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Synthesis and Phase Behavior of Side-Group Liquid Crystalline Polymers in Nematic Solvents

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ABSTRACT: A model system of side-group liquid crystalline polymers (SGLCPs) with systematically varied molecular weight (from 78 to 420 kg/mol; PDI ≤ 1.16) and spacer length (8−12 atoms long) was prepared by polymer analogous synthesis. Matching the structure of the mesogenic units to that of the nematic solvent produced excellent solubility, even at molecular weights an order of magnitude greater than in prior literature on SGLCP solutions. Addition of up to 10 wt % polymer did not affect the ordinary and extraordinary refractive indices of the nematic host (4-pentyl-4′-cyanobiphenyl, 5CB), indicating that the order parameter was not significantly affected by the polymer.

1. Introduction

Polymers are often used in electrooptic liquid crystalline materials such as polymer dispersed liquid crystals,[1,2] polymer stabilized liquid crystals,[3,4] and compensating films.[5] The use of polymers in these systems depends on such factors as their solubility, birefringence (Δn), electrooptic response, and rheological properties. Experiments performed by Gu et al.[6] found that side-group liquid crystalline polymers (SGLCPs) greatly increase the twist viscosity of a liquid crystal solution to an extent that depends on the spacer length between the backbone and the pendant mesogenic groups. The rheological response of an SGLCP in the melt or in nematic solution also depends on its conformation. If a polymer has a smectic phase, it is likely to have an oblate conformation in all its mesomorphic phases. However, Mattoussi and Ober[7] have shown that this does not necessarily apply to a mesomorphic solution: they found a prolate conformation in a nematic solvent for an SGLCP that had an oblate conformation in the melt.[8] Here we describe the preparation of a precisely defined series of polymers that is ideal for characterizing the effects of a dissolved polymer on a liquid crystal (LC) host and for studying the relationships between chemical structure, phase transition temperatures, and polymer conformation. The characterization of this polymer series is essential for studies[9,11] that test the predictions of the Brochard theory.[10]

The theory proposed by Brochard[10] predicts how the addition of a polymer to a nematic liquid crystal affects its orientational and rheological response to an applied shear stress. In this theory the anisotropy of a liquid crystal polymer in a nematic solvent determines its effect[11−13] on the Leslie−Erickson[14,15] viscosity coefficients. Brochard theory predicts that addition of a polymer with a prolate spheroid conformation can cause the director to flow align at a steady-state angle near the velocity direction (tumbling parameter $\lambda > 1$) even if the LC solvent itself is a tumbling nematic ($|\lambda| < 1$). In contrast, Brochard predicts that addition of a polymer with an oblate (or disklike) spheroid conformation to a flow aligning nematic host ($\lambda > 1$) can result in a material where the director tumbles in response to an imposed shear ($|\lambda| < 1$). The theory even admits the possibility that addition of an oblate polymer to an LC solvent could produce a solution that exhibits flow alignment near the velocity gradient direction ($\lambda < -1$)—roughly perpendicular to the usual alignment direction for calamitic, or rodlike, nematics. In previous work,[11] we demonstrated that the addition of ~7.5 wt % of the high molecular weight, oblate-type SGLCPs used in this study could indeed change the viscosity coefficients sufficiently to cause a solution with calamitic mesogenic units to align near the velocity gradient direction rather than near the velocity direction.

In this study a model series of large SGLCPs was synthesized. The backbone of the polymer was synthesized using living anionic polymerization, for low polydispersity,[16−19] and the mesogen was attached in a second step.[20−23] This approach allowed the synthesis of high molecular weight, low polydispersity polymers with identical degrees of polymerization (DP) but different mesogens. Similarly, a single mesogen was attached to polymers with varied length from DP = 200 to 1150.

Prior to this study the longest 1,2-polybutadiene that had been reportedly converted to the polyalcohol poly(2-hydroxyethyl)ethylene (PBOH) had DP ≈ 900.[24] Preparing high molecular weight polymers is difficult since the kinetics of the reaction are greatly reduced, the polymers are less soluble at all stages of the reaction, and, most importantly, cross-linking reactions are increasingly difficult to eliminate.

Pronounced odd−even effects associated with alternation between parallel and perpendicular mean orientations of the mesogens relative to the polymer backbone with increasing spacer length have been observed for certain backbone structures (especially acrylates).[25−27] In the present system, the melt and solution thermodynamics only exhibit weak odd−even effects as the spacer length was increased.

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Along with melt studies, solution studies included the determination of solubility in nematic solvents and determination of the refractive indices (n_e and n_o) of the solutions. Since these SGLCPs have cyanobiphenyl mesogens, excellent solubility was found in the nematic solvents 4-pentyl-4′-cyanobiphenyl (5CB) and 4-pentoxy-4′-cyanobiphenyl (5OCB), and in the eutectic mixtures E7 and E44.[28] In the 5CB solutions, the small changes in the refractive indices upon addition of polymer indicated that the order parameter of these solvents was not significantly affected.

