

Optical Rheology of New Liquid Crystalline Thermosets (LCTs): Influence of Shear on Disclination Texture

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ABSTRACT

Liquid crystalline thermosets (LCTs) have been under intensive study because of their outstanding mechanical performance and low viscosity during processing. We have successfully synthesized four kinds of nematic bismaleimide thermosets that differ in the nature of a pendant group substitution and that feature a thermally stable nematic phase. Importantly, the pendant groups were found to be efficient in depressing the melting point to a level that allows for flow and cure at reasonably low temperatures. By blending two particular monomers with monofunctional maleimide that we synthesized, N-(4-hydroxyphenyl) maleimide (HPMI), the melting point is depressed and the curing process is postponed to higher temperatures. Such a blend has a processing window amenable to much-needed thermal and rheological characterization, particularly the evolution of disclination density during shear flow as cure progresses. Our previous work on disclination density measurements during shear flow has revealed particular scaling of dimensionless disclination density with dimensionless shear rate. The influence of shearing on the disclination density, flow patterns, and molecular orientation though gelation of thermosetting liquid crystals remains unexplored. In this presentation, we will follow a description of material synthesis with a report on the results of optical rheology experiments applied to the ternary blends containing HPMI and two bismaleimide monomers, detailing the influence of shear on disclination density though gelation.

INTRODUCTION:

Because of their outstanding mechanical performance and low viscosity during processing, liquid crystalline thermosets (LCTs) have received intensive study over the past two decades.¹⁻⁴ Control over the micron-scale texture in LCTs may provide particular improvement in fracture toughness behavior. In 1998, C. Ortiz⁵ *et. al.* studied one type of epoxy-based LCT. In curing the material under different conditions, they prepared epoxy resins with amorphous, nematic, or smectic-A structures and compared their fracture behavior. The results showed that the material with a smectic-A structure exhibited slow, stable crack propagation and so had the highest fracture toughness. In their proposed toughening mechanism for the smectic-A resin, it was envisioned that upon deformation, unfavorably oriented domains fail first leaving microscopic voids as defects ahead of the crack tip. As a result, domains adjacent to the voids undergo plastic deformation. This mechanism is similar to that of polycrystalline metals, which are characterized by admirable ductility.

In light of these findings, we anticipate a significant role of disclination density in the toughening of LCTs, resulting in a need to control this parameter during processing. In previous work^{6,7}, we studied the dependence of disclination density on shear rate in simple shearing flow of two well-understood liquid crystalline

compounds, 5CB and 8CB. In those works, it was found that disclination density increases substantially with shear rate, an effect sometimes termed *textural refinement*, but to a greater extent in the case of 8CB. Also, with a modified rheological microscope,⁸ we have studied the influence of shear on the texture of liquid crystalline polymers, revealing quite distinct phenomena, including band formation on flow direction reversal⁹ and flow induced isotropic-nematic transition.¹⁰ However, the influence of flow on the disclination density, flow patterns, and molecular orientation through gelation of liquid crystalline thermosets has not been studied. In this paper, we will describe preliminary steps toward achieving this goal, including the synthesis of a series of the nematic bismaleimide (BMI) compounds and nematic oligomeric reactants (NORs) bearing the BMI group. We further present representative results of an optical rheology study on the synthesized materials for direct comparison to the behavior of 5CB and PSHQ6, the latter being a model thermotropic polymer. Our idea is that curing of LCTs traverses rheological characteristics of these two model systems and thus direct comparison should be revealing.

EXPERIMENTS:

Materials:

Chloro-hydroquinone, methoxy-hydroquinone, and *t*-butyl hydroquinone were obtained from Aldrich and purified by vacuum sublimation before use. Ethanol-free chloroform, used as solvent during etherification, and triethylamine were separately refluxed on CaH₂ and then distilled immediately before use. Other chemicals and solvents such as maleic anhydride, *p*-amino benzoic acid, oxalyl chloride, thionyl chloride, and hydroquinone were obtained from Aldrich and used without further purification. Poly-[(phenylenesulfonyl)-*p*-phenylene 1,6-hexamethylene bis(4-oxybenzoate)] (PSHQ6) was kindly supplied by Prof. C.D. Han of University of Akron.

Instrumentation:

DSC Differential Scanning Calorimetry (DSC) was performed using a Perkin-Elmer DSC7 with a nitrogen flow rate of 20 mL/min. The heat rate was 10 °C/min. Sample weights used were typically 10 mg.

