Soft Matter

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Journal:	*Soft Matter*
Manuscript ID	SM-ART-08-2023-001084.R1
Article Type:	Paper
Date Submitted by the Author:	30-Oct-2023
Complete List of Authors:	Bauman, Grant; University of Colorado Boulder, Chemical and Biological Engineering White, Tim; University of Colorado Boulder, Chemical and Biological Engineering; University of Colorado Boulder, Materials Science and Engineering

ARTICLE

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Oligomers containing significant quantities of liquid crystalline monomers display thermotropic liquid crystalline behavior. Of particular interest is the formation of an aligned nematic phase in response to shear flow experienced when liquid crystalline oligomers are 3-D printed via direct ink write. The procession from a macroscopically disordered phase to a macroscopically ordered phase is distinct and depends on the initial state of the oligomers. When the oligomers begin in a polydomain nematic state, the transition to an aligned nematic state occurs gradually over a wide range of shear rates. Conversely, when the oligomers begin in an isotropic state they behave as a Newtonian fluid until a critical shear rate is reached, at which point they align in a critical manner. It is shown that by either decreasing liquid crystalline content or increasing temperature, the viscosity of the oligomer melt decreases while this critical shear rate increases. In addition, the normal stress of oligomers is positive over all shear rates but decreases significantly in magnitude with increasing temperature. By combining the analysis of both temperature and liquid crystalline content, it is demonstrated that the temperature relative to the nematic-isotropic transition temperature is key to the oligomers' unique flow behaviors.

Introduction

Liquid crystalline phases are a byproduct of an intermolecular force balance that minimizes free energy via orientational ordering of molecules. The simplest type of liquid crystalline ordering is the nematic phase in which molecules have one degree of orientational order.[1,2] In a nematic domain, liquid crystalline molecules are aligned on average in a single direction. The orientation of these molecules is referred to as the nematic director.[3] On the macroscale, materials in the nematic state can be described as polydomain[4,5] (many domains, with random distribution of orientation) or monodomain (a single or many domains, with a consistent nematic director). Because of the balance of attractive and repulsive forces between molecules, nearly all liquid crystalline phases are naturally thermotropic. As a result, a liquid crystal (LC) will transition from the nematic phase to the isotropic phase when heated above the nematic-isotropic transition temperature (T_{NI}).[2]

The characteristics of the nematic state lead to a number of unique rheological behaviors which have long been a subject of scientific interest. Broadly, the materials which have been studied fall into two distinct classes: small molecule liquid crystals and liquid crystalline polymers (LCPs). Occupying the space between these two classes of materials are liquid crystalline oligomers. These molecules are made of a small number of repeat units that gives them properties between those of small molecules and LCPs. Recently, there has been a growing interest in LC oligomers as starting materials for direct ink write 3-D printing of liquid crystalline networks.[6–12] Of particular interest are their well-demonstrated tendency to align during extrusion from a 3-D printer, accessible T_{NI} (often below 60°C)[13,14], and ability to flow at moderate temperatures as a solvent-free melt.[9,13] As LC oligomers become more common in 3-D printing applications, there is a need to understand the fundamental rheology of these materials, particularly in situations relevant to direct ink writing.

There are decades of studies which have reported on the rheological behavior of both small molecule liquid crystals and LCPs.[5] From these reports, there are several rheological phenomena unique to liquid crystalline systems that are of interest. One of the more noteworthy findings is the observation that the nematic director of an LC can react to an applied shear flow in multiple ways.[15,16] In some small molecule LCs or lyotropic LCPs, a phenomenon known as director tumbling will occur.[17–19] In a director tumbling regime, the hydrodynamic torques on the liquid crystalline molecules are unbalanced and the angle of the nematic director never reaches a steady state, instead fluctuating over time.[20] Director tumbling LCs stand in contrast to LCs that align along the direction of shear flow.[15] So-called flow-aligning LCs will reach a steady state after some period of time in shear flow. Many thermotropic LCPs have been found to be flow-aligning. There are many factors, such as temperature, that contribute to whether an LC molecule will respond to shear flow with director tumbling or flow alignment. It has been shown that increasing

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

the temperature of small molecule LCs causes them to exhibit more flow-aligning properties.[21,22] In addition, high shear rates tend to promote flow alignment while low shear rates are more likely to produce director tumbling.[23,24] The numerous reports of monodomain nematic networks printed from LC oligomers suggest that LC oligomers exhibit flow aligning behavior, which is consistent with the behavior of most thermotropic LCPs.