Solubility of a polymer in a nematic solvent at high molecular weights is a significant achievement. The additional order of a nematic fluid reduces the entropy of solvation and often results in only slight solubility of low molecular weight polymers. In our system the similarity of structure resulted in the solubility of polymers an order of magnitude larger than those typically examined by prior researchers.

The present development of a synthetic approach and examination of phase behavior (in the melt and in nematic solutions) provides a foundation for coordinated studies of chain conformation (showing the present polymers are oblate with $R_\perp/R_\parallel = 1.6$)[29] and rheology (showing that access to high polymers with DP > 1000 reveals unprecedented effects of dissolved SGLCPs on the flow behavior of LC solutions).[9,11]

2. Experimental Methods

2a. Multiangle Laser Light Scattering. Gel permeation chromatography (GPC) was carried out on two Polymer Labs 30 cm long PLgel 5 mm mixed-C columns (200−2 000 000 g/mol) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer, both from Wyatt Technology. The MALLS detector used a 30 mW, 690 nm, gallium arsenide linearly polarized laser, and the differential refractometer used 690 nm light with a Wollaston prism. Tetrahydrofuran (THF) at a flow rate of 1 mL/min at a temperature of 35 °C was used as the eluent. No calibration standards were used, and dn/dc values were obtained for each injection assuming 100% mass elution from the columns using only the data near the polymer peak.

2b. Phase Transition Determination. The transition temperatures and phases of the SGLCPs were determined using both a Zeiss polarized optical microscope (POM) with a Mettler FP82 hot stage and a differential scanning calorimeter (DSC) (Perkin-Elmer DSC7). In the microscope the temperature was slowly raised at 5 °C/min and the phases were identified along with the temperature at which phase transitions began. In the DSC method the samples were heated well into the isotropic phase to remove the thermal history. Then the temperature was raised at 10 °C/min and the computer software was used to determine the onset temperature of the various phase transitions. The DSC was calibrated using indium and zinc as standards at a heating rate of 10 °C/min.

2c. Refractive Index Measurement. The refractive indices of solutions of SGLCP in 5CB were measured using an Abbe refractometer[30] equipped with a band-pass filter for 633 nm light. Alignment of the liquid crystal was obtained by washing the surfaces of the prisms with a solution of 1% lecithin in chloroform to promote homeotropic (perpendicular) alignment. Since the liquid crystal was birefringent, light entering this phase was split into two beams with different polarization states. Therefore, the ordinary and extraordinary refractive indices, n_o and n_e, could be determined. Instead of a single transition from a light to a dark state, two transitions from bright to dim and from dim to dark were seen.[31]

2d. Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FTIR). ^{1}H NMR was performed on a Mercury-Vx 300 MHZ NMR spectrometer with the software package VNMR Version 6.1B using 32 scans with a 1 s delay time.

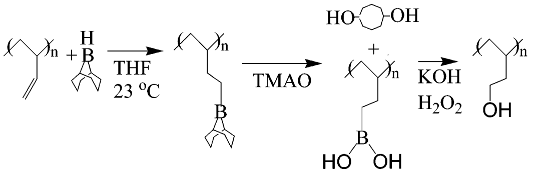

Figure 1. Conversion of 1,2-polybutadiene to a polyalcohol (PBOH) using hydroboration/oxidation. In the second step the TMAO is shown cleaving only secondary organoborane bonds even though a small fraction of the primary bonds are also cleaved.

FTIR was performed on a Nicolet Nexus 470 spectrometer with a DTGS detector, a KBr beam splitter, and a 1 mW He−Ne laser (633 nm). The chamber was purged using dry N_2 gas and a background was taken using a blank card (3M type 2 IR cards, poly(tetrafluoroethylene) substrate). The samples were prepared by dissolving the material in a volatile solvent, placing a few drops of the solution on the card, and allowing the solvent to evaporate.

3. Materials Synthesis

3a. Polyalcohol Synthesis. The 1,2-polybutadiene polymer used in these experiments was synthesized using anionic polymerization in cyclohexane with *tert*-butyllithium as an initiator at 16 °C and a pressure of ∼25 psig.[16−19] Unless otherwise stated, all chemicals were obtained from Aldrich Chemical Company and used as received. Approximately 5 mol of 1,2-dipiperidinoethane[32,33] (98% pure, purchased through ACROS Chemicals) was added per mole of initiator as a reaction modifier to favor the production of 1,2 over 1,4 repeat units. For long-term storage the polymers were kept at −20 °C with ∼1 wt % Irganox or with octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxphenyl)propionate as an antioxidant. All the 1,2-polybutadiene samples used in these experiments had ∼98% 1,2 repeat units as detected by ^{1}H NMR at 300 MHz and polydispersity indices (PDI) of ∼1.04 as detected by GPC with MALLS detection.

