*Chapter 4*

# EFFECTS OF SOLVENT QUALITY AND VISCOSITY ON THE BEHAVIOR OF END-ASSOCIATIVE POLYMERS

## 4.1   Introduction

Hydrocarbon fluids in vehicles, such as many fuels, lubricants, and heat transfer fluids, can pose hazards upon accidental release, particularly when in the form of sprays, where drops can evaporate and contribute to flammable gases in the presence of potential spark sources.[1,2] Using long polymer additives as mist control agents, preventing the formation of small droplets that readily evaporate and biasing droplet distributions towards larger droplets, has been known as a mechanism for preventing hydrocarbon fluid fires;[3–6] however, long polymers are subject to degradation due to high shear forces during pumping,[7–10] which occurs in transport to and use in a vehicle.

Prior work in the Kornfield group for preventing jet fuel fires utilized long end-associative telechelic polycyclooctadiene (PCOD) to act as megasupramolecular mist-control agents that survive pumping events by disassociating during what would be a chain scission event for a covalently bonded long polymer and reassociating afterward.[6,11,12] Much as in jet fuel, lubricant mists are a potential fire hazards, motivating adapting this polymer system for mist control in polyalphaolefin (PAO) lubricant and heat transfer fluid.

Using the megasupramolecular PCOD system in PAO presents a number of challenges due to differences in the solvent compared to jet fuel. Both the backbone and end-groups are less soluble in PAO than in jet fuel and other hydrocarbon solvents studied by our group; and PAO, like many other lubricants, is substantially more viscous than jet or diesel fuel. Effects of variations

in chemical structure of backbone and end-group on solubility is planned to be discussed in the thesis of Hojin Kim. Here, the effects of solvent quality and viscosity on non-associative and end-associative polymers are investigated using the backbone and end-group structures developed by Dr. Ming-Hsin Wei.[6,12] To inform engineering criteria for further development of additives for mist control in lubricant systems, this study integrates efects on shear and extensional flow. In collaboration with Dr. Jacob Temme at Army Research Laboratory, we examine the effects of a homopolymer and an end-associative polymer on spray breakup in relation to their effects on shear and extensional properties.

## Relationship between Extensional Properties and Mist Control

High molecular weight polymeric additives have been proposed as mist-control agents (as known as anti-mist agents) over the past 50 years for hydrocarbon fluids as a route to suppressing highly flammable fine-droplet mists.[3,5,6] The effect of these polymers is two-fold—the average droplet size is increased[3,4,13,14] and, in particular, small satellite droplets are substantially suppressed.[10,15] The driving force for both of these effects is hypothesized to be the resistance of the polymer additive to the highly extensional flow during ligament pinchoff, which has been experimentally supported.[13,16] Imaging of sprays of viscoelastic fluids with sufficiently high resistance to extension (characterized as a high extensional relaxation time) demonstrates thin filaments connecting proto-drops to larger fluid formations, resulting in many would-be satellite droplets returning to the main drops.[10,15,16]

The improvement in mist control, however, is lost with degradation of the polymer due to mechanical chain scission (such as during pumping) as the efficacy is directly tied to the extensional properties and thus the molecular

weight.[10,13,17,18] See Chapter 1 for further description of the physics of polymeric mist control and Chapter 2 for measurements of how chain scission affects extensional properties.

**Effects of Solvent Quality and Viscosity in Extension and Chain Scission**

The body of literature on extension of chains contains multiple, contradicting discussions of the effects of solvent quality on extensional properties of polymer solutions, likely due to the complexity of interpreting polymer conformations under different flow conditions.[19] For example, the critical extension rate for observations of birefringence ($\dot{\epsilon}_c$), which is tied to the coil-stretch transition, was initially predicted to depend on the solvent quality dependent through the relationship between $\dot{\epsilon}_c$ and molecular weight ($M$), of the form $\dot{\epsilon}_c \sim M^{-3\nu}$, where $\nu$ is the Flory exponent (a measure of the solvent quality).[20] Follow-up experimental results showed universality of the molecular weight dependence regardless of solvent quality, i.e., $\dot{\epsilon}_c \sim M^{-1.5}$,[21] and the theory was revised to a dependence of the form $\dot{\epsilon}_c \sim M^{-(1+\nu)}$, which yields exponents in the range of -1.5 to -1.6 across the range of solvent qualities for flexible polymers from $\Theta$ solvent ($\nu = 0.5$) to good solvent ($\nu = 0.6$),[20,22] although literature results report a larger range of exponents.[20] Solvent viscosity, on the other hand, has a relatively clear role in extensional flow—increasing solvent viscosity increases extensional relaxation time, based on theory[23] and on experiments.[21]

Prior literature has demonstrated that chain scission increases with a poorer solvent in laminar and turbulent flow.[24,25] In a poorer solvent, the chains are more compact and thus from the above, we would expect that coil-stretch transition would occur at higher extensional rates (more difficult to stretch) and that the ratio of extended length to the coil size would be larger. If
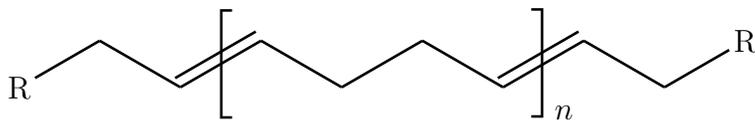
Scheme 4.1: Telechelic polycyclooctadiene (PCOD), end-groups R in Scheme 4.2.

increased chain scission is occurring, it implies that the extensional rate at scission is lower for the poor solvent, indicating that there is possibly increased drag from the solvent on the backbone occurring during the strong extension events or due to the poorer solubility. When designing potential additives, poor solvent quality thus imposes a limit on the molecular weight of the polymer additive.

In this study, I will simultaneously be considering the effects of solvent quality and viscosity on the behavior of the PCOD backbone in shear and extension, as well as the changes in association strength due to changing solvents.

## 4.2 Experimental Methods

**Materials**

Polycyclooctadiene samples prepared by Hojin Kim, utilizing the methods outlined in Appendix B using cyclooctadiene purified using zeolite molecular sieving. Decahydronaphthalene was acquired from Sigma-Aldrich. Polyalphaolefin compliant with MIL-PRF-87252E (BRAYCO 889 MIC) was acquired from QC Lubricants.

Telechelic polycyclooctadiene samples of the form in Scheme 4.1 were used in this study, where R groups are either a diacid group (Scheme 4.2(a), DA), a dibase group (Scheme 4.2(b), DB), or a C6 alkane chain (non-associative), as appropriate.

(a) R: Di-acid (DA) end-group       (b) R: Di-base (DB) end-group
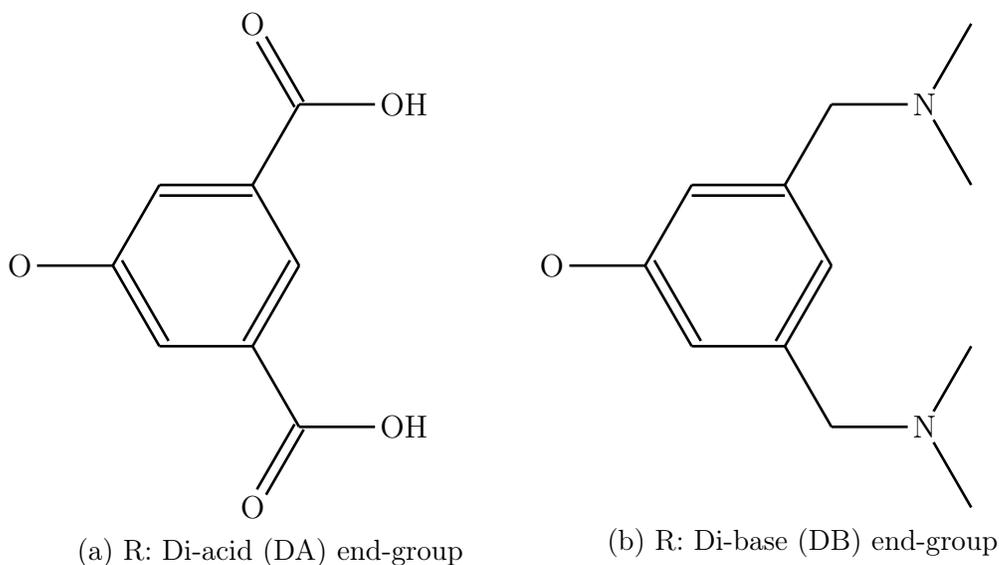
Scheme 4.2: Associative end-groups for telechelic polycyclooctadiene, "R" in Scheme 4.1.

