Chapter 5

END-FUNCTIONALITY DETECTION THROUGH SHEAR RHEOLOGY

5.1   Introduction

End-functional polymers offer diverse opportunities, from responsive drug delivery vehicles to polymer compatibilizers.[1,2] Very long associative α,ω-telechelic polymers (>40,000 backbone atoms, bba) act as highly potent additives that resist degradation while conferring turbulent drag reduction and mist control.[3,4] In hydrocarbons, like most fuels and lubricants, long end-associative polymers could improve safety and energy efficiency.[3,5] To form multi-million molecular weight supramolecules at the low concentrations (i.e., <0.2 wt %) relevant to drag reduction and mist control,[3] the individual units must both be long and be successfully α,ω-functionalized, demanding end-group fidelity even at high molecular weights.[4] To produce hydrocarbon-soluble telechelic polymers of controlled molecular weights, our group has employed ring-opening metathesis polymerization (ROMP) of emphcis,*cis*-1,5-cyclooctadiene (COD). ROMP enables high fidelity installation of functional groups at both ends of growing chains by the use of di-functional chain-transfer agents (CTAs) and a two-step polymerization process.[5,6] Targeting long chains with low additive loading by mass points to ROMP monomers with all of the heavy atoms in the backbone (e.g., cyclobutene, cyclooctene, and cyclooctadiene). For comparison to other polymers that have been extensively studied and used in hydrocarbons, the mass of polymer per bba is 85 g/mol for polyhexylmethacrylate, 80 g/mol for poly(t-butyl-styrene), 29 g/mol for polyisobutylene, and a mere 13 g/mol for polycyclooctadiene (PCOD). Among the atom-efficient candidate

cycloolefins for ROMP, COD (Figure 5.1a) has the advantages of high ring strain paired with good hydrocarbon solubility in the final product.

Although ROMP of COD has been used previously to prepare a variety of telechelic PCODs,[5,7–10] high molecular weight telechelic polymers (>500 kg/mol) with high end group fidelity were often inaccessible due to COD's isomer, 4-vinylcyclohexene (VCH) (Figure 5.1b), historically a common contaminent in commercially available COD.[5,11,12] The pendant vinyl group of VCH acts as an undesired CTA during ROMP of COD, terminating a growing chain[5,11] and leaving a non-functional end. Separation of the isomers, VCH and COD, is difficult at a lab-scale because of their close boiling points (131 and 150 °C, respectively, at atmospheric pressure).[5,12] Repeated distillations can reduce VCH levels to approximately 1000 ppm, limiting the average degree of polymerization (DP) to $\sim$1000 (8000 backbone atoms).[5] To produce telechelic PCOD with $>$ 40,000 bba (DP $>$ 5000) requires less than one unintentional chain transfer per 50,000 monomers incorporated ($<$ 20 ppm VCH), motivating removal of VCH and subsequent validation of end-groups post-polymerization.