The 1,2-polybutadiene prepolymer was converted to PBOH using a procedure similar to that of Chung et al.,[20] Adams and Gronski,[21] and Mao et al.[22,23] Hydroboration with 9-borabicyclo-[3.3.1]nonane (9-BBN) (0.5 M in THF under nitrogen in Sure/Seal bottles) was followed by oxidation under basic conditions; see Figure 1. In the first step, a 50% excess of 9-BBN under argon (28 mL, 0.014 mol) was added to the polybutadiene solution (0.50 g, 0.0092 mol) in anhydrous THF (25 mL) and the reaction was run at room temperature for 2−3 days.

A 3:1 mole ratio of trimethylamine *N*-oxide dihydrate (TMAO, 98%) to 9-BBN was added (4.7 g, 0.042 mol, in 20 mL of H_2O). Since the reaction mixture separated into two phases and TMAO is much less reactive than H_2O_2, the reaction was allowed to proceed for 1 day at room temperature.

Solutions of KOH (0.52 g, 0.0092 mol) and hydrogen peroxide (1.13 mL, 0.011 mol, 30 wt % in water) were used to complete the oxidation of the polymer.[20−22] Other researchers[22] using smaller molecular weight starting polymers found that the product PBOH was soluble in THF with small quantities of water. At our high molecular weight, the polyorganoborane was soluble in THF, but the PBOH product was not. Therefore, to avoid precipitation, the H_2O_2 and KOH were each dissolved in methanol (200 mL) and the polymer solution was added slowly (over 30 min) to this solution at 0 °C.

After the reaction the solution turned cloudy due to the precipitation of a water-soluble borate salt. These salts were removed by dissolving the polymer (0.5 g) in methanol (3.5 mL or ∼20 wt %) along with a small amount of KOH (∼0.02 g) and precipitating the polymer three times by the direct addition of H_2O (5 mL) while stirring. Starting with 1,2-polybutadiene with a PDI of about 1.04, a final polymer with a PDI between 1.08 and 1.15 was obtained at a yield of 85%. The disappearance of peaks between 4.8 and 5.6 ppm in the

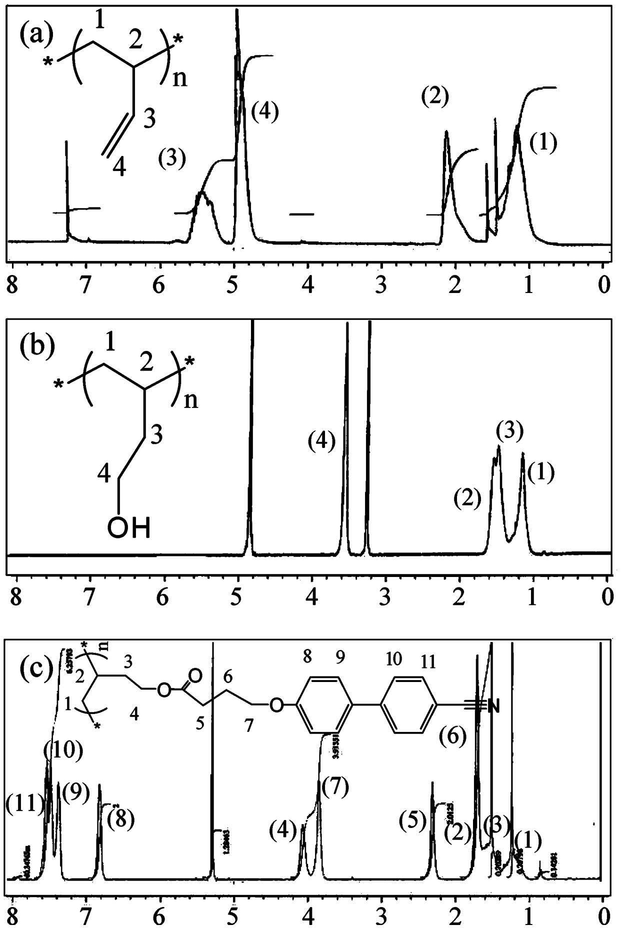

Figure 2. ^{1}H NMR spectra of (a) 1,2-polybutadiene in $CDCl_3$ and (b) PBOH in CD_3OD. The signals from the vinyl groups between 4.8 and 5.6 ppm were absent, indicating that all vinyl groups had been hydrated. The peaks at 3.3 and 4.9 ppm are due to the solvent CD_3OD. (c) ^{1}H NMR spectrum of PBCB4 in CD_2Cl_2. The peak at 3.6 ppm in PBOH was replaced by a peak at 4.04 ppm, indicating complete attachment of the mesogen.