**Rheological Solution Preparation**

To examine th eeffect of solvent quality and viscosity, three solvents were used. Of technological interest, PAO was selected as one of the three. As a partially unsaturated solvent that was known as a good solvent for polycyclooctadiene, decalin was selected as one of the solvents. To create a partially unsaturated solvent with shear viscosity at 15°C matched to PAO ($\sim$8.8$\pm$0.1 mPa-s at 15 °C), the third solvent was a mixture of decalin and 9.3 wt % 5 kg/mol polybutadiene.

Stock solutions in transparent glass vials were prepared by measuring a desired mass of solid polymer samples and adding to 5-10 mL, measuring the mass, of decahydronapthalene (decalin) or polyalphaolefin (PAO) as appropriate. For decalin stock solutions, 0.1 wt % butylated hydroxytoluene (BHT) was added as an anti-oxidant. For PAO samples, BHT was added at 5 times the polymer concentration. BHT acts as a solubilizer for when associative end-groups were present in addition to its anti-oxidant properties as discovered by Hojin Kim,[26] and was added to both the non-associative and associative solutions in PAO to

keep solvent viscosity and quality consistent between these samples. Solvent viscosity and extensional behavior of PAO alone was not substantially modified by the addition of 5 wt % of BHT. BHT was added to solvents prior to heating. Stock solutions were heated using two infrared (IR) lamps while rolling at 10 rotations per minute. Stock solutions were rolled under the IR heating until visibly homogeneous—3–5 days for samples in decalin and 5-10 days in PAO. After stock solutions preparation, dilutions were made by measuring out stock solution by mass into a separate vial and adding decalin or PAO until the desired PCOD concentration was reached. Diluted samples were rolled for at least 8 hours.

Shear rheological measurements were conducted at 15°C because the extensional measurements occur at ambient conditions (15 $\pm$ 1°C); however, solutions of high molecular weight PCOD in PAO were observed to precipitate out of solution after extended storage at these temperatures. In the case of PAO dilutions, all samples were heated with rolling until immediately prior to use for shear measurements (follow by 5 min at 15 °C after loading into the cone-and-plate geometry as a part of equilibration on the rheometer) or $\sim$30 minutes prior to use for extensional measurements, to avoid temperature inhomogeneties in the sample during an experiment.

For overlap concentration measurements, dilutions in decalin were first measured in shear, and then 9.3 wt % (measured relative to the decalin solvent only) of 5 kg/mol polybutadiene (Sigma-Aldrich), diluting the polymer concentration relative to the original solution. The resulting concentration of PCOD was used in intrinsic viscosity calculations. For solutions used in matched non-associative and associative shear and extensional measurements, stock solutions of non-associative and associative PCOD in decalin were measured to result in the correct polymer concentration after addition of the 9.3 wt %

5kg/mol polybutadiene, and then the polybutadiene was added. In both cases, dilutions were rolled overnight.

For the solutions of associative PCOD containing both diacid (DA) and dibase (DB) telechelic PCOD, separate stock solutions were prepared as described above, and measured aliquots of each stock solution were added to a vial to result in a DA:DB ratio within 1% of stoichiometry, and then these solutions were diluted with the appropriate solvent to the desired concentration.

**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 15 $\pm$ 0.1 °C using a Peltier plate to regulate temperature and samples were allowed to thermally equilibrate and relax for 5 min after reaching 15 °C. Shear rate sweeps were performed from 1 to 100 1/s. The sample edge was examined to check for evidence of evaporation and none was observed.

**Dripping-onto-Substrate Extensional Rheometry (DoSER)**

A dripping-onto-substrate extensional rheometry (DoSER) instrument was constructed by Robert Learsch and Red Lhota consisting of a GSVitec MultiLED G8 with QT lamp head (12000 lumen light source, Figure 1.7**A**), a Harvard Elite 11 syringe pump on an adjustable track (solution delivery, **B**), Photron FASTCAM Nova S12 type 1000K-M-32GB (high-speed camera, **C**) equipped with an optical train as described below, and a custom holder for aluminum substrates (**D**). The optical train consisted of a Resolve4K 7:1 Zoom
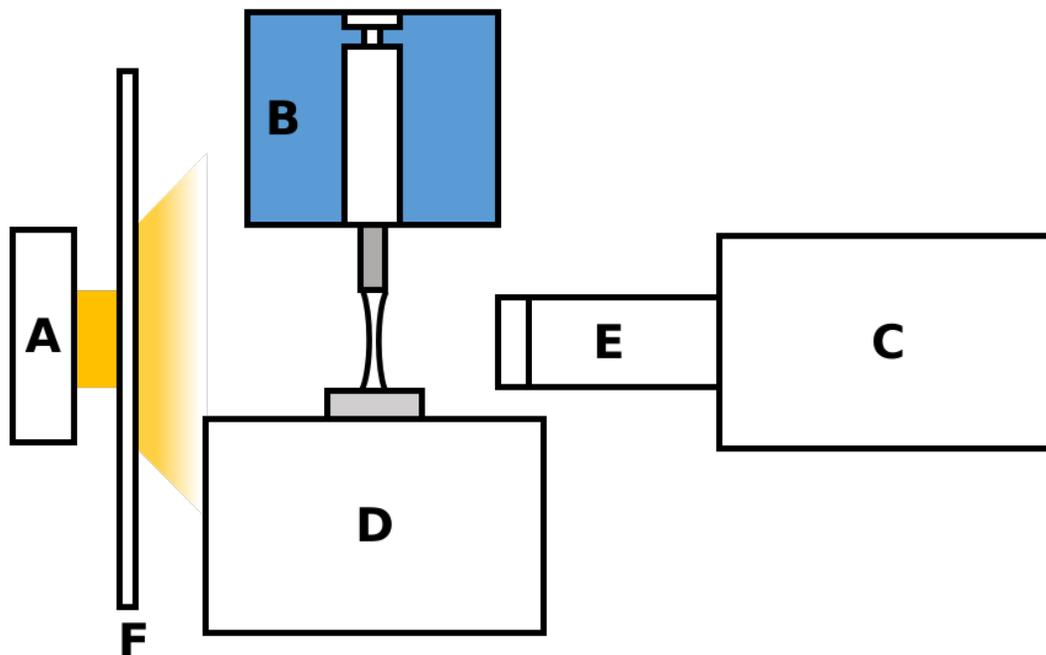
Figure 1.7: Schematic of dripping-onto-substrate extensional rheometer (not to scale). (repeated from page 14)

Video microscope lens, two rear projection lenses, a 1.0x objective lens, and a coupler, resulting in a resolution limit at full zoom of 3.5 µm (**E**). The camera was operated at 25,000 frames per second with a shutter speed of 150,000 Hz (i.e., 7 µs exposure). The light passes through a diffuser before reaching the measurement plane (**F**).

A syringe with a 22G blunt-tip polytetrafluoroethylene needle (outer diameter 1.0 mm) was mounted to the syringe pump. The substrate was positioned at a height of 2.8 mm below the tip of the needle, corresponding to a height-to-needle-diameter ratio of 3 or a height-to-free-drop-diameter ratio of 1, which is within the optimal range for hydrocarbon solutions.[27] Ambient temperature was measured with each experiment and was in the range 15 ± 1 °C.

For each solution, DoSER was performed using the following procedure. An aliquot was slowly loaded into a syringe through a 22G polytetrafluoroethy-

lene blunt-tip needle. The syringe was attached to the syringe pump and the syringe pump was slowly advanced until solution was observed to drip from the needle, and then the needle tip was cleaned. A clean set of aluminum substrates was loaded onto the substrate holder and the first substrate was aligned below the needle tip. The light was turned on and the camera was focused and aligned with the needle tip. The substrate was then raised or lowered to the correct height (as describe above) relative to the needle tip. A drop was dispensed from the needle tip by the syringe pump at a rate of 0.02 mL/min, until the drop was nearly touching the substrate. The syringe pump was stopped prior to droplet-substrate contact. The events of droplet contact through liquid bridge formation and pinchoff were recorded (referred to as an experimental video or "run"). A background video was acquired after each run. A clean substrate was then placed below the needle tip. Dispensing drops onto a clean substrate was repeated until five total runs were recorded. The videos were analyzed using the *dosertools* Python package, described in detail in Appendix A, to obtain the normalized diameter as function of time after the critical time (time of transition between solvent behavior and elastocapillary response). The decay of the normalized diameter is used to evaluate the extensional relaxation time. In our experiments, run-to-run variation on the DoSER instrument was observed to be more significant than errors in fitting–errors in measured relaxation times are thus quantified using the run-to-run variation. Solutions with relaxation times of 0.05 ms and lower were difficult to consistently characterize on our instrument.