As molecular weight increases, traditional methods of detecting end-group fidelity, like nuclear magnetic resonance (NMR), become less able to distinguish between di-telechelic, mono-telechelic, and non-functional polymers due to the small number of end-group atoms compared to the backbone.[13,14] In this work, we detect the relative extent of α,ω-functionalization by using shear rheology to characterize the polymers produced from COD where VCH was removed by two different methods—competitive hydroboration of VCH and COD, the route recommended by the literature,[5] and molecular sieving by a zeolite, ZSM-5 (Figure 5.1c).[15–17]
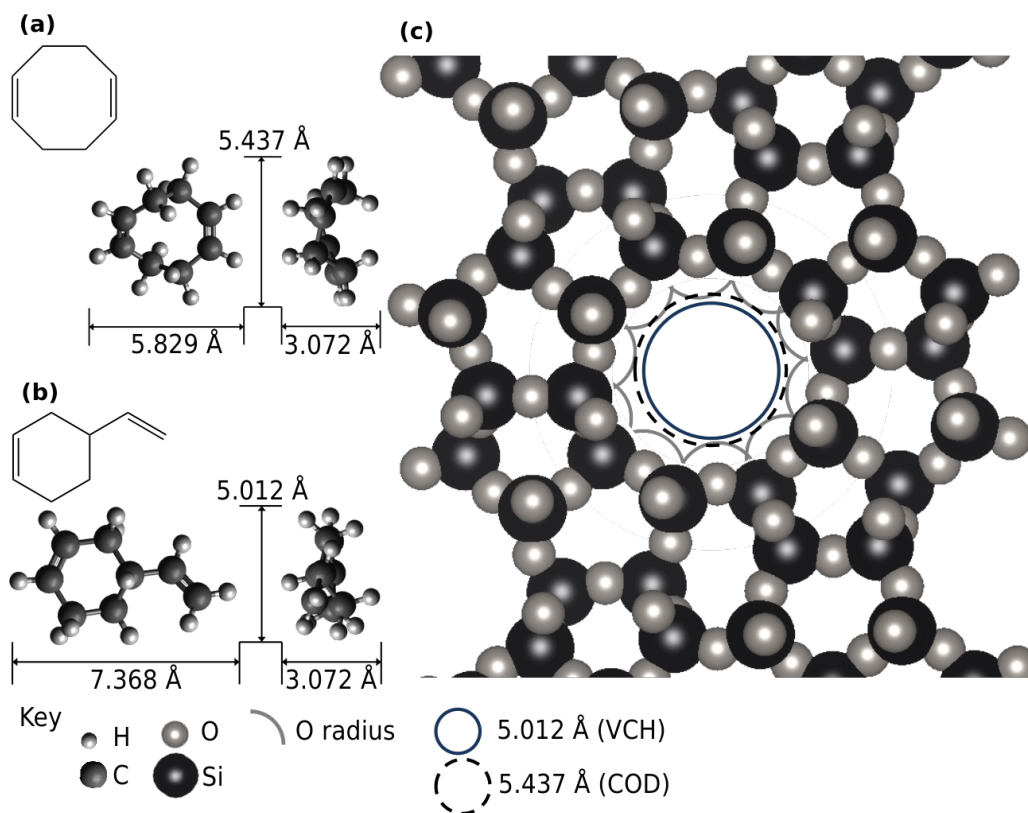
Figure 5.1: (a) Chemical structure and ball-and-stick model of cyclooctadiene (COD) demonstrating molecular dimensions of 5.437 Å by 5.829 Å by 3.072 Å. (b) Chemical structure and ball-and-stick model of 4-vinylcyclohexene (VCH) demonstrating molecular dimensions of 5.012 Å by 7.368 Å by 3.072 Å. COD and VCH ball-and-stick models optimized in Avogadro.[18,19] (c) Structure of a representative layer of ZSM-5, showing the opening of the straight channel pores, which are 5.4-5.6 Å wide.[20] Structure drawn in VESTA.[21] Gray arcs represent an oxygen radius of 1.52 Å,[20] black dashed circle represents a 5.437 Å diameter circle corresponding to the size of COD, blue solid circle represents a 5.012 Å diameter circle corresponding to the size of VCH.

5.2   Experimental Section

Treatment of COD and Synthesis of PCOD

Treatment of COD and synthesis of all PCOD samples were performed by Hojin Kim. See Appendix B.

PCOD Solutions in Decahydronaphthalene for Rheology

Solutions of PCOD in decahydronapthalene (decalin), a solvent with similar unsaturation to fuel with relatively low volatility and limited interference with hydrogen-bonding, were prepared for rheology by Hojin Kim. Approximately 10 ml of decahydronapthalene (mixture of *cis + trans*) was poured into a 20 ml glass vial with PTFE lined cap and the solvent weight was recorded. To this, 0.01 g of BHT and an appropriate amount of PCOD for the desired concentration were added with a stir bar. The head space was purged with argon, and the cap was sealed with parafilm. The mixture was stirred at 60°C for 4-12 hours and used for rheological experiments within 2 days.