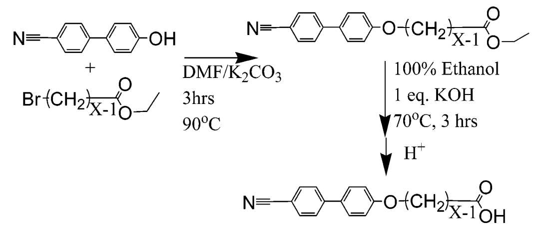

Figure 3. Spacer attachment to the cyanobiphenyl-based mesogen.

^{1}H NMR spectrum of 1,2-polybutadiene and the appearance of a peak at 3.6 ppm in PBOH confirmed >99% vinyl group conversion to alcohol; see Figure 2a,b.

3b. Attachment of Mesogen. A cyanobiphenyl mesogen was chosen for this study to confer SGLCP solubility in extensively characterized cyanobiphenyl-based small molecule LCs; see Figure 3. The spacer was made from an ethyl-ω-bromine ester with different numbers of carbon atoms. Esters with four, five, and six carbon atoms were purchased from Aldrich (95%, 98%, and 99% pure, respectively) and esters with seven and eight carbon atoms (96% and 97% pure, respectively) were purchased from TCI America and Narchem, respectively. The esters (12.8 mL for ethyl 6-bromohexanoate, 0.072 mol) were attached to the mesogen 4-cyano-4′-hydroxybiphenyl (95%) (10 g, 0.051 mol) (purchased from TCI America) by a Williamson ether synthesis reaction in anhydrous *N*,*N*-dimethylformamide (99.8% pure under nitrogen in Sure/Seal bottles) (100 mL) with anhydrous K_2CO_3 (>99%) (7.0 g, 0.051 mol) at 90 °C for 3 h while the reaction was monitored by TLC. The product was purified by fractionation on a silica gel column using 30% ethyl acetate in hexanes and was recrystallized in ethanol (190 proof) providing a 90% yield.

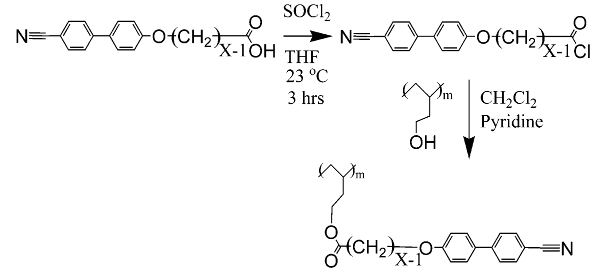

Figure 4. Procedure for attaching the cyanobiphenyl-based mesogen to the polymer backbone. PBCB*x* denotes a 1,2-polybutadiene backbone, with a cyanobiphenyl mesogen. The "*x*" in the polymer name indicates the size of the spacer, where $x + 4$ is the number of atoms between the mesogen and the polymer backbone. In these experiments $x = 4-8$.

The ethyl protecting group was removed by reaction with KOH (2.9 g, 0.051 mol) in anhydrous ethanol (99.5%) (150 mL) at 70 °C for 3 h. The reaction mixture was poured into a 0.1 M aqueous $NaHCO_3$ solution, and the pH was adjusted to 6 by dropwise addition of glacial acetic acid to precipitate the mesogen with its attached spacer in an acid form (CBA*x*). The product CBA*x* was further purified by dissolution in an acetone/H_2O solution followed by filtration to remove insoluble byproducts. The yield for the attachment of the spacer was 90%.

The final step in the polymer synthesis was the attachment of CBA*x* to the polymer backbone following a procedure similar to Adams and Gronski[21] and Coleman et al.;[34] see Figure 4. CBA*x* (2.0 g for CBA6, 0.0065 mol) was dissolved in anhydrous THF (20 mL) with anhydrous K_2CO_3 (0.89 g, 0.0065 mol). A large excess of thionyl chloride (99+%) (3 mL, 0.041 mol) was added, producing the acid chloride after 3 h at room temperature. The $SOCl_2$ and THF were removed under vacuum at room temperature, and the mesogen was redissolved in anhydrous toluene which was also removed under vacuum. The remaining solids were hot filtered in a solution of anhydrous hexane (100 mL, dried by reaction with CaH_2) at 70 °C. Upon cooling to ~0 °C, the acid chloride product precipitated; then the solvent was decanted, and the precipitate was washed with additional cold anhydrous hexane.