Optical Microrheometry (OMR) The optical microrheometer used in this study was previously described in detail.^{8,10} With this device, a thin polymer film is sheared between heated quartz plates through the use of a stepper motor driving a ball screw. The stepper motor is controlled by a Compumotor™ indexer and drive system as commanded from a PC and the top and bottom disks are independently thermostated with embedded mica heaters and Eurotherm™ PID controllers. The sample thickness is set using a micrometer-based kinematic mount yielding a sample thickness of 50 μm, unless otherwise noted. This apparatus is mounted on an aus Jena microscope with the polarizer and analyzer crossed and the polarizer oriented at an angle 45° to the flow direction. The sample thickness and temperature is varied for different materials and thus is detailed individually for each experiment described in the discussion section.

In this paper, we employ a reciprocating shearing action in which the shear

rate is constant, but the direction of flow is periodically reversed. That is, at time zero, the shear begins at certain shear rate until reaching a prescribed value of strain. Once the strain is reached, the flow is reversed but with the same shear rate. When the absolute strain returns to zero, one period of shearing is completed.

Synthesis:

LCTs trimers and their blends

The chemical structure of the various LCT trimers and their nomenclature are listed in Figure 1, along with PSHQ6 and NOR6 (described below). The syntheses of the trimers and N-(4-hydroxyphenyl) multimode (HPMI) are essentially same as described previously¹¹⁻¹³. The preparation of the blends of LCTs trimers was conducted using a cosolvent and precipitation. Details of this processing and characterization by DSC and NMR will be described and discussed separately.¹⁴

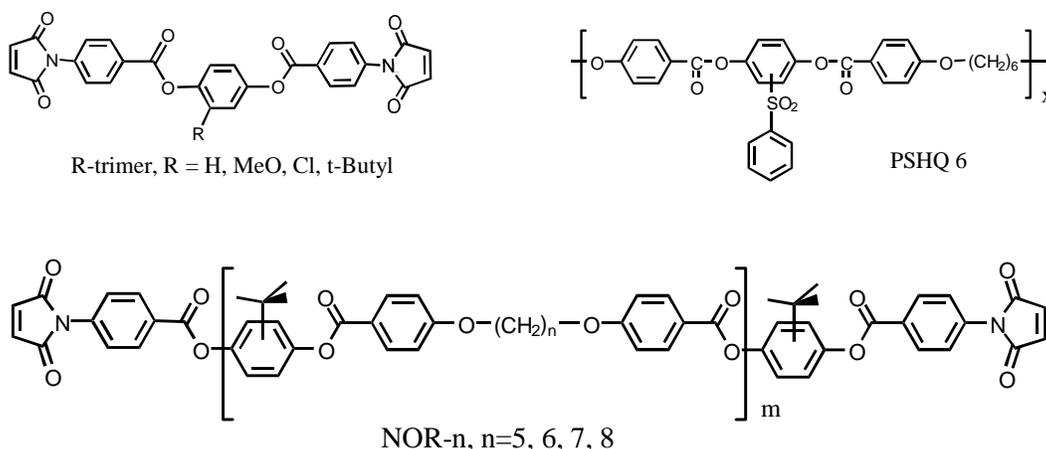


Figure 1. Chemical structure and nomenclature of the LCT trimers, PSHQ-6, and NOR-n.

Nematic oligomeric reactants (NORs)

The synthesis scheme for NORs is shown in Figure 2. Here we will describe the synthesis of NOR-6 as an example. In a three-necked flask, 3.95 g of 4, 4'-dichloroformyl- α,ω -diphenoxyhexane (10 mmol) and 1.83 g of t-butyl hydroquinone (11 mmol) were dissolved in anhydrous chloroform. 5 mL (36 mmol) of anhydrous triethylamine was then added slowly into the reaction mixture that was subsequently refluxed under nitrogen for three days. The solution was next chilled to 0 °C using an ice bath and 0.5 g of the *p*-maleimidobenzoylchloride (2.2 mmol) was added. The mixture was then stirred for 2 more days under a nitrogen atmosphere.

The reaction mixture was purified by twice dissolving and precipitating in chloroform and cold methanol, respectively. DSC and hot-stage polarizing optical microscopy (POM) characterizations revealed a T_g of 95 °C and T_{NI} of 190 °C. Gel permeation chromatography (GPC) yielded number- and weight-average molecular weights of 2915 and 4865 g/mol, respectively, as calibrated by narrow polydispersity polystyrene standards in THF at 30 °C.