Shear Rheological Measurements

Shear viscosity measurements were performed on an Anton Paar MCR 302 WESP rheometer using a cone-and-plate fixture of 50 mm diameter and 2.007° angle, with a truncation of 0.207 mm. Samples were loaded by depositing 1.1 mL of the sample on the center of the plate, lowering the cone to 0.217 mm, removing excess to create a flat edge, and then lowering to 0.207 mm to create a spherical edge condition. The plate was cooled to 0 ± 0.1 °C using a Peltier plate to regulate temperature and reduce volatility and samples were allowed to thermally equilibrate and relax for 5 min. Shear rate sweeps were performed from 0.1 1/s to 100 1/s for solutions with concentrations above 1 wt % and from 1 to 100 1/s for concentrations below 1 wt %. The sample edge was examined to check for evidence of evaporation and none was observed.

5.3 Results

Rheological Consequences of Monomer Purity for Low Molecular Weight Telechelic Polycyclooctadiene

The viscosities of non-associative and self-associative polymers made using hydroboration and molecular sieving methods were measured at concentrations of 1.2, 1.5, 2.0, and 2.5 wt% in decalin (Figures 5.3-5.2).

Gelation and gel fracture was observed for self-associative polymers at a molecular weight of 60 kg/mol at all concentrations from both purification methods and at a molecular weight of 200kg/mol at 2.5 wt% for polymers from hydroboration-treated COD and at 2.0 wt% and 2.5 wt% for polymers from zeolite-treated COD (noted by hollow symbols in Figure 5.2). Gel fracture was characterized by the sample ejecting from the gap between the cone and plate and moving on top of the cone, resulting in the appearance of significant shear thinning in the recorded viscosities. These results are in line with network formation previously observed for DA PCOD in decalin.[22]

The peak specific viscosities for non-associative polymers at the same molecular weight and concentration were not statistically significantly different across purification methods at 95% confidence (Figures 5.3 and 5.4). Enhancements in the viscosity of the self-associative polymer solutions compared to non-associative polymer solutions at 60 kg/mol were substantial, reaching over 100,000% the viscosity of the equivalent non-associative solution at 2.5 wt% (Figure 5.5). At 60 kg/mol, self-associative telechelic polymers from zeolite-treated COD (z, DA) demonstrated statistically significantly higher enchancement than self-associative telechelic polymers from hydroboration-treated COD (hb, DA) for concentrations of 1.2 wt%, 1.5 wt%, and 2.0 wt%. Enhancements in the viscosity of the self-associative polymer solutions compared to non-associative polymer solutions at 200 kg/mol were significant (Fig-

ure 5.6), but less than at 60 kg/mol, resulting in lower specific viscosities for solutions of self-associative polymers at 200 kg/mol than 60 kg/mol at the same concentration (Figures 5.3 and 5.4). At 200 kg/mol, self-associative telechelic polymers from zeolite-treated COD (z, DA) demonstrated statistically significantly higher enchancement than self-associative telechelic polymers from hydroboration-treated COD (hb, DA) for concentrations of 1.5 wt%, 2.0 wt%, and 2.5 wt%.