Once purified, the acid chloride was dissolved in CH_2Cl_2 (20 mL) and the PBOH (0.31 g, 0.0043 mol of −OH groups) was dissolved in 5 mL of pyridine, which served as the reaction catalyst. Since PBOH was not soluble in CH_2Cl_2 but the product SGLCP was, the attachment of the mesogen could not be accomplished in a single solvent without precipitation. Therefore, the PBOH/pyridine solution was added slowly (5 min) to the acid chloride/CH_2Cl_2 solution, allowing mesogenic units to rapidly attach to the polymer and rendering it soluble in the reaction mixture. The reaction was allowed to progress for several hours before the polymer was precipitated twice from a solution of dichloromethane by the addition of methanol, removing any unattached mesogen, giving a final yield of 95% relative to the amount of PBOH used. The final polymers were designated PBCB*x*, where "*x*" indicates the number of carbon atoms in the ester group used to form the spacer.

4. Results and Discussion

4a. Reduction of Cross-Linking Reactions. To minimize cross-linking reactions, a mild oxidizing agent, TMAO, was used to avoid the presence of oxygen molecules from the decomposition of hydrogen peroxide. Since TMAO reacts much more quickly with secondary than with primary organoborane bonds, it would take an extremely long time for TMAO to cleave all three organoborane bonds. Therefore, TMAO did not eliminate

Table 1. MALLS Results[a]

polymer sample	predicted $M_n{}^b$ (g/mol)	measured M_n (g/mol)	PDI	butadiene prepolymer M_n (g/mol)	prepolymer PDI
PBCB4	388 000	540 000	1.16	63 000	1.04
PBCB6	78 000	92 000	1.14	11 500	1.03
PBCB6	364 000	427 000	1.13	54 000	1.04
PBCB6	420 000	504 000	1.09	63 000	1.04
PBCB7	437 000	525 000	1.09	63 000	1.04

[a] Because of the similarity of all the polymer structures and the difficulty of getting accurate d*n*/d*c* values for every sample, an average value of d*n*/d*c* = 0.16 mL/g was used for all samples. [b] The predicted molar mass was based on 100% attachment of the mesogen to the 1,2-polybutadiene prepolymer backbone. Since multiple samples of each polymer were made and the physical properties measured were the same, the predicted molar mass was used throughout the text.

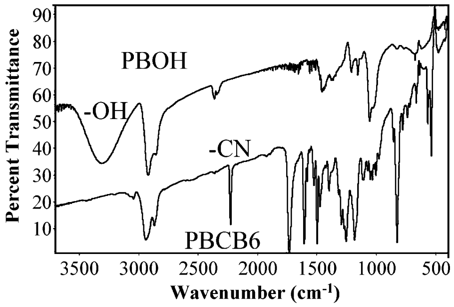

Figure 5. FTIR spectrum comparing PBOH to PBCB6. The loss of the broad peak at 3300 cm^{-1} and the addition of the peak at 2224 cm^{-1} indicated complete attachment of mesogen to the hydroxyl groups.

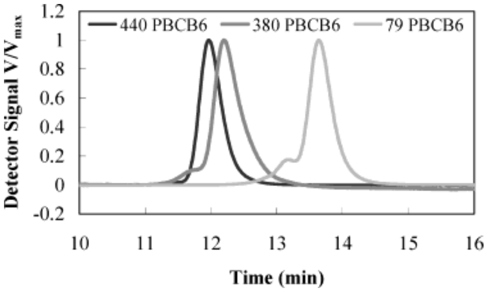

Figure 6. Sample GPC traces used to determine molecular weight and radius of gyration in an isotropic THF solution. Results are shown for the refractive index detector; traces based on the light scattering detector are virtually identical.

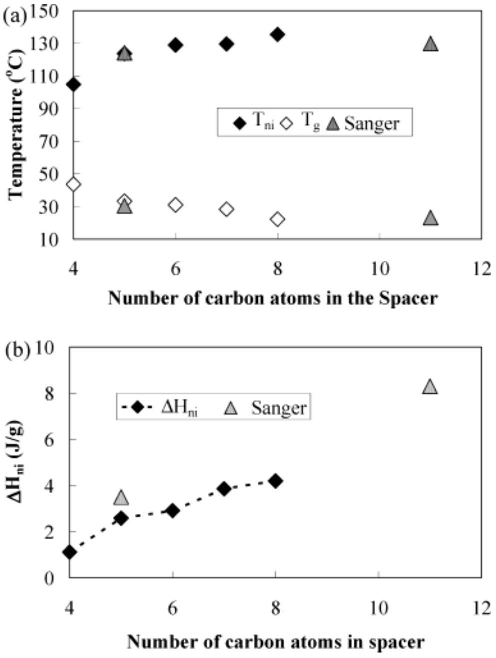

Figure 7. Effect of spacer length for PBCB*x* polymers in comparison to the results of Sanger[24] for similar polymers. (a) Transition temperatures T_g and T_{ni}; (b) ΔH_{ni} showing a small odd–even effect.

the need for hydrogen peroxide, but it reduced the requirement by a third.[35]

The extent of the attachment reaction was monitored by ^{1}H NMR and FTIR. The chemical shifts of the hydrogens in the α position relative to the hydroxyl group changes from 3.6 to 4.1 ppm upon addition of mesogen; see Figure 2b,c. FTIR further confirmed that the reaction proceeded to completion by the disappearance of a broad hydroxyl peak at 3300 cm^{-1} and the appearance of a sharp peak at 2125 cm^{-1} corresponding to a $-$C≡N group; see Figure 5.[20,22] This confirmed that greater than 99% of the available hydroxyl groups had reacted.