Further discussions of DoSER theory and analysis are available in Chapter 1 and Appendix A respectively.

**Spray**

Spray experiments and analysis were performed by Dr. Jacob Temme and coworkers at the Army Research Laboratory (ARL). Methods, data, and figures included with permission of ARL. Polymers and solutions for spray experiments presented in this chapter were prepared by Hojin Kim with concentrations based on measured rheological properties of preliminary solutions (Robert Learsch measured extension properties, I measured shear for these preliminary solutions).

The spray experiments were performed in an optically accessible atmospheric chamber. Two fields of view were observed using a Phantom SA-X2 high-speed camera paired with a Zeiss 50mm lens: the first from the nozzle tip to approximately 80 mm downstream and the second centered 30-35 mm downstream and 25 mm to the side of the orifice. In the first field of view, images were recorded at 10 kHz. The second field of view was imaged with high enough magnification to resolve features as small as 200 µm with recordings at 35 kHz. In each experiment, pressurized fluid at 120 psi (0.83 MPa) was released through a 5 mm orifice. Spray angle analysis was performed by MATLAB-based image analysis of spray videos (Figure 4.1), modified by ARL from Engine Combustion Tools.[28]

## 4.3   Results

**Solvent Quality**

Intrinsic viscosity as a function of weight-average molecular weight was measured for non-associative PCOD in three solvents: decalin, decalin with 9.3 wt % 5kg/mol polybutadiene added (9.3 wt % 5k PB decalin), and PAO (Figure 4.2). The intrinsic viscosity of 1Mg/mol PCOD in PAO was not measurable due to limited solubility. Logarithmic fits of the Kuhn-Mark-Houwink-
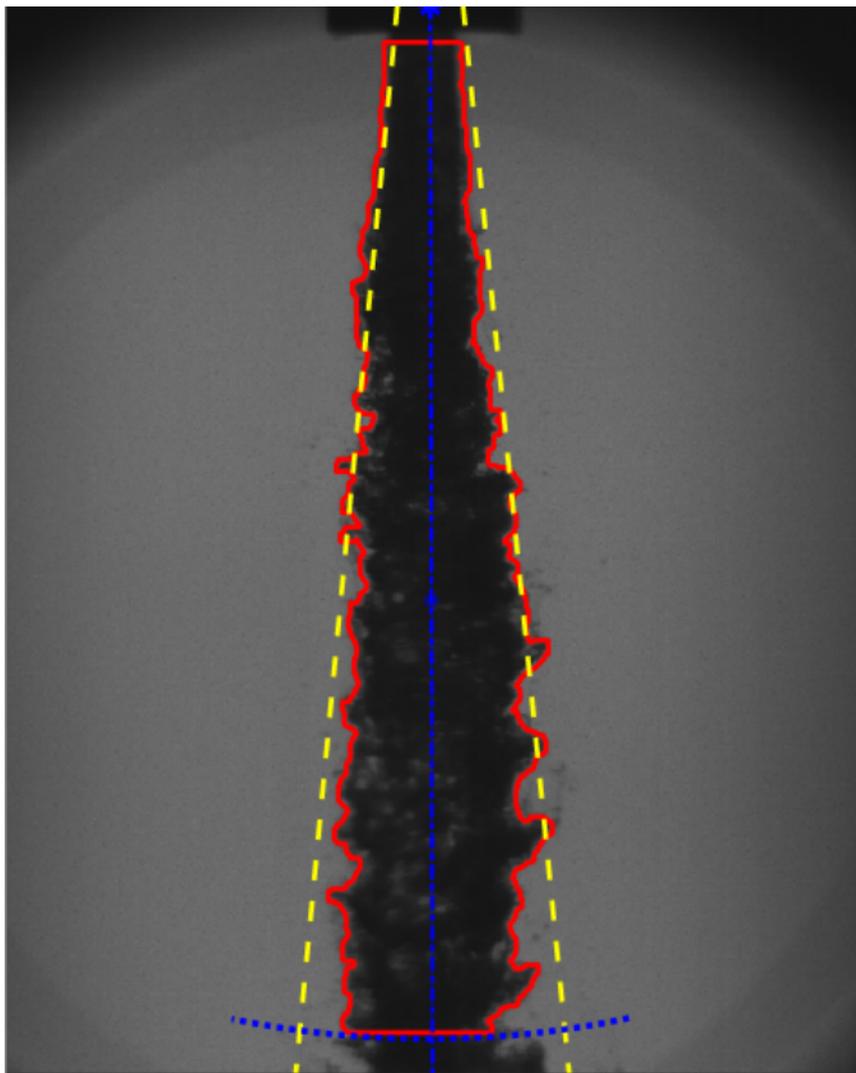
Figure 4.1: Example image for determination of spray angle. Red indicates edge of spray as determined by image analysis. Yellow indicates calculated spray angle.

| Solvent | $K * 10^4$ (1/wt %) | $a$ |
|---|---|---|
| decalin | 5.5 | $0.66 \pm 0.03$ |
| 9.3 wt % 5k PB decalin | 6.5 | $0.59 \pm 0.02$ |
| PAO | 1.3 | $0.68 \pm 0.04$ |

Table 4.1: Measured Kuhn-Mark-Houwink-Sakurada prefactor ($K$) and exponent ($a$) (Equation 1.2) for polycyclooctadiene in decalin, decalin with 9.3 wt % 5 kg/mol polybutadience added (9.3 wt % 5k PB decalin), and polyalphaolefin (PAO) at 15°C. ($a \pm$ one standard deviation, $K$ standard deviations were less than $10^{-8}$)

Sakurada equation (Equation 1.2) to the measured data produced $K$ and $a$ that show PAO has the highest value of $a$ among the three solvents (Table 4.1), although the values for decalin and PAO are within one standard deviation for the fit.

Recasting the intrinsic viscosity as overlap concentration using Equation 1.1, we observed much higher overlap concentrations for the same PCOD sample in PAO than in decalin (Figure 4.3). At the highest molecular weight in this study that was measurable in all three solvents, the overlap concentration in decalin is three times greater than in decalin.

**Shear Viscosity of End-Associative Solutions**

The effect of end-groups on the shear viscosity was measured for solutions of ~670 kg/mol PCOD in the three solvents of interest at three reduced concentrations ($c/c^* = 0.125, 0.25, 0.5$) where $c^*$ denotes the overlap concentration of the corresponding non-associative polymer, 670 kg/mol non-associative PCOD in that solvent. Comparing solutions at matched $c/c^*$ for the non-associative polymer corresponds to matching the volume pervaded by the polymer alone
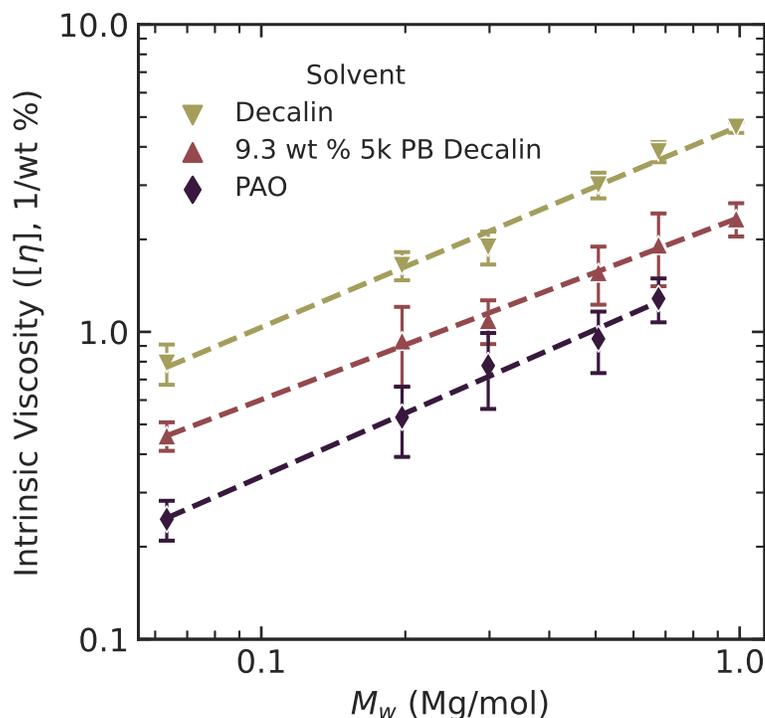
Figure 4.2: Intrinsic viscosity ($[\eta]$, 1/wt%) of polycyclooctadiene as a function of weight-average molecular weight ($M_w$, Mg/mol) in decalin, decalin with 9.3 wt % 5kg/mol polybutadiene added (9.3 wt % 5k PB decalin), and polyalphaolefin (PAO). Dashed lines represent the Kuhn-Mark-Houwink-Sakurada (KMHS) equation (Equation 1.2) fits to the data for each solvent at 15°C. KMHS fits are found in Table 4.1

(without end-groups), which requires greater mass concentration for solvents in which the chain adopts a more compact conformation (670 kg/mol PCOD has a $c^*$ of 0.2, 0.4, and 0.6 wt% for decalin, 9.3 wt % 5k PB decalin, and PAO, respectively). For each solvent and $c/c^*$, the specific viscosity of non-associative PCOD was compared to that of DA PCOD, DB PCOD, and a stoichiometric mixture of DA and DB PCOD (Figure 4.4).