Rheological Consequences of End-groups at Low Concentration

The highest accessible molecular weight is of particular importance for enhancing rheological properties using a low polymer concentration of end-associative polymers.[3,4] Therefore, we compared solution viscosity at concentrations less than or equal to 0.15 wt% of the highest molecular weight telechelic polymers made from hydroboration- and zeolite-treated COD (M_w ~200 kg/mol and ~1000 kg/mol respectively, see Appendix B for details on molecular weights). No shear thinning or gelation was observed in the shear rate range tested for these samples. The enhancement of the shear viscosity relative to the solvent alone, i.e., the specific viscosity, was consistently greater for z, DA than hb, DA (Figure 5.7): ($\eta_{z,DA}/\eta_{hb,DA}$) is 260 % ± 50% at 0.15 wt% and 350% ± 27 % at 0.10 wt% when compared to the longest DA-ended telechelic polymer from hydroboration-treated COD. A subtle but significant feature was the similarity between the non-associative and self-associative counterparts obtained using hydroboration-treated COD—in contrast to the greater viscosity for z, DA than for its non-associative counterpart (Figure 5.8). In summary, z, DA demonstrated significant enhancement of shear viscosity at low concentrations compared to both hb, DA and non-associative PCOD of similiar molecular weight.
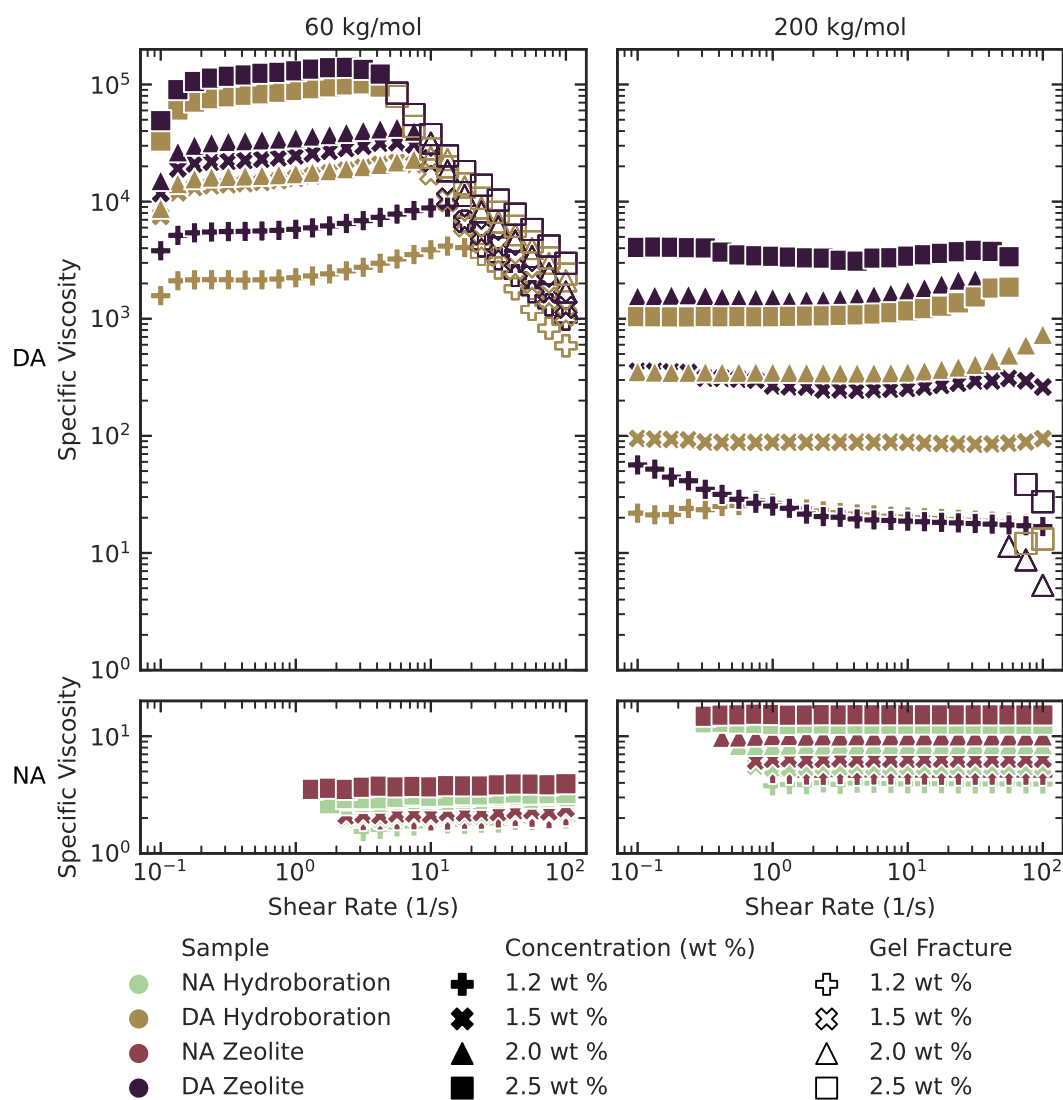
Figure 5.2: Specific viscosities as a function of shear rate of solutions of (bottom) non-associative (NA) and (top) self-associative (DA) polymers made from hydroboration-treated COD (hb) and zeolite-treated COD (z) at concentrations of 1.2 wt%, 1.5 wt%, 2.0 wt%, and 2.5 wt% in decalin with molecular weights of approximately (left) 60 kg/mol and (right) 200 kg/mol. Hollow symbols indicate gel fracture. Figures 5.3, 5.5, and 5.2 (left) depict the same data. Figures 5.4, 5.6, and 5.2 (right) depict the same data.
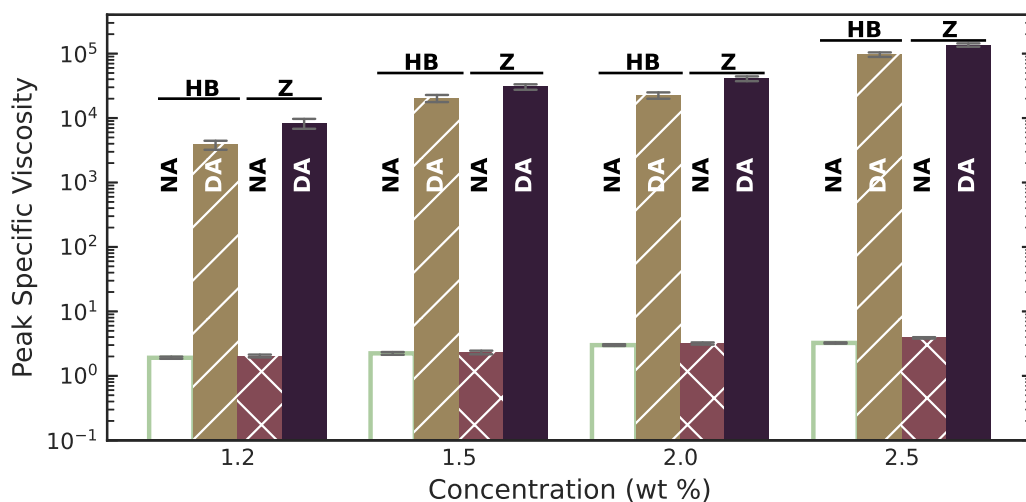
Figure 5.3: Peak specific viscosities of solutions of non-associative (NA) and self-associative (DA) polymers made from hydroboration-treated COD (hb) and zeolite-treated COD (z) at concentrations of 1.2 wt%, 1.5 wt%, 2.0 wt%, and 2.5 wt% in decalin with molecular weights of approximately 60 kg/mol. Error bars represent a 95% confidence interval. Figures 5.3, 5.5, and 5.2 (left) depict the same data.
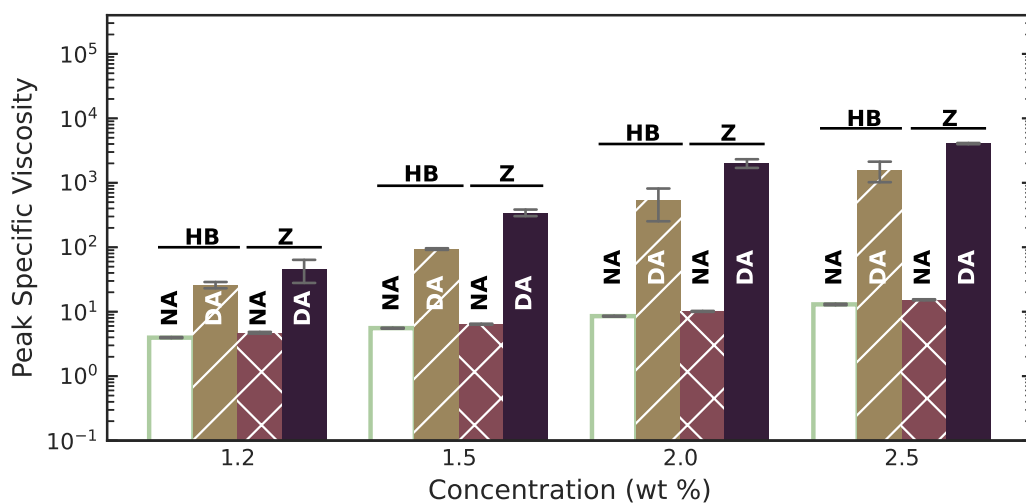

