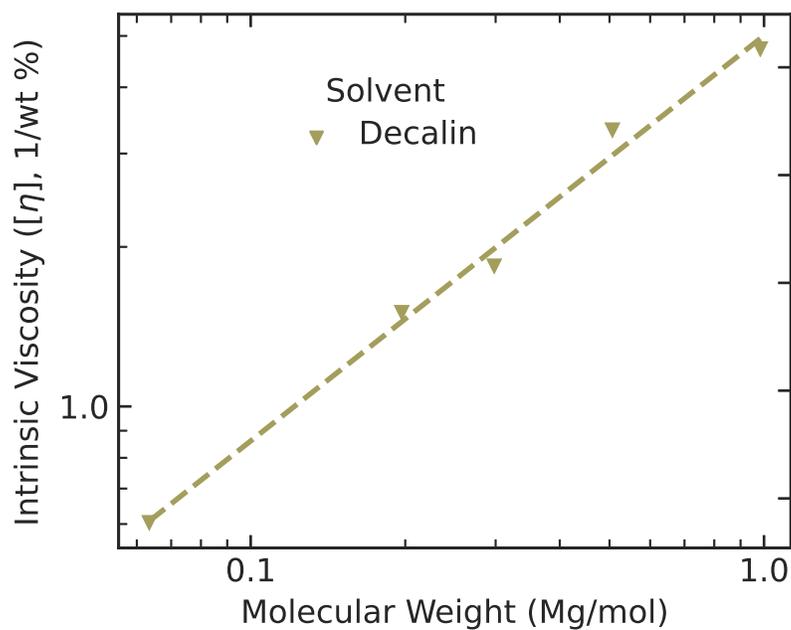


Figure C.2: Intrinsic viscosity ($[\eta]$, 1/wt %) as a function of weight-average molecular weight (M_w , g/mol) for polycyclooctadiene in decalin at 0°C (circles). Kuhn-Mark-Houwink-Sakurada equation fit to data (dashed line), $[\eta] = KM_w^a$ with $K = 1.4 * 10^{-4}$ and $a = 0.76 \pm 0.03$, with $[\eta]$ in (1/wt %) and M_w in g/mol. ($a \pm$ one standard deviation, K standard deviations were less than 10^{-8})