Though an 85% yield could be achieved by this method, the resultant polymer often had an unacceptably large PDI. After repeated attempts a PDI of 1.08 for PBOH was achieved at molar masses as high as M_n = 89 000 g/mol. Similarly to Chung et al.,[20] Adams and Gronski,[21] and Mao et al.,[22] this method allowed us to maintain a PDI of 1.1–1.15 for the final PBCB*x* polymers even at high molar masses and to systematically vary both the molar mass and the spacer length.

4b. Multiangle Laser Light Scattering. A value for d*n*/d*c* of 0.16 mL/g was obtained for the PBCB*x* series of polymers from an average of several runs. The predicted molar masses were based on 100% conversion of vinyl group to alcohol and 100% attachment of mesogenic groups with no cross-linking of the polymers; see Table 1. When compared with the actual molar mass determined by MALLS, the measured was always higher than the predicted. The higher this discrepancy the higher the PDI. If the primary cause of the increase in PDI was intermolecular cross-linking, then the values of the measured molar masses are consistent with the measured PDIs of the samples. The molecular weight distribution of the final SGLCP verified that a final PDI ≤ 1.16 could be achieved starting with prepolymer having PDI ≤ 1.04; see Figure 6.

4c. Melt Properties. A series of polymers PBCB*x* (*x* = 4, 5, 6, 7, 8) were made using a 1,2-polybutadiene prepolymer with a molar mass of M_n = 63 000 g/mol. For the PBCB*x* polymers a characteristic nematic marbled texture was seen under POM. This present observation of a nematic phase is in accord with the phase behavior of PBCB5 reported by Sanger and Gronski.[24]

In the PBCB*x* series, the nematic phase exists between a glass transition (T_g) and an isotropization transition (T_{ni}); see Figure 7. As the spacer length was increased (PBCB4 to PBCB8), the range of this nematic phase broadened as T_g decreased and T_{ni} increased. Longer spacers increase the mobility of the side chains, increasing their entropy and therefore causing T_g to decrease with increasing spacer length. Similarly to T_{ni}, the enthalpy of the nematic−isotropic transition (ΔH_{ni}) increased with spacer length. In contrast to ΔH_{ni}, the change in heat capacity at the glass transition temperature was insensitive to spacer length ($\Delta C_p = 0.30 \pm 0.02$ J/g °C).

The increases in both ΔH_{ni} and ΔT_{ni} with spacer length accord with known effects of increasing the spacer or alkyl tail length on SGLCPs.[36−38] In WAXS studies by Sanger and Gronski,[24] an increased spacer length was found to promote the formation of a smectic phase in PBCB11. In our system a longer spacer increased the strength of the nematic field, increasing ΔH_{ni} and T_{ni}, but even for PBCB8 no smectic phases were seen.

For the largest spacer used, PBCB8, there were a total of 12 atoms between the polymer backbone and the biphenyl group, which makes it somewhat surprising that a smectic phase was not seen. Other researchers using cyanobiphenyl-based SGLCPs with silicon atoms on the backbone[39] or on the spacer[40] had found smectic phases with four to nine atoms and seven atoms, respectively, in the spacer. Percec and Lee[41] synthesized a system of polymers where a cyanobiphenyl mesogen was attached using ether links connecting the methylene spacer to the backbone and to the mesogenic unit. They also found smectic phases for polymers with seven or more atoms in the spacer. The presence of silicon atoms or ether links makes these spacers flexible, decoupling the mesogen from the backbone, which should favor the more disordered nematic phase. Therefore, it must be the greater incompatibility of the spacers containing siloxane or ether groups and the cyanobiphenyl mesogen that favors the formation of smectic LCs relative to PBCB*x*.

Experiments by Shibaev et al.[37] using a cyanobiphenyl-based mesogenic group with a polymethacrylate and a polyacrylate backbone found smectic phases only at larger spacer lengths. They found smectic phases for spacers of eight (but not five) atoms in polymethacrylates and 14 (but not eight) atoms in acrylates. Since these systems use both an ether and an ester bond to link the mesogens, the flexibility of the spacer must be similar to our system. For the polymethacrylate system, smectic phases were formed with eight atoms in the spacer; therefore, the cyanobiphenyl mesogen must be more incompatible with the polymethacrylate backbone than with the ethylene backbone of PBCB*x*.