Figure 5.4: Peak specific viscosities of solutions of non-associative (NA) and self-associative (DA) polymers made from hydroboration-treated COD (hb) and zeolite-treated COD (z) at concentrations of 1.2 wt%, 1.5 wt%, 2.0 wt%, and 2.5 wt% in decalin with molecular weights of approximately 200 kg/mol. Error bars represent a 95% confidence interval. Figures 5.4, 5.6, and 5.2 (right) depict the same data.
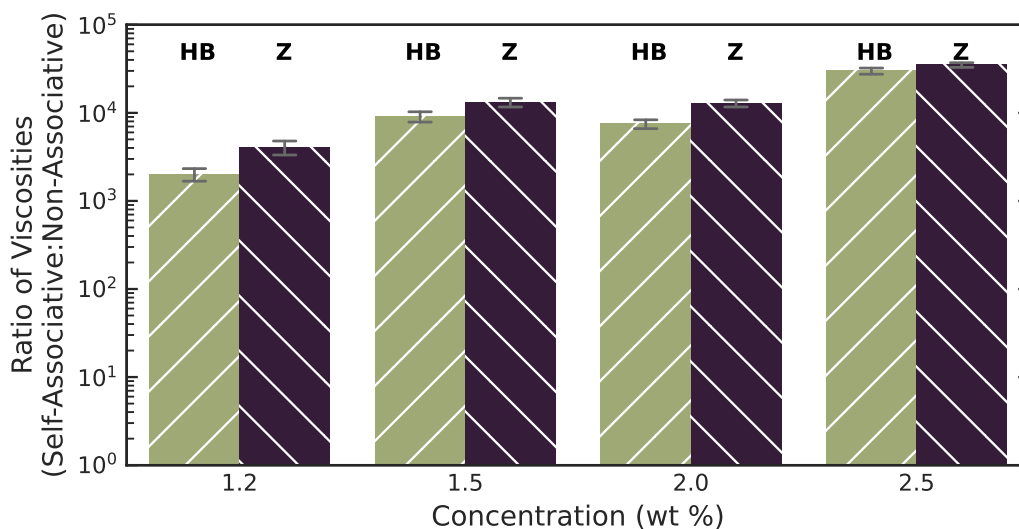
Figure 5.5: Ratio of peak viscosities of solutions of self-associative (DA) polymers to non-associative (NA) polymers made from hydroboration-treated COD (hb) and zeolite-treated COD (z) at concentrations of 1.2 wt%, 1.5 wt%, 2.0 wt%, and 2.5 wt% in decalin with molecular weights of approximately 60 kg/mol. Error bars represent a 95% confidence interval. Figures 5.3, 5.5, and 5.2 (left) depict the same data.
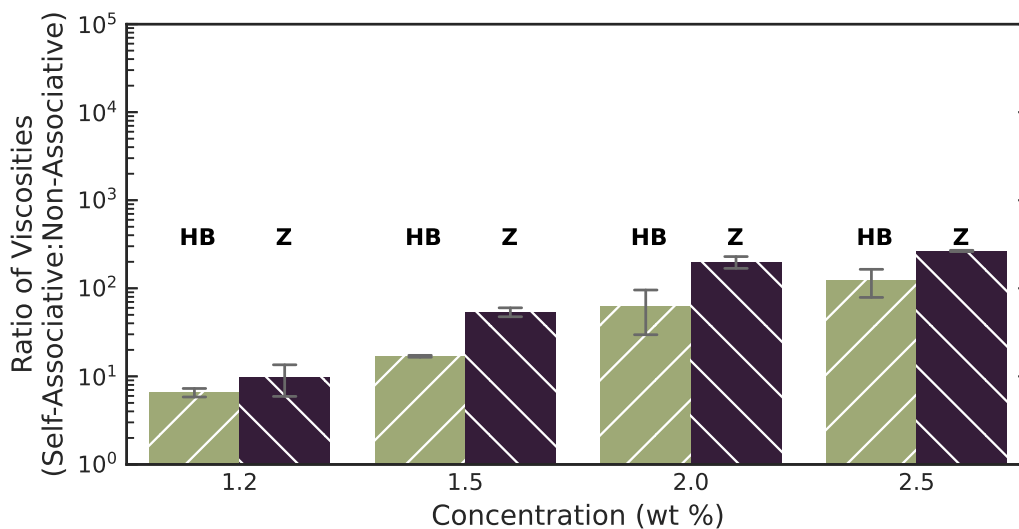