One important consequence of flow aligning behavior is a difference in viscosity that arises between aligned and unaligned materials.[25] This is a result which has been identified in both LCPs and more recently LC oligomers.[26] This allows the state of a liquid crystalline material to be monitored through viscosity measurements.[27] Specifically, the transition between a macroscopically unaligned state (polydomain or isotropic) and a monodomain nematic state is accompanied by a decrease in viscosity that may be as large as an order of magnitude.[26,28,29]

In addition to changes in viscosity, liquid crystalline fluids exhibit trends in normal stress due to their orientational ordering. As a viscoelastic liquid crystalline fluid aligns along the direction of shear, the anisotropic microstructure of the material leads to tension along streamlines which in turn results in normal stress.[30] Although there are many ways that normal stresses can develop in liquid crystalline fluids due to the numerous ways these fluids respond to flow, it is generally seen that flow-aligning thermotropic LCPs will display positive values of the first normal stress difference (N_1).[31–34] However, the analysis of normal stress during shear flow is complicated by the gradient in shear rate experienced by a fluid on a parallel plate rheometer. Parallel plate rheometers cannot directly measure N_1, instead reporting only the total thrust between the plates.[35] Although no quantitative analysis of N_1 is possible with a parallel plate rheometer, the thrust (and thus stress) between the plates does scale with the quantity ($N_1 - N_2$) through an equation that includes a Rabbinowitch-type correction.[35,36] Therefore, we propose that measuring the total normal stress generated by liquid crystalline oligomers in a flat plate rheometer can allow a purely qualitative assessment of the magnitude of normal forces in the fluid that result from liquid crystalline alignment.

While the rheology of small molecule LCs and LCPs has been the subject of considerable study, liquid crystalline oligomer rheology has received only cursory attention. Due to their molecular weights that fall between small molecules and polymers, oligomers possess rheological behaviors that have not been documented in other liquid crystalline materials. Multiple studies have analyzed the rheology of a diverse array of oligomer systems[37–39], but only recently has a study been directed towards oligomers that specifically possess thermotropic liquid crystalline character. In this report it was seen that LC oligomers for 3-D printing applications show large changes in their viscosity over time during shear flow inception and cessation.[26] In addition, a bifurcation in the behavior of the oligomers was seen where at temperatures below T_{NI} the material would align under a 10 s^{-1} shear flow but above T_{NI} would not. This finding stands in contrast to experimental reports of LC oligomers with T_{NI} below room temperature being 3-D printed into aligned liquid crystalline elastomers.[14] Although it is well-known that many LC oligomers in the nematic state align with shear flow, the behaviors of LC oligomers in the isotropic state is less understood. This preliminary study seeks to further elucidate the difference in rheology between thermotropic liquid crystalline oligomers above and below T_{NI}. To this end, the relationship between the liquid crystalline state of the oligomers and their rheological properties is assessed through variation of composition and temperature. Through viscosity measurements it is seen that while both nematic and isotropic oligomers can align with shear flow, the way this transition occurs is different for oligomers in each state. For nematic oligomers, the transition to a monodomain state takes place gradually over a wide range of shear rates. For oligomers in the isotropic state, they behave as Newtonian fluids until a critical shear rate is reached at which point they rapidly proceed to an aligned state. This critical shear rate is found to be directly linked to the temperature of the oligomers relative to T_{NI}. In addition, normal stress is found to be positive and highly temperature dependent for these oligomers which in conjunction with viscosity data provides further evidence of the flow aligning behavior of LC oligomers. Overall, LC oligomers display many behaviors similar to thermotropic LCPs but exhibit enough distinct trends to warrant further rheological characterization.