In SGLCPs an odd−even effect is often seen as the length of the spacer is varied. In some acrylate[25] and methacrylate-based[26,27] SGLCPs a strong odd−even effect results from the "hinge effect", where the mesogenic group alternates between a parallel and a perpendicular orientation relative to the polymer backbone. In our SGLCP series, only one property, $\Delta H_{ni,}$ displayed an odd−even effect: the change in enthalpy was greater from $x = 4$ to 5 and 6 to 7 than from 5 to 6 or 7 to 8; see Figure 7. Even though odd−even effects typically decrease with spacer length, work by Craig and Imrie[26,27] saw them in T_{ni} and ΔS_{ni} for polymers with up to 15 atoms between the mesogen and the backbone and attributed it to the "hinge effect." In our systems the longest spacer had 12 atoms; therefore, the absence of any strong odd−even effects suggests that these polymers had the same orientational relationship between the backbone and the mesogen. Neutron scattering results[29] confirm that this is the case (the orientational tendency is transverse with $R_{\perp}/R_{\parallel} \approx 1.6$ for the PBCB*x* series).

4d. Solution Properties: Transition Temperatures and Solubility limits. The solubility of these polymers was checked in a number of small molecule LCs. Samples of 5CB, E7, and E44 were purchased from Merck. All other small molecule LCs were purchased from Aldrich. Solutions were prepared by dissolving the polymer and LC in dichloromethane and then removing the dichloromethane under vacuum. The insolubility of our nematic polymer in the smectic LC 4′-octyl-4-cyanobiphenyl (8CB) was expected since smectic materials are most compatible with other smectic LCs having similar layer spacings.[42] Due to large differences in mesogen structure, the polymers were also insoluble in *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA). Once the phase and structure of the polymer and the solvent were matched more closely, good solubility was obtained. The polymer was found to be soluble in the cyanobiphenyl-based nematic LCs 5CB and 5OCB, and in the eutectic mixtures E7 and E44.[28]

The ability of these polymers to dissolve in cyanobiphenyl-based nematic LCs at high molecular weights is a significant property. The additional order of a nematic fluid reduces the entropy of dissolution of the polymer, reducing its solubility relative to isotropic solvents. Solubility issues often limit the choice of polymer and solvent, forcing experiments to be conducted at low molecular weights or at low concentration. The excellent solubility of our SGLCPs gives us the opportunity to extend research on SGLCPs in LC solvents to high polymers (DP > 1000).

The effect of PBCB6 on the phase transition temperatures of the small molecule LC solvents was to increase T_{ni}; see Figure 8. In 5CB the polymer also caused the formation of a biphasic region in low concentration solutions (≤10 wt %), but at 50 wt % the LC transitioned directly from the nematic to the isotropic phase; see Figure 8a. In 5OCB, a small biphasic region, ~0.5 °C, smaller than the symbol size in Figure 8b, was visible only when heating the sample. Since the T_{ni} of 5OCB was closer to the T_{ni} of the polymers and possibly because of a slightly better match in their structures, it transitioned into the isotropic state more directly. In 5OCB the addition of polymer not only increased T_{ni} but it also decreased the melting point. When the solutions of 5OCB were cooled through the freezing point, small amounts of polymer phase separated at the grain boundaries of the crystals.

The eutectic mixtures E7 and E44 are composed of mixtures of cyanobiphenyl-based LCs, primarily 5CB and 5OCB. These mixtures have a biphasic region, and the addition of PBCB6 (having a higher T_{ni}) increased the temperatures T_{ni} and T_c; see Figure 8a. The presence of a biphasic region is a common occurrence in solutions of polymers dissolved in small molecule nematic LCs.[43−45] Significantly, miscibility was observed over a wider temperature range in the nematic phase than the nematic temperature window of the host LC itself. In general, the addition of polymer increased the temperature range of the nematic phase (decreasing T_g, Figure 7a, or T_m, Figure 8b, and increasing T_{ni}, Figure 8a).

4e. Refractive Index. The refractive indices of solutions of 420 kg/mol PBCB6 in 5CB were measured using an Abbe refractometer.[30] Solutions of up to 10 wt % polymer were compared to bulk 5CB. The change in