For comparison with spray experiments described below, a separate batch of DA, DB, and 1:1 DA:DB 670 kg/mol solutions in PAO was prepared and characterized at concentrations of 0.05 wt % and 0.5 wt % (Figure 4.5).
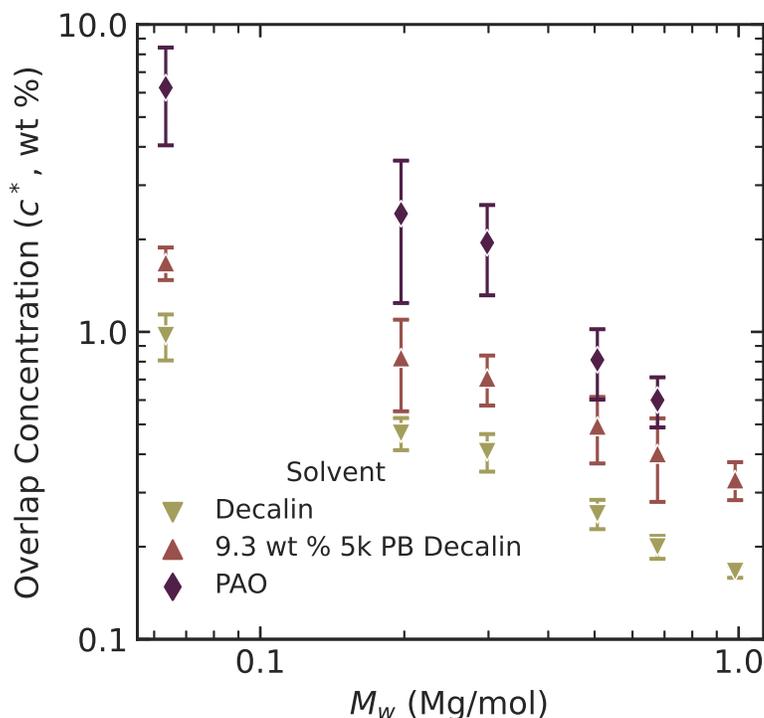
Figure 4.3: Overlap concentration ($c^*$, wt%) of polycyclooctadiene as a function of weight-average molecular weight ($M_w$, Mg/mol) in decalin, decalin with 9.3 wt % 5kg/mol polybutadiene added (9.3 wt % 5k PB decalin), and polyalphaolefin (PAO) at 15°C. Error bars indicate 95% confidence intervals.

**Extensional Relaxation Time of End-Associative Solutions**

Normalized diameter ($D/D_0$) was measured by image analysis of high-speed videos of dripping-onto-substrate extensional rheometry experiments as described in Appendix A. Fits to the normalized diameter in the elastocapillary regime as described in Appendix A were used to determine the extensional relaxation time ($\lambda_E$) for each of the solutions measured in the shear rheology in Figure 4.4, in addition to solutions at a $c/c^* = 1$ (Figure 4.6).

Extensional relaxation times of DA, DB, and 1:1 DA:DB 670 kg/mol PCOD in PAO from a separate batch of solutions were measured at additional concentrations (0.05 wt %, corresponding to spray measurements later in this work, and 0.5 wt %) by Robert Learsch—corresponding non-associative PCOD measure-
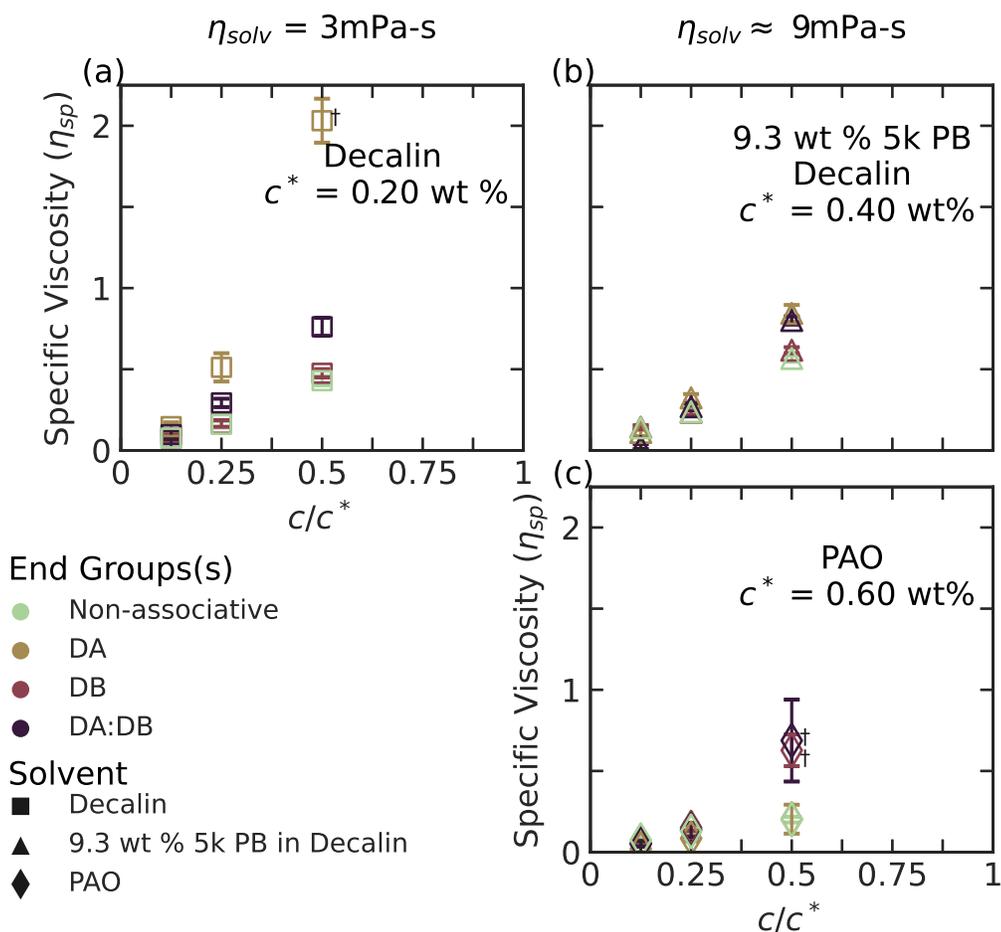
112



Figure 4.4: Specific viscosity ($\eta_{sp}$) averaged over low shear rates as a function of reduced concentration ($c/c^*$) and presence of end-groups for telechelic 670 kg/mol polycyclooctadiene dissolved in (a) decalin, (b) decalin with 9.3 wt % 5kg/mol polybutadiene added (9.3 wt % 5k PB decalin), and (c) polyalphaolefin (PAO) at 15°C. Error bars indicate 95% confidence intervals. Where error bars are not visible, the corresponding interval is within symbol size. † indicates samples in which shear-thinning was observed.

Figure 4.5: Specific viscosity ($\eta_{sp}$) averaged over low shear rates as a function of concentration (wt %) and presence of end-groups for telechelic 670 kg/mol polycyclooctadiene dissolved in polyalphaolefin (PAO) at 15°C. Measurements at 0.05 wt % and 0.5 wt % performed with a separate batch of solutions. Error bars indicate 95% confidence intervals. Where error bars are not visible, the corresponding interval is within symbol size. † indicates samples in which shear-thinning was observed.
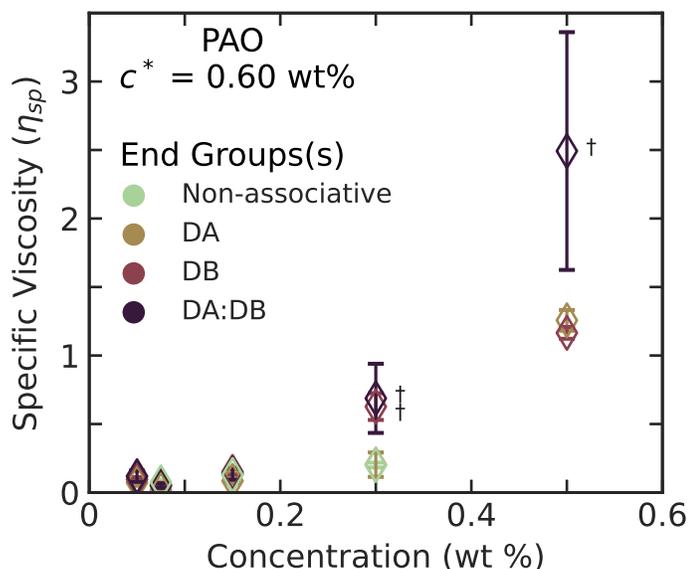
ments at the same molecular weight and concentrations were not performed (Figure 4.7).