Experimental

Materials

The oligomers used in this study were synthesized via a previously reported thiol-Michael addition reaction.[13,26,40] In this procedure, diacrylate monomers are mixed with the dithiol monomer EDDT (2,2’-(ethylenedioxy)diethanethiol, Aldrich) in a molar ratio of 0.8 acrylate groups : 1 thiol groups. Two diacrylate monomers were used in this study: the liquid crystalline monomer C6M (1,4-bis[4-(6-acryloyloxy-hexyloxy)benzoyloxy]-2-methylbenzene, Wilshire Technologies) and the non-liquid crystalline monomer DEGDA (Di(ethylene glycol) diacrylate, Aldrich). The ratio of these two monomers was varied to create a series of eight oligomers containing different concentrations of the liquid crystalline monomer. The oligomers are labeled TMO_x, where x is the mass of the liquid crystalline monomer divided by the total mass of the material. Formulation details are provided in the Supplemental Information. Based on the reactants utilized here, we expect the oligomers to be linear. A tetra-functional ene crosslinking monomer (glyoxal bis(diallyl acetal), Aldrich) is included at a molar ratio of 0.2 ene functional groups : 1.0 thiol functional groups. Although the crosslinking reaction was not initiated in any of the materials in this study, the crosslinker is included to relate this study to compositions relevant to 3-D printing. The addition reaction between acrylate and thiol functional groups is facilitated by 1 wt% of dipropylamine (Aldrich) in the mixture. Also included in the mixture are 1 wt% of the inhibitor butylated hydroxytoluene (Acros Organics) and 1.5 wt% of the photoinitiator 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure 369, IGM Resins). All reagents were used as received. After melting and vortex mixing all components in a glass vial, the vial is placed on a 65°C hotplate for three hours. After three hours, the vial is transferred to an 80°C oven for one hour to ensure completion of the thiol-Michael addition reaction. After completion of this reaction, the mixture is a viscous liquid which will be referred to as the "oligomers". When analyzed via GPC and referenced to a polystyrene standard, the oligomers have an M_n of between 4000 g/mol and 8000 g/mol which corresponds to a number of repeat units of between 8 and 11 (Fig. S2). Additionally, each oligomer mixture was subjected to differential scanning calorimetry to determine T_{NI}. In Fig. S3, it can be seen that T_{NI} decreases as the liquid crystalline content of the oligomers decreases until the point that a nematic phase is not present at any temperature.

Shear Rheology

All rheology experiments were performed on a TA Instruments ARES G2 rheometer equipped with a Peltier plate and 20 mm stainless steel parallel plates geometry. The sample thickness was set at 0.3 mm for all tests to minimize edge fracture of the oligomers at high shear rates. After loading onto the rheometer, the thermal history of the oligomers was cleared by briefly heating to 60°C and then slowly cooling to the desired test temperature. After equilibrating at the experimental temperature for 1 minute, samples were subjected to a flow sweep from 0.01 s^{-1} to 100 s^{-1}. Data points were recorded when the measured value was within 5% for three consecutive 10 second periods.

Results

Rheology of Oligomers with Varied Liquid Crystalline Content

We first explored the effect of liquid crystalline content on the rheological alignment of oligomers. Flow sweeps of $TMO_{0.72}$, $TMO_{0.6}$, and TMO_0 show the effect of changing liquid crystalline content on the viscosity of the oligomer melts as well as the presence of shear thinning behavior (flow sweeps for full TMO_x series included in Fig. S4). $TMO_{0.72}$, which is nematic at room temperature, shows a gradual shear thinning which begins after a viscosity maximum that occurs at a shear rate of approximately 0.025 s^{-1} and continues through 100 s^{-1} (Fig. 1a). This corresponds to the liquid crystalline elements of the oligomers aligning along the direction of shear over a broad range of shear rates. This type of behavior is in good agreement with a previous report that LC oligomers align under shear over considerable lengths of time.[26] $TMO_{0.6}$, which is isotropic at room temperature but still possesses a high degree of liquid crystalline content, displays a much sharper onset of shear thinning. Such a critical onset of shear thinning and mesogen alignment has been previously observed in legacy examinations of the rheology of thermotropic LCPs and was not accompanied by noticeable edge failure of the oligomers.[28,41] Until a shear rate of approximately 30 s^{-1}, $TMO_{0.6}$ behaves as a Newtonian liquid with only slight fluctuations in the measured viscosity. It is not clear if these viscosity oscillations represent a small degree of director tumbling or are associated with experimental fluctuations. The sharp onset of shear thinning in $TMO_{0.6}$ is distinctive in showing that isotropic oligomers can be aligned by shear at sufficiently high applied shear rate. This critical shear rate, which is indicative of the shear rate necessary to see a degree of nematic alignment, is an important input in the preparation of aligned LCE via rheological printing methods.