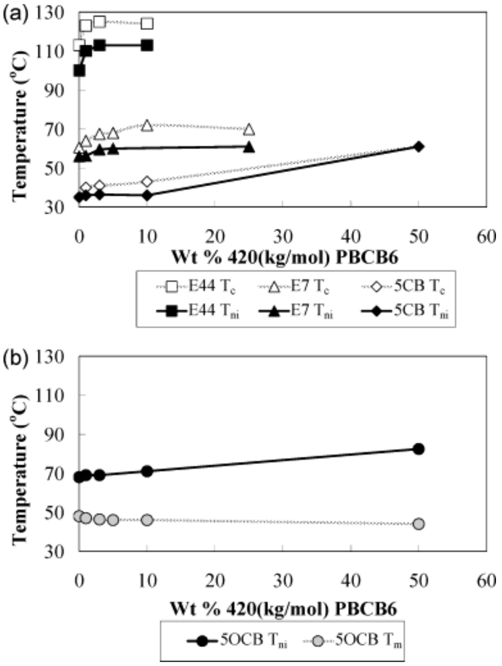

Figure 8. Phase diagram for solutions of 420 kg/mol PBCB6 dissolved in cyanobiphenyl-based small molecule liquid crystals. Phases were determined by DSC and POM. Similar results were found for solutions of the other polymers in this series, PBCB*x*. (a) T_{ni} indicates the transition from one nematic phase to a biphasic nematic/isotropic phase. T_c indicates a transition from biphasic to an isotropic phase. (b) T_{ni} is the transition from a nematic to isotropic phase with a small biphasic region only visible while heating. T_m is the melting point of the crystalline phase.

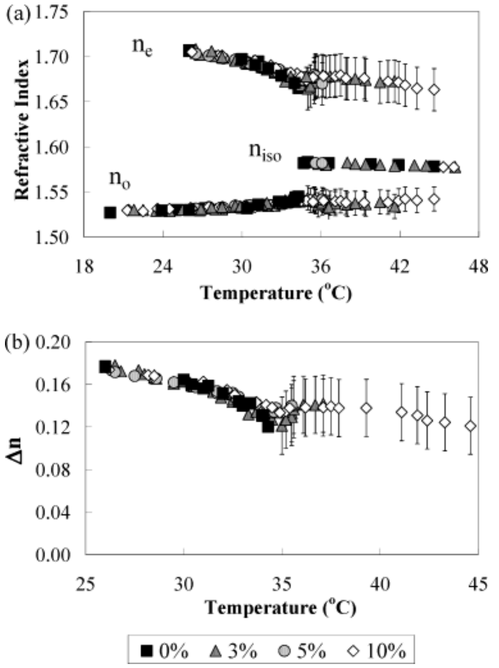

Figure 9. Effect of dissolved polymer 420 kg/mol PBCB6 on (a) refractive indices and (b) birefringence of solutions in 5CB. At temperatures above 35 °C, the solution was biphasic with the largest fraction in the isotropic phase. For temperatures below ~32 °C, within experimental uncertainties, the birefringence of the solutions was the same as that of bulk 5CB.

Δn, n_o, and n_e due to the addition of polymer was less than the experimental uncertainty for temperatures below ~32 °C; see Figure 9. In Figure 9b near T_{ni}, a larger Δn is seen for the solutions of 10 and 5 wt %. This behavior was expected since the polymer had a significantly higher T_{ni} than 5CB and served to stabilize the nematic phase.[46,47]

When the solution went through T_{ni}, a biphasic region was encountered in which the refractive index of the larger isotropic phase was easily discerned. Since the polymer-rich LC phase was present in significantly smaller quantities and was poorly aligned, it was difficult to measure its refractive indices. The uncertainty in measurements below T_{ni} were smaller than the symbol size in Figure 9, but in the biphasic region the uncertainties were much larger, as indicated.

Coles and Bancroft[48] using a cyanobiphenyl-based SGLCP dissolved in E7 demonstrated that changes in Δn were correlated with a reduction in the order parameter and K_{11}. In our system the negligible changes in Δn upon addition of polymer indicated that the order parameter was not significantly affected except near T_{ni}.

5. Conclusion

Using a cyanobiphenyl-based mesogenic unit in these SGLCPs confers excellent solubility in nematic cyanobiphenyl-based small molecule LCs even with high molecular weight polymers. This allowed us to explore concentration and molecular weight regimes that were previously unexamined. Because of their similarity in structure, the addition of polymer to 5CB did not change Δn for temperatures below 32 °C. This indicated that even up to 10 wt % polymer the order parameter of the solvent was not significantly altered, which allows parameters, such as the Frank elastic constants, for bulk 5CB to be used as an estimate for those of the solutions.

Studying solutions of model polymers in LCs allows us to evaluate the effects of polymers on a nematic host as a function of molecular weight and spacer length. Since this series of SGLCPs extends to chain lengths an order of magnitude larger than that previously investigated in LC solutions, it has revealed new phenomena that were previously inaccessible, such as flow alignment of a calamitic LC near the velocity gradient direction.[11] This series of polymers also provides a way to evaluate Brochard's predictions regarding the effect of a dissolved polymer on the Leslie−Erickson viscous parameters,[10] and to compare the rheologically inferred anisotropy with the anisotropy measured using small angle neutron scattering.[29]

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