## Comparing Sprays with and without Polymer Additives

Measurements and analysis of sprays performed at Army Research Laboratory (ARL) by Dr. Jacob Temme and coworkers.

The spray of polyalphaolefin (PAO) with no additives (left, Figure 4.8) was observed to spread intermittently during instabilities in the observed time period, kicking out thin ligaments that broke up into small droplets down to the resolution limit (200 µm). Adding non-associative 1Mg/mol polycyclooctadiene (PCOD) to PAO modified the spray angle, ligament structure, and droplet formation. Solutions of 0.05 wt % 1 Mg/mol PCOD in PAO (center Figure
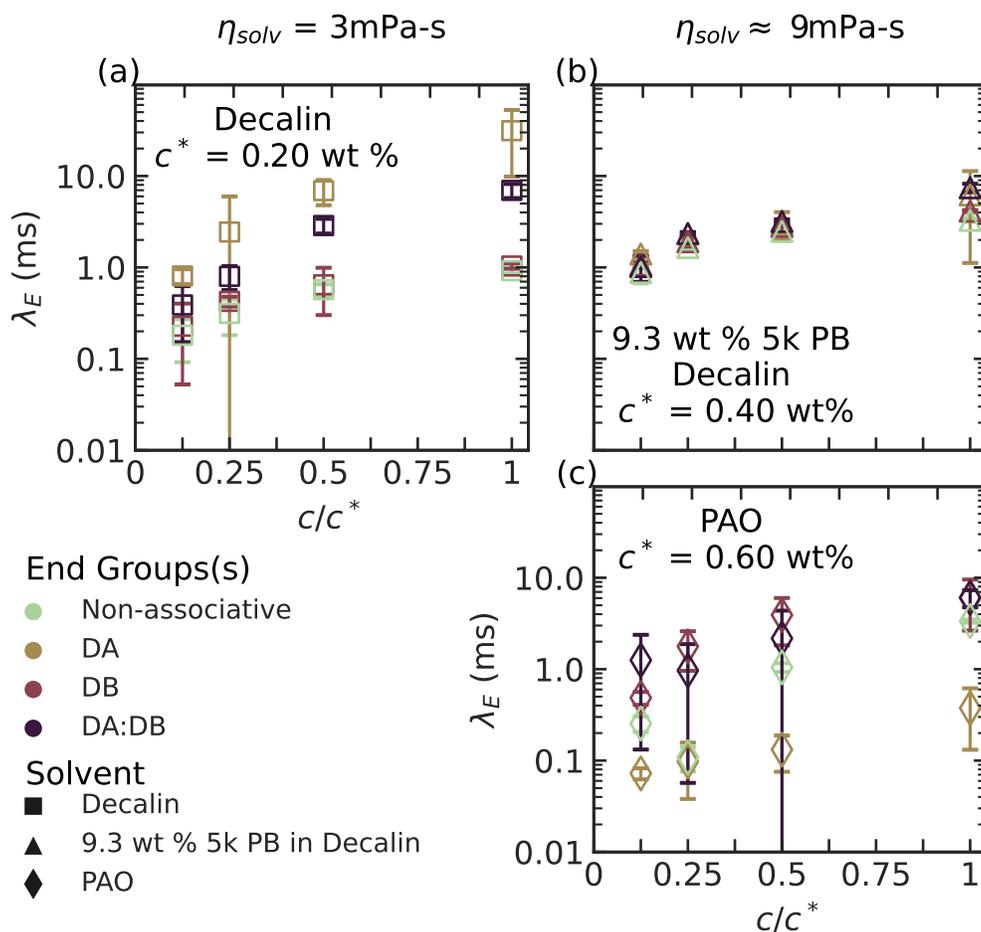
Figure 4.6: Extensional relaxation time ($\lambda_E$, ms) as a function of reduced concentration ($c/c^*$) and presence of end-groups for telechelic 670 kg/mol polycyclooctadiene dissolved in (a) decalin, (b) decalin with 9.3 wt % 5kg/mol polybutadiene added (9.3 wt % 5k PB decalin), and (c) polyalphaolefin (PAO) at 15°C. Error bars indicate 95% confidence intervals representing run-to-run variation in DoSER measurements (fitting errors are substantially smaller). Where error bars are not visible, the corresponding interval is within symbol size.

Figure 4.7: Extensional relaxation time ($\lambda_E$, ms) as a function of concentration (wt %) and presence of end-groups for telechelic 670 kg/mol polycyclooctadiene dissolved in polyalphaolefin at 15°C. Measurements at 0.05 wt % and 0.5 wt % performed with a separate batch of solutions by Robert Learsch. Error bars indicate 95% confidence intervals representing run-to-run variation in DoSER measurements (fitting errors are substantially smaller). Where error bars are not visible, the corresponding interval is within symbol size.
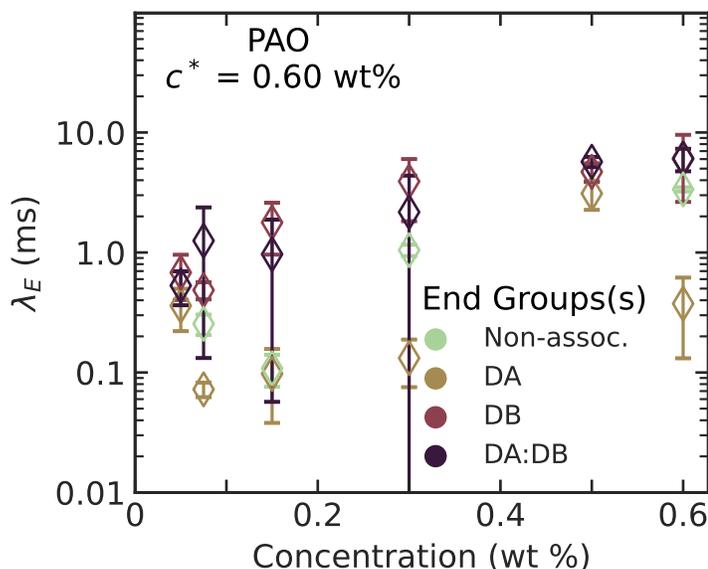
4.8) demonstrated some instabilities and spreading, though less dramatic than the PAO alone. The ligaments formed were thicker and produced few observable droplets. Solutions of 0.1 wt 1 Mg/mol % PCOD in PAO further modified spreading and increased ligament size, leading to large attached ligaments that stayed close to the main body of the jet.