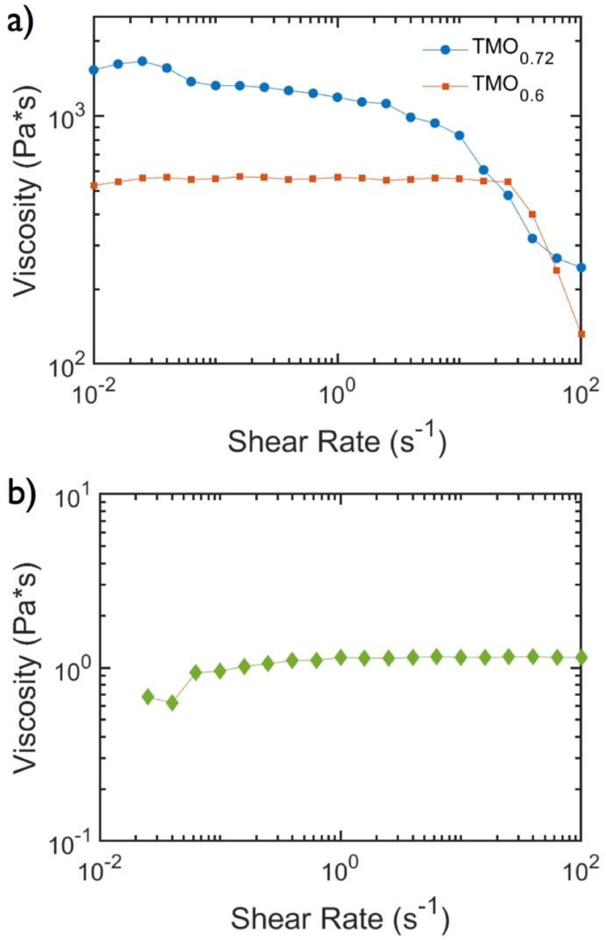

Figure 1. a) Flow sweep of $TMO_{0.72}$ and $TMO_{0.6}$ at ambient temperature showing the different shear thinning behavior of nematic and isotropic oligomers. b) TMO_0 shows no shear thinning behavior at ambient temperature

Here, we define a critical shear rate ($\dot{\gamma}_c$) as the shear rate at which the viscosity reaches a value of 75% of the maximum value recorded during the flow sweep. Prior studies have indicated oligomers which align will reach a viscosity lower than this while oligomers that do not align will remain above this value.[26] As evident in Fig. 1b, an entirely non-liquid crystalline material (TMO_0) exhibits Newtonian flow over the entire range of shear rates tested.

The critical shear rates of the TMO_x series of oligomers are shown in Fig. 2. It can be seen the critical shear rate needed to align the oligomers increases exponentially as liquid crystalline content is decreased. The increased shear rate needed to align the oligomers is due to the decrease in intermolecular interactions between mesogens that promote a nematic phase. Expectedly, as the temperature of the oligomers increases, the critical shear rate also increases. Increased thermal energy of the oligomers causes them to prefer an isotropic configuration which in turn increases the hydrodynamic force which must be applied to align them into a nematic phase. It is worth emphasizing the maximum shear rate tested in these experiments was 100 s^{-1} and oligomers with lower LC contents or higher temperatures may still align at higher shear rates even though they are not shown here. Nonetheless these results demonstrate the importance of maintaining a sufficiently high liquid crystalline content which is necessary to realize nematic alignment under typical 3-D printing conditions.