Figure 5.6: Ratio of peak viscosities of solutions of self-associative (DA) polymers to non-associative (NA) polymers made from hydroboration-treated COD (hb) and zeolite-treated COD (z) at concentrations of 1.2 wt%, 1.5 wt%, 2.0 wt%, and 2.5 wt% in decalin with molecular weights of approximately 200 kg/mol. Error bars represent a 95% confidence interval. Figures 5.4, 5.6, and 5.2 (right) depict the same data.
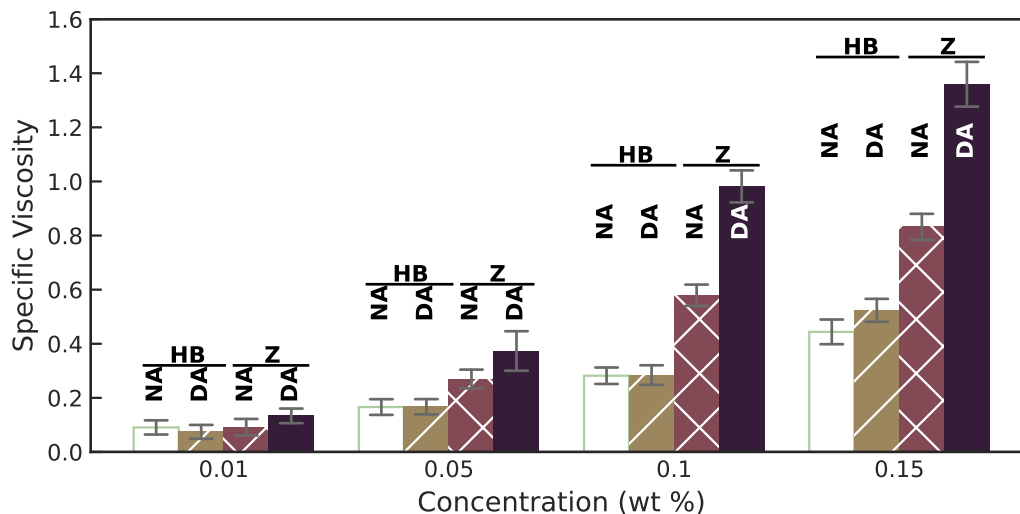
Figure 5.7: Specific viscosities of solutions of the highest readily accessible molecular weights of non-associative (NA) and self-associative (DA) polymers made from hydroboration-treated COD (hb) at approximately 200 kg/mol and zeolite-treated COD (z) at approximately 1 Mg/mol at concentrations of 0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.15 wt% in decalin. Error bars represent a 95% confidence interval. Figures 5.7 and 5.8 depict the same data.
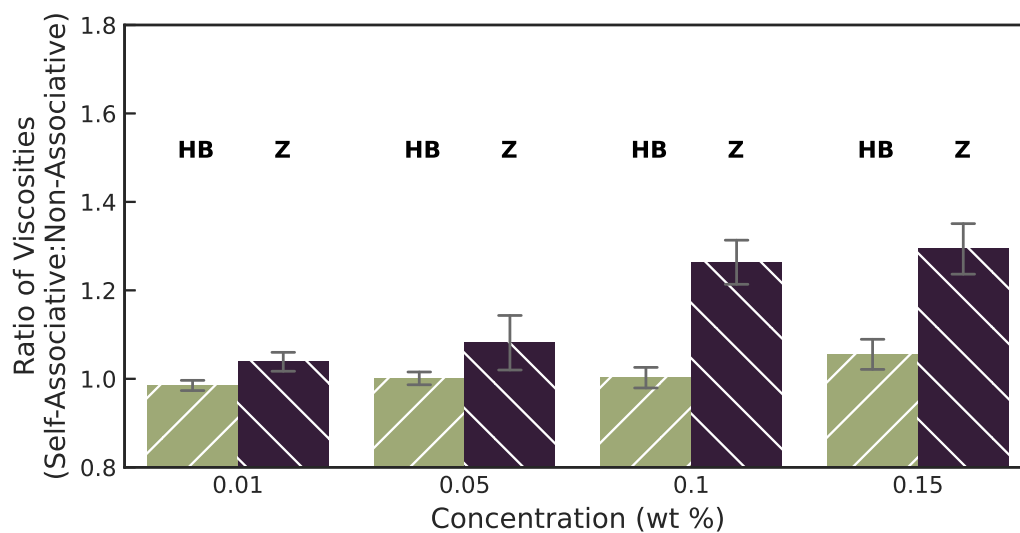