Quantitative measurement of the spray angle as a function of time demonstrated significant differences between PAO with and without the non-associative additive. PAO with no additives experienced frequent large spray angle events, while adding 0.05 wt % 1 Mg/mol PCOD reduced the amplitude of those events, and 0.01 wt % 1 Mg/mol PCOD suppressed them in the time period observed (Figure 4.9). Averaging over the period observed showed that 0.05 wt% reduced the spray angle by nearly 50 % (Table 4.2). Spray angle is related
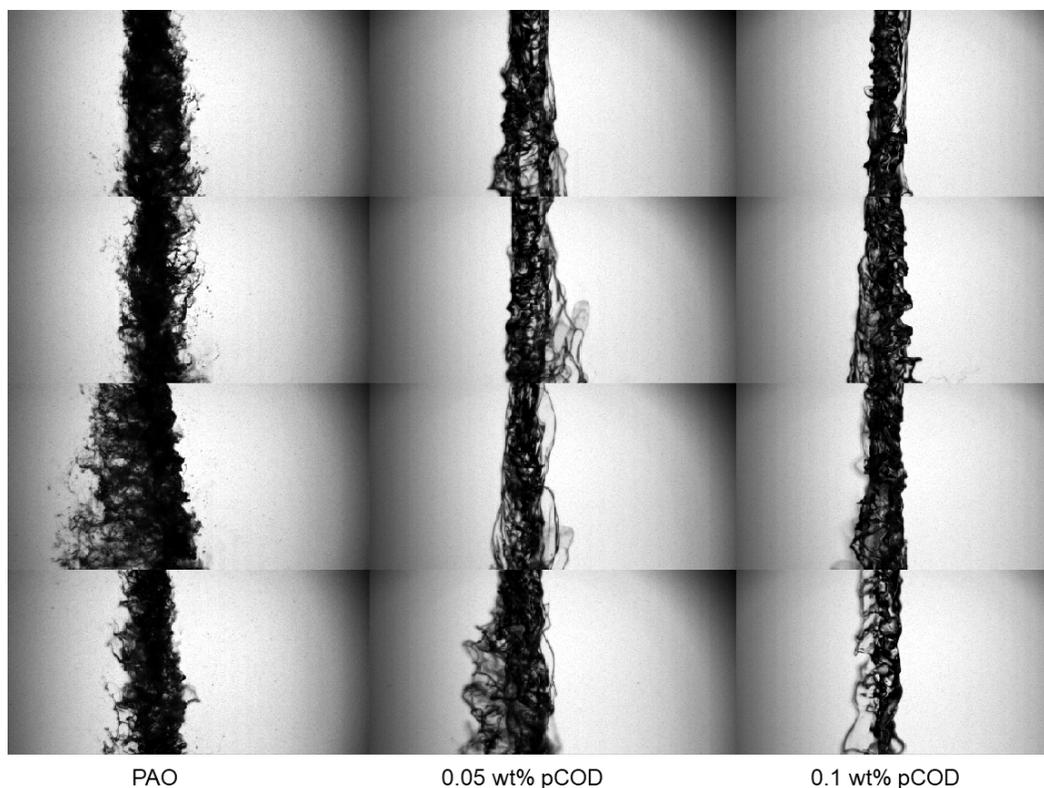
| PAO | 0.05 wt% pCOD | 0.1 wt% pCOD |

Figure 4.8: Representative spray images 30-35 mm downstream of the orifice for (left to right) PAO, 0.05 wt % 1 Mg/mol PCOD in PAO, 0.1 wt % 1 Mg/mol PCOD in PAO at ambient temperature. Images produced and provided by Dr. Jacob Temme, ARL.

to ignitability—a larger spray angle increases likelihood that a potential spark source will be in range for ignition.

As seen in the representative images in Figure 4.8, the addition of PCOD largely suppressed the formation of droplets in the range resolvable by the camera and optical setup used in these experiments ($> 200\mu$m). As a result, average droplet diameter was only determinable for the PAO with no additive (Table 4.3). Ligament diameter can act a proxy for expected diameter size—as ligaments detach from the spray, their pinchoff will create droplets of similar diameter (described in Chapter 1). Average ligament diameter increased 30 % with the addition of 0.05 wt % 1 Mg/mol PCOD and 85 % with the addition of 0.1 wt % 1 Mg/mol PCOD (Table 4.3). The formation of ligaments or filaments
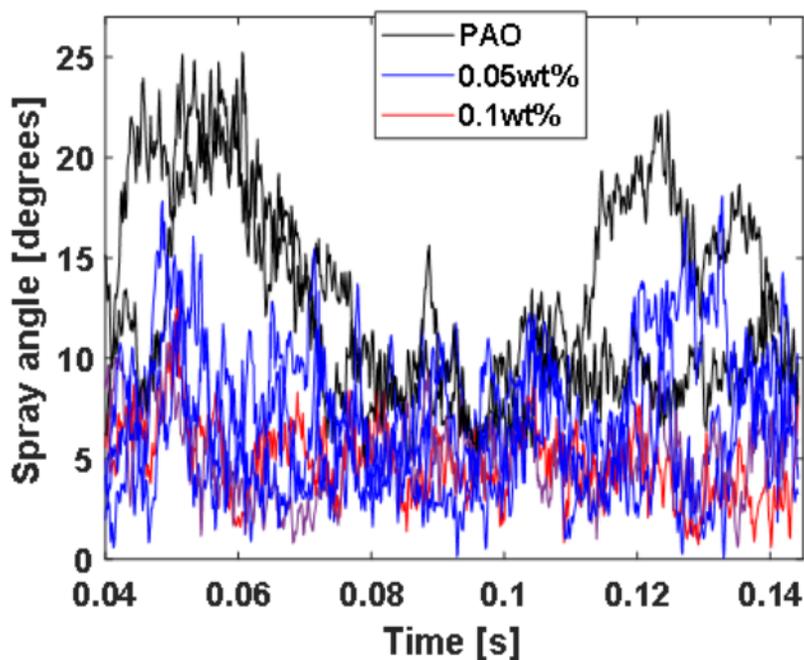
Figure 4.9: Spray angle as a function of time for PAO (black), 0.05 wt %
1 Mg/mol PCOD in PAO (blue), 0.1 wt % 1 Mg/mol PCOD in PAO (red).
Figure produced and provided by Dr. Jacob Temme, ARL.

Table 4.2: Average measured spray angle observed in quasi-steady state jetting
of PAO fluids. Values are ± one standard deviation. Processing performed by
Dr. Jacob Temme, ARL.

| Fluid | Average Quasi-Steady State Spray Angle [degrees] |
|---|---|
| PAO | $12.6 \pm 0.2$ |
| 0.05 wt % 1 Mg/mol PCOD in PAO | $6.7 \pm 0.1$ |
| 0.1 wt % 1 Mg/mol PCOD in PAO | $5.1 \pm 0.1$ |

PAO: Polyalphaolefin,
PCOD: Polycyclooctadiene

has been previously tied to ignition suppression, even at concentrations lower
than full droplet suppression.[3]

Adding associative PCOD (specifically 0.03, 0.05, and 0.1 wt % of 1:1 DA:DB

Table 4.3: Average droplet diameter and ligament diameter observed in jetting of PAO fluids. Image analysis performed by Dr. Jacob Temme, ARL.

| Fluid | Average Droplet Diameter [μm] | Average Ligament Thickness [μm] |
|---|---|---|
| PAO | 230 | 260 |
| 0.05 wt % 1 Mg/mol PCOD in PAO | - | 340 |
| 0.1 wt % 1 Mg/mol PCOD in PAO | - | 480 |

PAO: polyalphaolefin,
PCOD: 1 Mg/mol polycyclooctadiene



PAO          0.03 wt% DA:DB          0.05 wt% DA:DB          0.1 wt% DA:DB
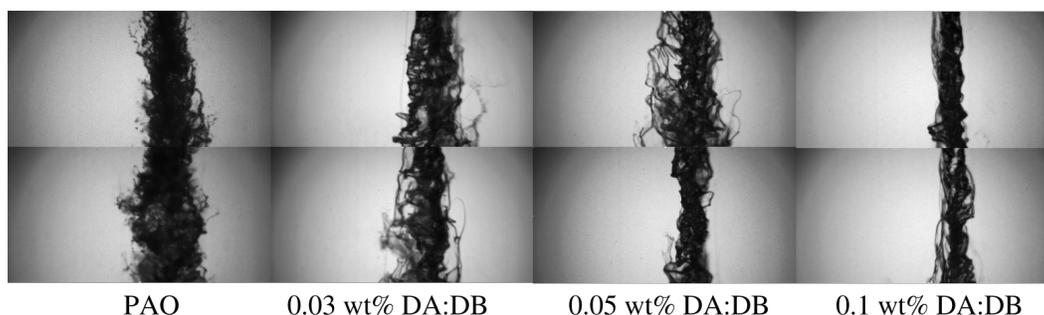
Figure 4.10: Representative spray images 30-35 mm downstream of the orifice for (left to right) PAO, 0.03 wt % DA:DB 670 kg/mol PCOD in PAO, 0.05 wt % DA:DB 670 kg/mol PCOD in PAO, 0.1 wt % DA:DB PCOD 670 kg/mol in PAO. Images produced and provided by Dr. Jacob Temme, ARL.

670 kg/mol PCOD) to PAO had a similar effect as the non-associative (but longer backbone) PCOD. As concentration of polymer additive increased, spray angle decreased, droplet formation was suppressed, and ligament diameter increased (Figure 4.10).