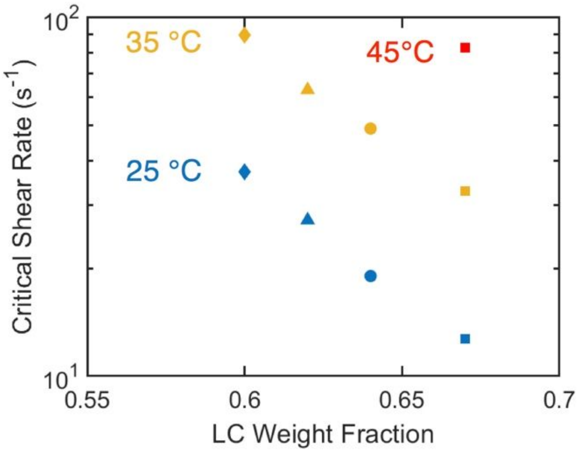

Figure 2. Critical shear rate of TMO$_{0.67}$ (squares), TMO$_{0.64}$ (circles), TMO$_{0.62}$ (triangles), and TMO$_{0.6}$ (diamonds) at 25 °C, 35 °C, and 45 °C. The critical shear rate is defined as the shear rate at which a 25 percent decrease in viscosity is observed during flow sweep experiments.

Rheology of Liquid Crystalline Oligomers as a Function of Temperature

While changing the liquid crystalline content of the oligomer melts is one way to affect the state they are in, changing temperature provides more straightforward control over oligomer morphology. By varying temperature, the rheological properties of a single oligomer melt can be probed in both the nematic and isotropic phases. To this end, TMO$_{0.72}$ (T$_{NI}$=43°C) was subjected to flow sweeps at several temperatures between 20°C and 80°C. Much as in the TMO$_x$ series of oligomers, the TMO$_{0.72}$ oligomers show markedly different shear thinning behavior depending on the state of the oligomers. When TMO$_{0.72}$ is at 22°C and in the nematic state, it displays the gradual shear thinning expected of a polydomain oligomer melt aligning to a monodomain state (Fig. 3a). At 55°C and in the isotropic state, TMO$_{0.72}$ behaves as a Newtonian liquid until a sudden drop in viscosity is seen at approximately 25 s^{-1}. Expanding the analysis to a wider temperature range, it can be seen that the maximum observed viscosity of TMO$_{0.72}$ during flow sweeps decreases exponentially with increasing temperature (Fig. 3b). It is notable that the slope of simple exponential functions fitted to the data in the nematic phase and the isotropic phase have significantly different slopes.