Figure 5.8: Ratio of viscosities of solutions of self-associative (DA) polymers to non-associative (NA) polymers at the highest readily accessible molecular weights of non-associative (NA) and self-associative (DA) polymers made from hydroboration-treated COD (hb) at approximately 200 kg/mol and zeolite-treated COD (z) at approximately 1 Mg/mol at concentrations of 0.01 wt%, 0.05 wt%, 0.1 wt%, and 0.15 wt% in decalin. Error bars represent a 95% confidence interval. Figures 5.7 and 5.8 depict the same data.

5.4 Discussion

Comparing the peak specific viscosities of polymer solutions made from zeolite-treated and hydroboration-treated COD at high concentrations, the effect of molecular weight on end-group fidelity is observed. The self-associative polymers made from zeolite-treated COD significantly increase the viscosity at both 60 and 200 kg/mol at multiple concentrations compared to the self-associative polymers made from hydroboration-treated COD, but the relative effect at the higher molecular weight is larger, indicating that end-group control is diminished as molecular weight increases. As molecular weight increases, the proportion of intentional di-acid-functionalized CTA to potential contaminant CTAs present in the treated COD will decrease. A reduction in rheological potency of association for polymers from hydroboration-treated COD compared to those from zeolite-treated COD is evidence for unintentional chain transfer and unwanted non-associative end-group installation.

At low concentrations (< 0.1 wt%), comparing the nominally "self-associative" and non-associative polymers from hydroboration-treated COD at a COD/CTA ratio of 14,000 showed indistinguishable specific viscosities. This evidence suggests the majority of chain ends in the nominally "self-associative" polymer from hydroboration-treated PCOD have unknown end-group structure from impurities rather than CTA, qualitatively agreeing with population balance models of mixtures of non-functional and functional chain ends.[4] In contrast, polymers from zeolite-treated COD showed substantially greater viscosity compared to their non-associative counterparts at these same concentrations. The difference in viscosity versus concentration suggests a twofold reduction in apparent overlap concentration due to end-to-end association. Maintaining control of associative end-groups to a high degree of polymerization is essential for formation of a distribution of supramolecules that includes ultralong

species responsible for mist control and drag reduction.[3,4]

5.5   Conclusion

Highly-potent long end-associative polymers ($> 40,000$ backbone atoms, bba) resist shear degradation and retain efficacy compared to traditional polymers with $\geq 10^6$ bba,[3] even at low concentrations (< 0.1 wt%). This efficacy depends on end-group fidelity–the presence of mono-telechelic polymers causes "termination" of what would otherwise be the most effective long linear chains.[4] Although it is difficult to use NMR to quantify the fidelity of end-functionalization as molecular weight increases,[14] the rheological properties of solutions of the resulting polymers provide a sensitive indicator of the loss of end-group control.

Using shear rheology as our detection tool, we were able to reveal differences in monomer purity not visible in NMR through the diminished self-association present in the polymers synthesized from hydroboration-treated COD. By distinguishing between polymer candidates obtained through different routes that look similar under other detection tools such as gel permeation chromatography and NMR, we can select more effective mist control and drag reduction agents for such safety and sustainability applications as suppressing fire in lubricant leaks and decreasing pump power requirements.

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