## 4.4   Discussion

**Role of Solvent Quality and Viscosity for Non-associative PCOD in Shear and Extension**

The measured solvent quality of PCOD in PAO using the Kuhn-Mark-Houwink-Sakurada exponent yields a Flory exponent ($\nu$) of 0.56, implying PAO is a

better solvent for PCOD than decalin ($\nu = 0.55$) and the 9.3 wt % 5 kg/mol PB decalin ($\nu = 0.53$) (see discussion of the Kuhn-Mark-Houwink-Sakurada equation and the relationship to the Flory exponent in Chapter 1); however, we repeatedly observed solubility issues in PAO, including observations of inhomogeneties forming in solutions stored at 15 °C and lack of sufficient solubility of 1 Mg/mol PCOD to perform intrinsic viscosity measurements. Additionally, the higher overlap concentrations in PAO (and correspondingly the lower intrinsic viscosities) imply a highly compacted coil size compared to decalin. The poor solubility for PCOD in PAO compared to decalin implies that the maximum unimer molecular weight that can survive chain scission will be lower in PAO compared to decalin or jet fuel, motivating further study of these polymers under pumping conditions and adaptation of the backbone to be more soluble.

Our initial hypothesis was that adding low molecular weight PB to decalin would either keep the PCOD solvent quality constant or increase solvent quality relative to decalin alone, based on the similarity between polybutadiene and the PCOD backbone. The exponent and the overlap concentrations for 9.3 wt % 5 kg/mol PB decalin, however, indicate that it is a worse solvent than decalin.

Looking at the shear specific viscosity results (i.e., measuring increase over solvent viscosity), despite matched reduced concentrations ($c/c^*$), the specific viscosity of non-associative PCOD in decalin statistically significantly exceeds that of PAO at $c/c^* = 0.5$, and the specific viscosity of 9.3 wt % 5 kg/mol PB decalin is further increased over decalin. The relatively lower specific viscosity of the PAO at the same expected pervaded volume of the chains in solution suggests that at finite concentrations, PCOD in PAO is even further collapsed than what is anticipated by matching expected pervaded volumes with $c/c^*$ and thus not contributing as expected to the shear viscosity.

Because PCOD is much less soluble in PAO, particularly as temperature decreases, we must view the extension results as a transient measurement of the properties—because the temperature history was similar among the samples (kept above solubility temperature until removed from heat from equilibration to ambient temperature 30 minutes before measurement), we are still able to compare the effects of concentration and association among PAO samples, as well as assess qualitative differences compared to decalin and decalin with 9.3 wt % 5kg/mol PB.

Comparing extensional relaxation times, one pair of datapoints stands out as either subject to concern over solubility or over sample labeling. Despite having a higher shear viscosity, the $c/c^* = 0.25$ sample of non-associative PCOD in PAO was measured to have a lower extensional relaxation time than the $c/c^* = 0.125$ sample. Two explanations reasonably fit these two points: if the higher concentration sample experienced PCOD precipitating out of solution before measurement (observed in a previous solubility study) or if the syringes containing the two samples were switched prior to measurement due to human error. Due to very limited material available, these measurements were not repeated.

Looking at the matched shear viscosity samples (decalin with 9.3 wt % 5kg/mol PB and PAO), the non-associative PCOD in PAO demonstrated lower relaxation times than the viscosity-matched decalin at concentrations below overlap. Additionally, despite having nearly three times the solvent viscosity, the relaxation times for PCOD in PAO below overlap are substantially less than three times that of decalin, even though the Zimm relationship for relaxation times of dilute solutions predicts a linear relationship between relaxation time and solvent viscosity.[29] These results are in line with the observed specific viscosities, and might suggest that the PCOD chains in PAO are not interacting

as strongly with the flow as the polymers in better solvent. However, comparing the decalin with and without the short polybutadiene added, we see an outsized increase in extensional relaxation time relative to their ratio of solvent viscosities, suggesting that a lower solvent quality might be increasing the relaxation time, contradicting that conclusion about the chains in PAO. One hypothesis to explain both results is that the poor solubility of PCOD in PAO resulted in polymer coils that are not stretching, acting more like semi-flexible polymers; while the decalin with polybutadiene still allows the chains to stretch. This hypothesis is in line with chain scission measurements in the literature that point towards increased chain scission in poorer (but still fully soluble) solvent[25]—the chains in poorer solvent resist extension more, leading to higher extensional relaxation times and chain scission at lower extension rates. These contradictory results suggest further interogation of the role of solvent quality in extension of dilute solutions, while controlling for solvent viscosity effects.

**Role of Association in Shear and Extension**

DA PCOD in decalin is highly self-associative (see Chapter 5 for further discussion of DA self-association and network formation). At low temperatures, the self-association has previously been shown to result in higher specific viscosities than pairwise association due to network formation.[30] In both shear and extension, DA in decalin demonstrated the highest measured specific viscosity and extensional relaxation time, shear thinning at $c/c^* = 0.5$, and high variance in extensional measurements, evidence of large megasupramolecular formations and possible network formation and disruption. In contrast, the shear and extensional measurements demonstrated significantly reduced effect of DA alone compared to DA:DB in PAO, implying the network self-association

of DA is suppressed in PAO.

On the other hand, DB in decalin is not self-associative, and has similar shear and extensional properties to non-associative PCOD, while DA:DB paired shows evidence of association in both shear and extension in decalin, in line with prior studies.[30] Surprisingly, in PAO, DB demonstrated similar shear viscosity and extensional relaxation time as DA:DB, implying that some kind of self-association directly between DB end-groups or indirectly via the BHT additive may be occurring for DB PCOD samples in PAO.

**Changing Behavior in Spray**

Even at small amounts of polymer additive ($\leq 0.05$ wt %), both non-associative and associative, the spray behavior of PAO under the typical accidental release conditions substantially changed. By decreasing the spray angle and suppressing small droplets, the spray would be less likely to ignite in an accident. Additional PCOD (i.e., 0.1 wt % compared to 0.05 wt %) led to thicker ligaments and substantially modified spray behavior, which could overshoot the desired properties—we want to suppress small droplets, but not interfere with the flow through pumps inside the vehicle, or in the case of using an additive in fuel, still allow the fuel to ignite under the high-pressure conditions in an engine. Keeping the polymer additive content low is also desirable for use in the field—standards for lubricants and fuels require minimal additions of solids and increasing concentration can cause solubility issues.

## 4.5   Conclusion

Adding associative polycyclooctadiene to polyalphaolefin accomplishes our goal of controlling the droplet formation of a spray under simulated accidental release of a hydrocarbon lubricant using a pumping-tolerant additive. The increase in extensional relaxation time of the polymer solution is correlated with

the increased ligament diameter and suppression of small droplets. Even in a solvent for which this additive was not designed, the end-groups are shown to associate via increased shear viscosity and extensional relaxation time.

While DA:DB PCOD acted as a functional mist-control agent around room temperature in PAO, two directions of improvement are suggested by this work. First, PCOD has relatively low solubility in PAO, particularly as temperature decreases, which leads to collapsed coils and high overlap concentrations, leading to lower extensional performance per unit mass of polymer. Tailoring the backbone of the polymer to be better suited to PAO would likely improve performance of the additive to allow further decrease in the application concentration and assist in meeting standards that require solubility at low temperatures. Second, the DA:DB association was not as strong in PAO as in decalin, and more dramatic behavior changes per unit mass of polymer added could come from creating longer megasupramolecules and thus higher extensional relaxation time with larger association strength. Work on alternate associative groups could accomplish two tasks: lower additive loading for the same effect and eliminate the need for the excess of BHT added to solubilize the end groups. Further discussion of the optimization of additives for PAO will appear in the thesis of Hojin Kim.

## References

[1] L. Yuan. "Ignition of Hydraulic Fluid Sprays by Open Flames and Hot Surfaces". In: *Journal of Loss Prevention in the Process Industries* 19.4 (July 2006), pp. 353–361. ISSN: 09504230. DOI: `10.1016/j.jlp.2005.09.001`. URL: `http://linkinghub.elsevier.com/retrieve/pii/S095042300500166X` (visited on 12/21/2018).

[2] S. Gant. *Generation of Flammable Mists from High Flashpoint Fluids: Literature Review*. Research Report RR980. Derbyshire: Health and Safety Executive, 2013.

[3] K. K. Chao et al. "Antimisting Action of Polymeric Additives in Jet Fuels". In: *AIChE Journal* 30.1 (Jan. 1984), pp. 111–120. ISSN: 0001-1541, 1547-5905. DOI: `10.1002/aic.690300116`. URL: `http://doi.wiley.com/10.1002/aic.690300116` (visited on 03/23/2016).

[4] R. S. Marano et al. "Polymer Additives as Mist Suppressants in Metalworking Fluids Part I: Laboratory and Plant Studies - Straight Mineral Oil Fluids". In: *S.A.E. Transactions* 104 (Section 5 1995), pp. 136–146.