$$\text{viscosity} = k \times 10^{(m\text{T})} \qquad (1)$$

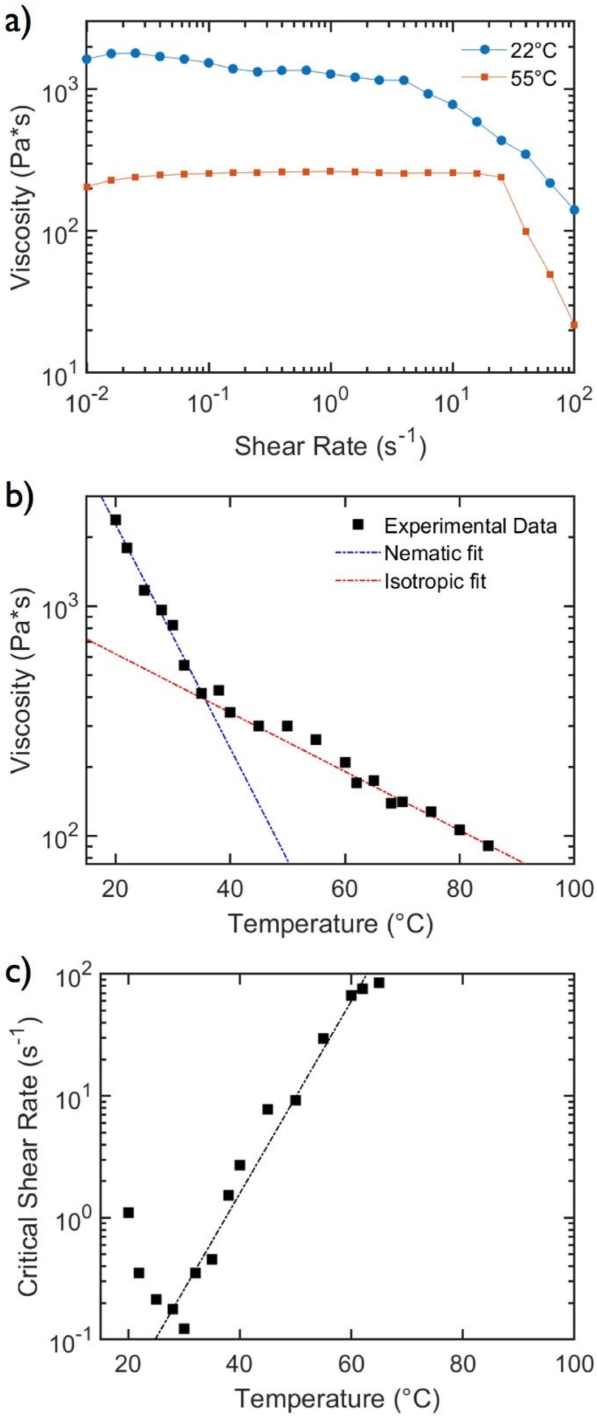

Figure 3. a) Flow sweeps of TMO$_{0.72}$ at 22 °C and 55 °C. In the nematic state, shear thinning occurs much more gradually than in the isotropic state. b) Viscosity of TMO$_{0.72}$ as a function of temperature. The dashed lines are exponential functions fitted to the data in the nematic phase and isotropic phase. c) Critical shear rate of TMO$_{0.72}$ as a function of temperature along with an exponential function fitted to the data above 30 °C.

Whereas the fitted value of *m* for the TMO$_{0.72}$ oligomers in the nematic state was found to be -0.49, the oligomers in the isotropic state were fitted with a value of *m* of -0.13. The steeper slope in the nematic region may be due to a combination of effects where the viscosity is decreasing due to temperature overcoming LC interactions that inhibit molecular mobility as well as the increased thermal energy of the oligomer chains. When the material is in the isotropic state, the LC interactions of the mesogens have already been overcome by thermal energy and thus this contribution to decreasing viscosity is absent.

In Fig. 3c, the critical shear rate of the $TMO_{0.72}$ oligomers reveals more important information about this material in flow. It can be seen at temperatures well below T_{NI}, the critical shear rate is below 1 s^{-1} which is indicative of oligomers which readily align with shear flow. Intriguingly, between 20°C and 30°C the critical shear rate decreases which could be due to greater ability of the mesogens to rotate due to decreased viscosity. Above 30°C, the critical shear rate monotonically increases until 65°C at which point no critical shear rate is observed. The trend of the data in this region is captured reasonably well by a simple exponential function such as Eq. (1). It is highly likely that this trend continues and a critical shear rate exists for the $TMO_{0.72}$ oligomers above 65°C, however it would be outside of the range of shear rates tested in this study.

Normal Stress of $TMO_{0.72}$ Oligomers

The flow aligning behavior of $TMO_{0.72}$ is further evidenced by the normal stress experienced during flow sweeps at several temperatures (Fig. 4). In general, normal stress increases with increasing shear rate. However, it is apparent that the magnitude of the normal stress is largely dependent on the temperature of $TMO_{0.72}$. At 22°C, normal stress reaches a maximum of approximately 50 kPa while at 80°C normal stress reaches a maximum of less than 1 kPa. Because positive values of normal stress are related to anisotropic microstructure in the fluid, this trend suggests that LC oligomers are less able to align at elevated temperature. In addition to a larger magnitude of normal stress, oligomers at lower temperature show an increase in normal stress at lower shear rates than oligomers at higher temperature. This is analogous to oligomers experiencing shear thinning and nematic alignment at lower shear rates as presented in Fig. 3c. From this data it is evident LC oligomers will more readily align and achieve a greater degree of anisotropic microstructure at lower temperatures.

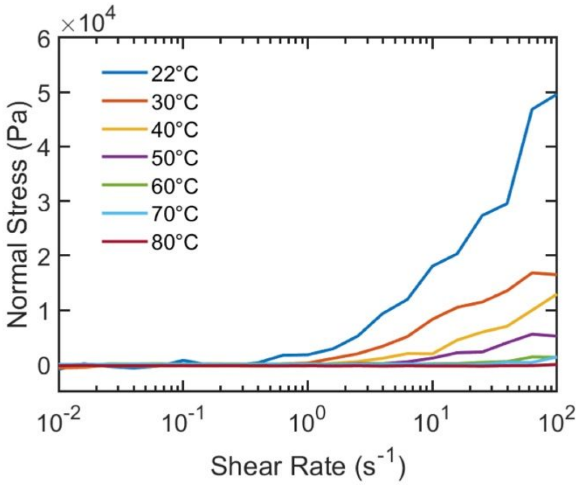

Figure 4. Normal stress of $TMO_{0.72}$ as a function of shear rate at seven temperatures. As temperature increases, the magnitude of N decreases and the shear rate at which it rises increases.