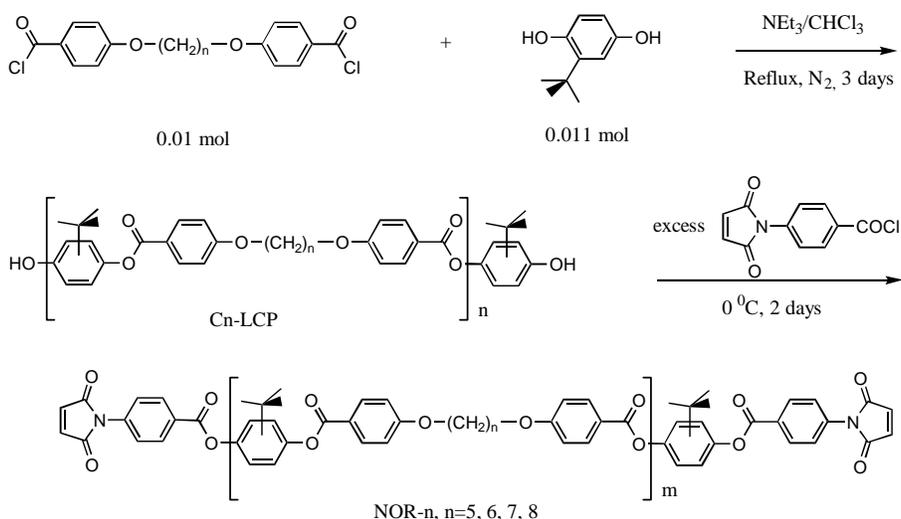


Figure 2. Schematic of the synthesis and of the NORs. See text for details.

RESULTS AND DISCUSSION:

Figure 3 presents the optical micrographs during shear of nematic pentylcyanobiphenyl (5CB). The sample thickness was 50 μm and the sample temperature was 30 $^\circ\text{C}$ (the melting and clearing transitions of this material are 22.4 $^\circ\text{C}$ and 34.5 $^\circ\text{C}$, respectively). From these micrographs, we can see that at low shear rate the microstructure is strongly dominated by surface anchoring that is heterogeneous due to a lack of surface treatment (other than standard cleaning). For the shear rates employed, 1, 5 and 10 s^{-1} , Erickson number, Er , values of 17.5, 87.5 and 175 result. Thus, low Er flows yield surface-dominated textures, while high Er flows yield texture dominated by the shearing flow, as expected. Apparently a shear rate of 5 s^{-1} ($Er = 87.5$) yields a response intermediate between surface-dominated and flow-dominated.

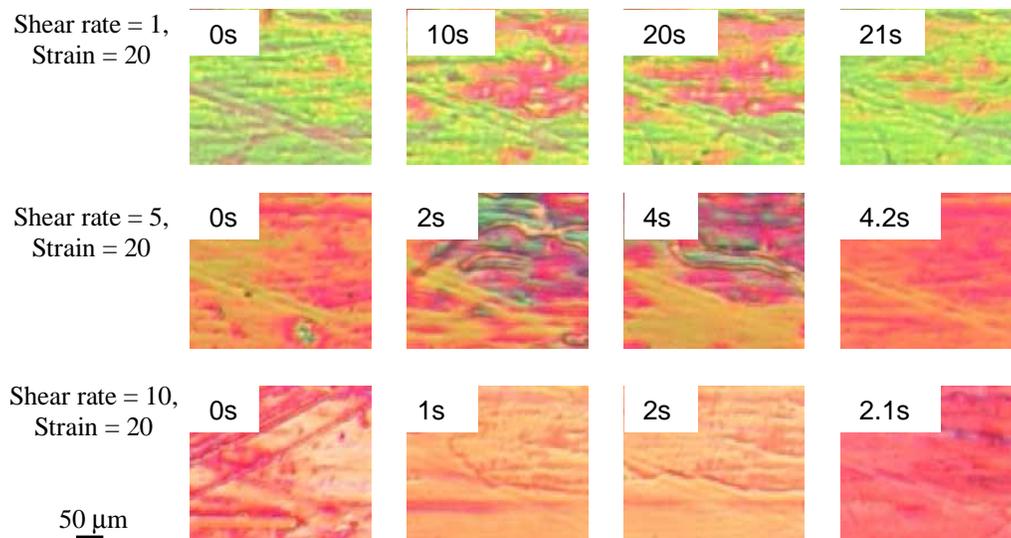


Figure 3. POM pictures of 5CB sheared at $T = 30\text{ }^\circ\text{C}$. The strain before reversal was 20, while the shear rates were 1, 5 and 10 s^{-1} from the first row to the last row. The flow direction was from left to right at first and then reverses after the third picture of each row. The crossed polarizers were oriented 45° to the flow. The observation times in seconds are shown in the right upper corner of each picture. The sample thickness was 50 μm .

