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Increased Order−Disorder Transition Temperature for a Rod−Coil Block Copolymer in the Presence of a Magnetic Field

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Supporting Information

INTRODUCTION

Block copolymers, capable of self-assembling on the 10 nm length scale, are of interest for a broad range of applications including ion transport, nanolithography, and optoelectronics, many of which require tunable, periodic, and aligned structures.[1] While electric field, shear, and surface-induced alignment have all been used to control nanostructure orientation and long-range order in classical polymer systems, all these techniques require restrictive geometries and direct contact with the block copolymer surface in order to achieve alignment. Nanostructured conjugated polymers are of interest for photovoltaic applications, and previous work demonstrates that these materials may be aligned via magnetic fields.[2] In order to optimize the performance of these materials, alignment of the nanostructure is important to improve properties such as charge transport in these devices. Magnetic alignment offers unique advantages because it may be carried out without direct contact with the sample enabling efficient processing techniques while still obtaining highly aligned materials.

Liquid crystalline molecules, including many conjugated polymers, are often highly anisotropic, leading to an inherent magnetic anisotropy which allows them to be easily aligned even in relatively modest magnetic fields. Since the anisotropic magnetic susceptibility of a single molecule is low, typically magnetic alignment of liquid crystals requires that the magnetic field acting on the director of a large liquid crystalline domain made up of many ordered molecules to overcome thermal fluctuations. By utilizing a block copolymer with a conjugated, rigid (rod-like) moiety, molecular anisotropy is introduced into one of the block copolymer domains, and an anisotropic magnetic susceptibility can be achieved in the material which produces a driving force for alignment in a magnetic field. For a rod−coil block copolymer, the backbone of the main-chain rod-like polymer aligns parallel to the applied field, forcing the block copolymer interface to be perpendicular to the field.[2] Similarly, magnetic alignment is possible in polymers with liquid crystalline mesogen side chains leading to interfaces parallel to the field; however, this can lead to multiple degenerate orientations which satisfy the alignment conditions.[3−8] It has been shown by rotating the sample within the magnetic field this degeneracy can be broken, resulting in highly aligned lamellar samples.[9]

While alignment of a smectic liquid crystalline phase for either side chain or main chain liquid crystalline block copolymers is possible, typically alignment within the nematic phase produces a higher degree of alignment and requires lower fields since the nematic phase contains only orientational order, intramolecular interactions are diminished, and the system has increased mobility. Previous work using liquid crystalline main chain rod−coil block copolymers has shown that annealing in the isotropic or nematic phase increases the order parameter 2−3 times greater than that for samples annealed only in smectic phase.[2] Additional work has shown aligned samples can be annealed in the smectic phase outside of a magnetic field and preserve much of their original orientation.[10] Osuji and co-workers have used a side chain liquid crystalline block copolymer where lithium ion conducting poly(ethylene oxide) cylinders were aligned, optimizing the ionic transport in a polymer electrolyte membrane, and were able to show that the transport within the polymer membrane was improved 10-fold over the randomly oriented morphology.[4,6] In the above studies, the highest degrees of order were achieved by cooling from above both the point at which the block copolymer chains become miscible (block copolymer microphase order−disorder transition temperature (T_{ODT})).[2,7] It has been postulated that by cooling from above these transition temperatures kinetic trapping can be prevented by aligning block copolymer domains as they nucleate and grow. While it has not been previously observed, it is clear that the presence of the field may affect the transition temperatures by modulating both block copolymer interactions and providing an exterior directionality to the liquid crystal.

The effect of fields on the order−disorder transition temperature has been explored in the similar but more classical case of insulating coil−coil block copolymers in electric fields. In most cases the electric field is thought to act on the difference in the dielectric constants of the two block copolymer domains, resulting in a minimum energy when the block copolymer interfaces are oriented parallel to the electric field.[11] Unfortunately, the difference in the dielectric constant of most block copolymer systems is relatively low requiring high electric fields which are often near the dielectric breakdown threshold of the polymer. Since the dielectric contrast between polymers is relatively small, it has been shown that the salt concentration within the polymer can increase the driving force for alignment lowering the required field strength and increasing the degree of alignment even when