[5] G. H. McKinley and T. Sridhar. "Filament-Stretching Rheometry of Complex Fluids". In: *Annual Review of Fluid Mechanics* 34.1 (2002), pp. 375–415. URL: `http://www.annualreviews.org/doi/abs/10.1146/annurev.fluid.34.083001.125207` (visited on 03/23/2016).

[6] M.-H. Wei et al. "Megasupramolecules for Safer, Cleaner Fuel by End Association of Long Telechelic Polymers". In: *Science* 350.6256 (Oct. 2, 2015), pp. 72–75. ISSN: 0036-8075, 1095-9203. DOI: `10.1126/science.aab0642`. URL: `http://www.sciencemag.org/cgi/doi/10.1126/science.aab0642` (visited on 03/17/2016).

[7] P. S. Virk. "Drag Reduction Fundamentals". In: *AIChE Journal* 21.4 (July 1975), pp. 625–656.

[8] S. A. Vanapalli, M. T. Islam, and M. J. Solomon. "Scission-Induced Bounds on Maximum Polymer Drag Reduction in Turbulent Flow". In: *Physics of Fluids* 17.9 (2005), p. 095108. ISSN: 10706631. DOI: `10.1063/1.2042489`. URL: `http://scitation.aip.org/content/aip/journal/pof2/17/9/10.1063/1.2042489` (visited on 05/05/2016).

[9] A. Somervaille, G. Betts, and C. F. I. Grains Research and Development Corporation (Australia). *Adjuvants: Oils, Surfactants and Other Additives for Farm Chemicals*. Kingston, ACT: Grains Research & Development Corporation, 2011. ISBN: 978-1-921779-32-9.

[10] R. W. Lewis et al. "Polymeric Drift Control Adjuvants for Agricultural Spraying". In: *Macromolecular Chemistry and Physics* 217.20 (Oct. 2016), pp. 2223–2242. ISSN: 10221352. DOI: `10.1002/macp.201600139`.

URL: https://onlinelibrary.wiley.com/doi/10.1002/macp.201600139 (visited on 03/23/2022).

[11]    R. L. A. David. "Associative Polymers as Antimisting Agents and Other Functional Materials via Thiol-Ene Coupling". Pasadena, California: California Institute of Technology, Mar. 7, 2008. 189 pp. URL: http://thesis.library.caltech.edu/2173/.

[12]    M.-H. Wei. "Synthesis and Potency of Long End-Associative Polymers for Mist Control". Pasadena, California: California Institute of Technology, 2014.

[13]    B. Keshavarz et al. "Studying the Effects of Elongational Properties on Atomization of Weakly Viscoelastic Solutions Using Rayleigh Ohnesorge Jetting Extensional Rheometry (ROJER)". In: *Journal of Non-Newtonian Fluid Mechanics* 222 (Aug. 2015), pp. 171–189. ISSN: 03770257. DOI: 10.1016/j.jnnfm.2014.11.004. URL: http://linkinghub.elsevier.com/retrieve/pii/S0377025714002055 (visited on 01/06/2017).

[14]    S. Kooij et al. "What Determines the Drop Size in Sprays?" In: *Physical Review X* 8.3 (July 20, 2018). ISSN: 2160-3308. DOI: 10.1103/PhysRevX.8.031019. URL: https://link.aps.org/doi/10.1103/PhysRevX.8.031019 (visited on 06/11/2020).

[15]    R. P. Mun, J. A. Byars, and D. V. Boger. "The Effects of Polymer Concentration and Molecular Weight on the Breakup of Laminar Capillary Jets". In: (1998), p. 13.

[16]    B. Keshavarz et al. "Ligament Mediated Fragmentation of Viscoelastic Liquids". In: *Physical Review Letters* 117.15 (Oct. 7, 2016). ISSN: 0031-9007, 1079-7114. DOI: 10.1103/PhysRevLett.117.154502. URL: https://link.aps.org/doi/10.1103/PhysRevLett.117.154502 (visited on 08/14/2017).

[17]    J. Dinic and V. Sharma. "Macromolecular Relaxation, Strain, and Extensibility Determine Elastocapillary Thinning and Extensional Viscosity of Polymer Solutions". In: *Proceedings of the National Academy of Sciences* 116.18 (Apr. 30, 2019), pp. 8766–8774. ISSN: 0027-8424, 1091-6490. DOI: 10.1073/pnas.1820277116. URL: http://www.pnas.org/lookup/doi/10.1073/pnas.1820277116 (visited on 05/05/2021).

[18]    V. Tirtaatmadja, G. H. McKinley, and J. J. Cooper-White. "Drop Formation and Breakup of Low Viscosity Elastic Fluids: Effects of Molecular Weight and Concentration". In: *Physics of Fluids* 18.4 (Apr. 2006), p. 043101. ISSN: 1070-6631, 1089-7666. DOI: 10.1063/1.2190469. URL: http://aip.scitation.org/doi/10.1063/1.2190469 (visited on 08/14/2017).

[19]  C. M. Schroeder. "Single Polymer Dynamics for Molecular Rheology". In: *Journal of Rheology* 62.1 (Jan. 2018), pp. 371–403. ISSN: 0148-6055, 1520-8516. DOI: `10.1122/1.5013246`. URL: `http://sor.scitation.org/doi/10.1122/1.5013246` (visited on 01/06/2018).

[20]  T. Q. Nguyen, G. Yu, and H.-H. Kausch. "Birefringence of a Polystyrene Solution in Elongational Flow: Effects of Molecular Weight and Solvent Quality". In: *Macromolecules* 28.14 (July 1995), pp. 4851–4860. ISSN: 0024-9297, 1520-5835. DOI: `10.1021/ma00118a010`. URL: `http://pubs.acs.org/doi/abs/10.1021/ma00118a010` (visited on 09/13/2016).

[21]  A. Keller and J. A. Odell. "The Extensibility of Macromolecules in Solution; A New Focus for Macromolecular Science". In: *Colloid & Polymer Science* 263.3 (Mar. 1985), pp. 181–201. ISSN: 0303-402X, 1435-1536. DOI: `10.1007/BF01415506`. URL: `http://link.springer.com/10.1007/BF01415506` (visited on 04/06/2022).

[22]  Y. Rabin, F. S. Henyey, and R. K. Pathria. "Scaling Behavior of Dilute Polymer Solutions in Elongational Flows". In: *Physical Review Letters* 55.2 (July 8, 1985), pp. 201–203. ISSN: 0031-9007. DOI: `10.1103/PhysRevLett.55.201`. URL: `https://link.aps.org/doi/10.1103/PhysRevLett.55.201` (visited on 04/05/2022).

[23]  M. Doi and S. F. Edwards. *The Theory of Polymer Dynamics*. International Series of Monographs on Physics. Oxford: Clarendon press, 1986. ISBN: 978-0-19-852033-7.

[24]  T. Moussa, C. Tiu, and T. Sridhar. "Effect of Solvent on Polymer Degradation in Turbulent Flow". In: *Journal of Non-Newtonian Fluid Mechanics* 48 (1993), pp. 261–284.

[25]  A. Dupas et al. "Mechanical Degradation Onset of Polyethylene Oxide Used as a Hydrosoluble Model Polymer for Enhanced Oil Recovery". In: *Oil & Gas Science and Technology – Revue d'IFP Energies nouvelles* 67.6 (Nov. 2012), pp. 931–940. ISSN: 1294-4475, 1953-8189. DOI: `10.2516/ogst/2012028`. URL: `http://ogst.ifpenergiesnouvelles.fr/10.2516/ogst/2012028` (visited on 01/15/2019).

[26]  H. Kim. "Megasupramolecules in Extremely Non-Polar Solvents: What to Do When 3000+ Backbone Units Fail to Drag Two End-Groups into Solution". International Congress of Rheology. 2020.

[27]  R. Learsch. "Investigation in Experimental Conditions and Automation of Dripping-onto-Substrate Rheology". American Chemical Society Spring Meeting (San Diego, CA). Mar. 23, 2022.

[28]  S. N. Laboratories. *Engine Combustion Network Schlieren Processing Code*. Engine Combustion Network. 2011. URL: `https://www.sandia.gov/ecn/code.php` (visited on 05/06/2022).

[29]   F. D. Giudice, S. J. Haward, and A. Q. Shen. "Relaxation Time of Dilute Polymer Solutions: A Microfluidic Approach". In: (), p. 12.

[30]   B. Li. "Ring/Chain versus Network: Architecture Induced by Self- versus Pairwise- Association of Telechelic Polymers". Pasadena, California: California Institute of Technology, 2016. 244 pp.