Discussion

Through flow sweeps performed on oligomers with changing LC content and temperature, the contributions of various factors can be difficult to isolate. For example, as the LC content of oligomers is decreased there is a corresponding decrease in the viscosity (Fig. S5). It is possible that either or both of these quantities are correlated with the increasing critical shear rate of the oligomers with decreased LC content. However, because many of the unique flow behaviors seen in these oligomers are due to the liquid crystalline nature of the material, one could expect the liquid crystalline properties of the oligomers to be key to their rheology. Specifically, the state of the oligomers is determined by the temperature of the oligomers in relation to T_{NI}. To see the effect of oligomer temperature relative to T_{NI} more clearly, several key metrics are plotted against a reduced temperature (T_r) defined as T_{sample}-T_{NI} in Fig. 5. Included in these plots are both the TMO_x series of oligomers with varied LC content tested at 25°C, 35°C, and 45°C and $TMO_{0.72}$ tested over a wide temperature range. In Fig. 5a, while the TMO_x and $TMO_{0.72}$ oligomers all display decreasing viscosity as T_r increases, the magnitude of the viscosity is not the same amongst these data sets. This emphasizes the effect temperature has on these oligomers, as oligomers at higher temperature tend to have lower viscosity regardless of T_r. While viscosity is primarily dependent on the temperature of the oligomers, $\dot{\gamma}_c$ shows a more consistent dependence on T_r (Fig. 5b). Both the TMO_x series and $TMO_{0.72}$ show an exponential increase in $\dot{\gamma}_c$ with increasing T_r (with the aforementioned exception of temperature well below T_{NI}) and are of a similar magnitude as well. What can be inferred from these data is that the hydrodynamic force needed to align the mesogens is strongly related to the thermal energy of the mesogens relative to the level that causes them to transition to the isotropic phase.

An interesting result of the viscosity being correlated to the temperature while the critical shear rate is correlated to T_r is that the maximum shear stress experienced by LC oligomers during a flow sweep from 0.01 s^{-1} to 100 s^{-1} shows three distinct regimes (Fig. 5c). At $T_r < 0$ °C the maximum shear stress experienced by the oligomers during the flow sweep decreases with increasing T_r as the viscosity of the oligomers decreases and $\dot{\gamma}_c$ remains small. This regime represents the conditions typically used in 3-D printing of LCEs, where the oligomers are in the nematic state and shear-align under even weak shear flows. Around T_r=0, this trend inverts, and the maximum shear stress increases with T_r. This regime represents isotropic oligomers aligned by shear flow, where rapidly increasing values of $\dot{\gamma}_c$ mean a greater shear stress is applied to the oligomers before they begin shear thinning. At T_r of approximately 20°C-40°C, a third regime is present in which the maximum shear stress once again decreases with increasing T_r. This regime represents isotropic oligomers that do not shear align at the flow rates tested here. This assertion is supported by the fact that oligomers do not exhibit a $\dot{\gamma}_c$ above the T_r at which this regime begins. Consequently, at temperatures suitably above T_{NI}, LC oligomers can be treated simply as Newtonian fluids due