Inspection of Figure 3, and consideration of other dynamic observations, we observe the proliferation of disclination lines on continued shearing and in proportion (more or less) to the shear rate. This follows previous work on 5CB using a rotational optical rheometer.⁶ Interestingly, we can see upon flow reversal that disclination lines formed during shearing disappear immediately, indicating rapid reversibility of disclination nucleation and deformation.

In contrast to the flow behavior of small-molecule nematics, thermotropic LCPs show dramatically different rheological and textural responses, owing to their macromolecular architecture. For example,¹⁰ we found that upon the shear reversal, a banded texture may appear, with such band formation occurring during the early stage of birefringence oscillations associated with flow reversal. According to these observations, it seems plausible that band formation is conditional on strain before reversal, shear rate, and relaxation time, the latter being related to molecular weight. Figure 4 shows POM micrographs upon shear reversal of PSHQ6 at $T = 210\text{ }^{\circ}\text{C}$ (nematic phase) and at different strains for two shear rates. From these micrographs, we find that band formation occurs for strains (before reversal) of 100, 50 and 40 at a shear rate of 0.5 s^{-1} . When strain reduced to a value below 30, no band formation occurs.

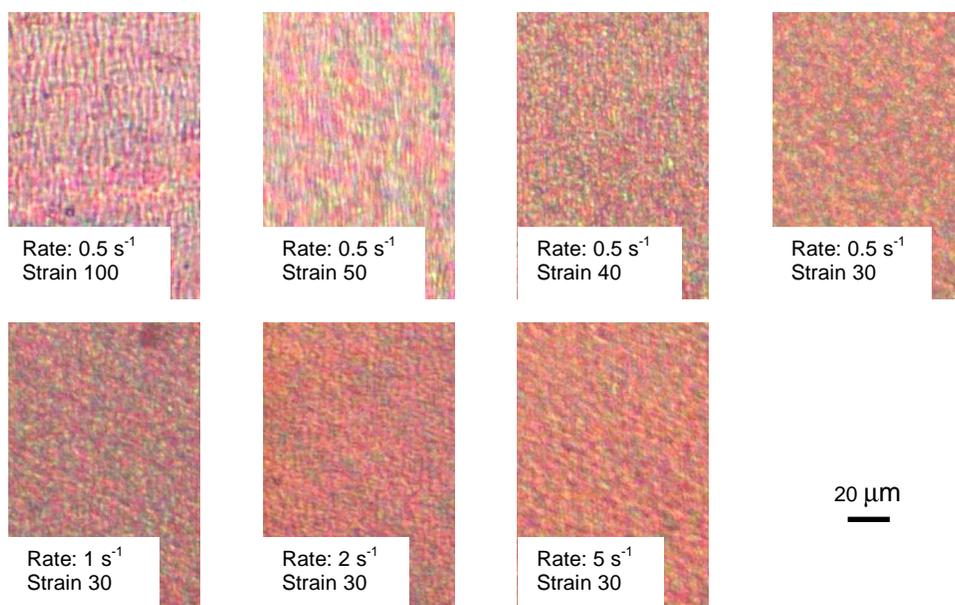


Figure 4. The POM pictures of optical rheology of PSHQ-6 upon the flow reversal. The temperature was $210\text{ }^{\circ}\text{C}$, The shear rates and strains are listed at the bottom of each picture. The crossed polarizers were oriented 45° to the flow. The sample thickness was $50\text{ }\mu\text{m}$. We can see a critical strain value of 30 for the bands formation for the 0.5 s^{-1} shear rate.

To compare with these model system observations, Figure 5 presents the optical rheology studies of a ternary blend contained 77.6 wt% Cl-trimer, 19.4 wt% MeO-trimer and 3 wt% HPMI. The crystal-nematic transition of this blend is $229\text{ }^{\circ}\text{C}$ and no isotropization is observed. The experimental temperature is $240\text{ }^{\circ}\text{C}$. We find with mechanical rheology methods (not shown) that the gelation of this kind of

material happens within a few minutes at this temperature. From Figure 4, we can see some gel particles in a sea of disclination-filled nematic liquid. This modified nematic fluid maintains low viscosity until a dramatic gelation point. As curing proceeds, no band formation is observed at flow reversal. We conclude that such ternary blends follow a non-homogenous polymerization during cure. That is, as the BMI groups polymerize, the molecular weight increases dramatically in a nonhomogeneous manner forming crosslinked particulate in the melt of uncured material. This procedure, reminiscent of precipitation polymerization of chloroethylene, is expected to lead to a low fracture toughness of the cured resin due to coarse inhomogeneity in crosslink density.

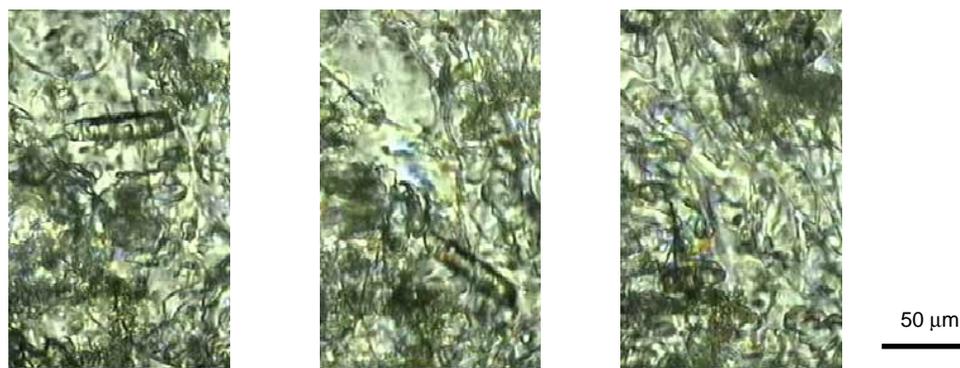


Figure 4. POM micrographs during shear of ternary trimer blend with 3 wt% HPMI at 240 °C. The three images are just before, during, and after flow reversal (resp.) from left to right. Gel particles are convected in flow with disclination lines. No bands form upon flow reversal. The shear rates and strains were 1 s^{-1} and 30 respectively, the crossed polarizers were oriented 45° to the flow and the sample thickness was 100 μm .

Finally, we examined NOR-6 as the example in our optical rheology study of the NOR-n architecture. Because this material has a lower clearing point than the cure temperature, we adopted the following thermal history: First, we made optical

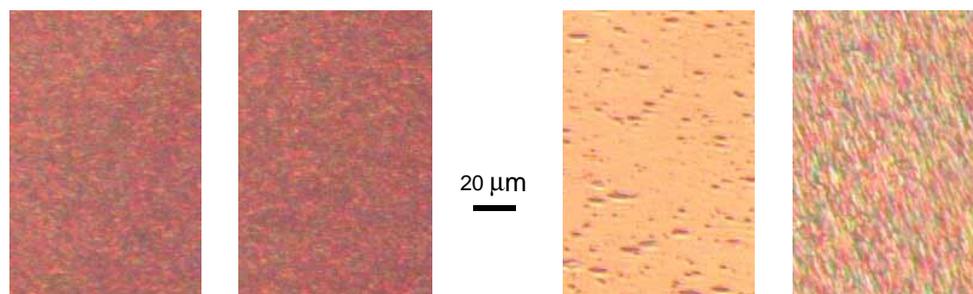


Figure 5. Optical rheology study of uncured (left) and partially cure (right) NOR-6. The first micrograph was taken 5 seconds before flow reversal, the second just upon the flow reversal. The third and fourth micrographs are of the sample cured at 240 °C for two hours. The third one was taken 5 seconds before the flow reversal, showing a near-monodomain nematic structure. The fourth picture reveals bands formed upon flow reversal. $T = 150 \text{ }^\circ\text{C}$ and the shear rates and strains were 1 s^{-1} and 30 respectively. The crossed polarizers were oriented 45° to the flow. The sample thickness was 50 μm .

rheology observations at 150 °C, with no cure reaction occurring, then we raised the temperature to 240 C (2 hours) to particularly cure the sample, and finally cooled it to 150 °C, for further study in the nematic phase.

From Figure 5, we can see that before cure, NOR-6 does not show any band formation on reversal even for strains greater than 50. After cure at 240 °C for two hours, however, we observe clear band formation even at lower strain values (30). This reflects a significant increase in molecular weight. In addition, shearing of the partially cured NOR-6 leads to a near-monodomain structure during shear; i.e., shearing such a sample may have the effect of lowering, rather than raising, the disclination density at high degree of cure. Also, in this material, no disruptive gel particles were observed, suggesting a homogenous cure procedure.

Conclusion:

In this study, we compared the optical rheology behavior of four kinds of liquid crystals: small molecular liquid crystal (5CB), polymeric liquid crystal and liquid crystalline thermosets of two types. The ternary blend showed non-homogenous cure procedure, characterized by the formation a suspension of gel particles in the sea of nematic melt of the monomer. This cure procedure is not desirable due to coarse heterogeneity in chemical and physical properties. In the cure of NOR-6, however, we observe a homogenous cure procedure. In addition, we also observed that shear engenders significant molecular alignment as high cure extent and at last produces a monodomain nematic structure. These observations show promise for use of architectures like NOR-6 for mechanical applications.

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