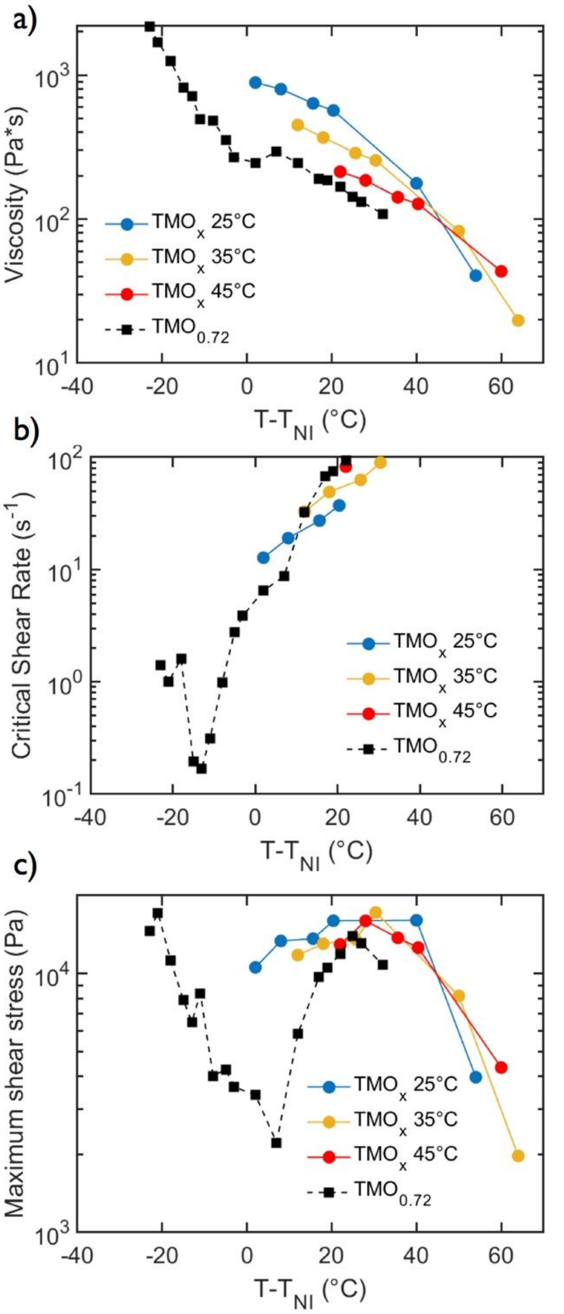

Figure 5. a) Viscosity of TMO$_x$ series of oligomers at 25 °C, 35 °C, and 45 °C plotted with TMO$_{0.72}$ viscosity at multiple temperatures. b) Critical shear rate of TMO$_x$ series of oligomers at 25 °C, 35 °C, and 45 °C plotted with TMO$_{0.72}$ critical shear rate at multiple temperatures. c) Maximum shear stress measured for TMO$_x$ series of oligomers at 25 °C, 35 °C, and 45 °C plotted with maximum shear stress measured for TMO$_{0.72}$ at multiple temperatures.

to the intermolecular interactions between mesogens being outweighed by the thermal energy of the molecules.

Conclusions

The rheology of liquid crystalline oligomers has been subject to systematic examination. Attributable to their intermediate molecular weight, they exhibit behaviors that deviate both from low-molar mass liquid crystals and also liquid crystal polymers. In the nematic state, oligomers display gradual shear thinning while in the isotropic state they show a dramatic onset of thinning. This bifurcation in the onset of shear thinning is consistent when the liquid crystalline content or temperature of the oligomers is changed. The normal stress of the oligomers under shear reinforces that oligomers at higher temperature require a greater shear rate to achieve nematic alignment and exhibit more weakly flow-aligning behavior. Experiments with both varied liquid crystalline content and temperature show that while viscosity is largely dependent on temperature, the critical shear rate required to observe shear thinning is closely linked with temperature of the oligomers relative to T$_{NI}$. As a result of these trends, the maximum shear stress LC oligomers experience during a flow sweep shows several different regimes which correspond to distinct material responses. These findings highlight some of the unique flow behaviors of liquid crystalline molecules of intermediate molecular weight and should be of some interest to applications where LC oligomers are being printed.

Author Contributions

G.E. Bauman: Conceptualization; Methodology; Writing - original draft preparation; Writing – review and editing (equal). **T.J. White:** Funding acquisition; Supervision; Writing – review and editing (equal)

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge financial support from the U.S. Department of Defense through a National Defense Science and Engineering Graduate Fellowship to G.E.B. The authors would like to thank Prof. Christopher Bowman for allowing extensive use of the ARES G2 rheometer and GPC. We appreciate the assistance of Dr. Benjamin Fairbainks for aiding with GPC experiments. We acknowledge Dr. Jeremy Koch for initial project inspiration, ideation, and guidance.

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