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only trace levels of salts are present, making electric field alignment sensitive to synthetic and processing conditions.[12] It has been predicted that the presence of an electric field may favor mixing of the block copolymer domains, causing a decrease in the T_{ODT},[13,14] while others have predicted an increase in the T_{ODT} because the electric field will reduce fluctuations, stabilizing the ordered phase.[15] Recently, experiments have shown a small decrease in the T_{ODT} which may confirm that electric fields favor mixing near the ODT.[16] All of these predictions and observations also show the effect of applying an electric field on the T_{ODT} for most polymer systems should be rather small (~2 °C). While electric field alignment and magnetic field alignment of block copolymers appear similar, they interact with the polymer in fundamentally different ways potentially resulting in different behavior. Liquid crystalline block copolymers lack any driving force for increased mixing at high magnetic fields, and therefore we would not expect the T_{ODT} to decrease when a magnetic field is applied.

Here we show using *in situ* small-angle X-ray scattering (SAXS) that a magnetic field can significantly alter the thermodynamics of a main chain liquid crystalline rod–coil block copolymers. The presence of a magnetic field increases the order–disorder transition temperature substantially and can have major implications on optimizing the alignment of these materials. The magnetic field couples to the rod-like liquid crystalline block stabilizing the ordered phase. In addition, the lamellar block copolymer microstructure enhances the smectic ordering leading to a much larger increase in the T_{ODT} than would be expected. Since obtaining highly aligned block copolymer structures using magnetic fields relies on accessing a disordered phase, the fact that the T_{ODT} may be dramatically increased by the presence of a magnetic field shows we must understand the *in situ* phase behavior in order to intelligently optimize alignment procedures.

EXPERIMENTAL SECTION

Poly(2,5-di(2′-ethylhexyloxy)-1,4-phenylenevinylene)-*b*-polyisoprene diblock copolymers (PPV–PI) were synthesized as previously described.[17] This study focuses on a particular polymer with total molecular weight (M_N) of 12 kg/mol, PDI of 1.10, and polyisoprene volume fraction of 70% as this polymer has been previously shown to demonstrate a lamellar phase (Figure 1) with an accessible microphase order–disorder temperature.[18,19] Molecular characterization including GPC and NMR was used to confirm the block copolymer molecular weight, composition, and lack of residual homopolymer. Small-angle X-ray scattering and polarized optical microscopy (POM) were used to quantify the zero-field block copolymer order–disorder transition temperature (T_{ODT}) and liquid crystalline nematic–isotropic transition temperature (T_{NI}).

At room temperature the PPV domain of the block copolymer is crystalline and upon melting (T_M) at 60 °C, the block copolymer lamellae contain liquid crystalline smectic ordered rods. As the temperature is increased, the system undergoes a simultaneous block copolymer order–disorder transition and liquid crystalline smectic–nematic transition at 115 °C where the rods and coils become miscible and the PPV rods lose translational order while retaining orientational order. The block copolymer phase separation in this system is dominated by liquid crystalline interactions because the rod–rod interactions, as parametrized by a Maier–Saupe parameter (μN), are much stronger than the Flory–Huggins interaction between the blocks (χN).[19] Further heating above the nematic–isotropic transition temperature (T_{NI}) at 140 °C results in a second transition to an isotropic system with no block copolymer or liquid crystalline order.

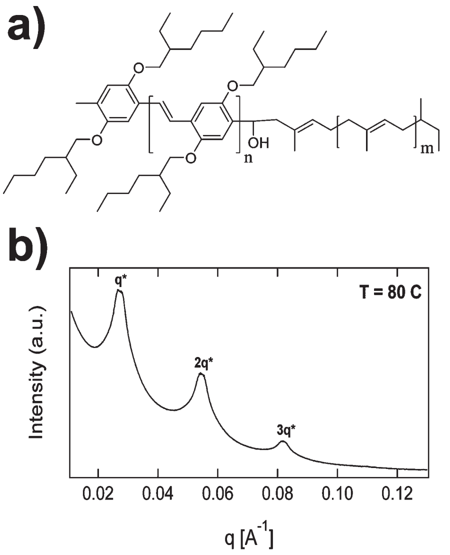

Figure 1. (a) Chemical structure of the model rod–coil block copolymer, PPV–PI, with easily accessible phase transitions and an anisotropic magnetic susceptibility, which self-assembles into (b) lamellae without the presence of any magnetic field confirmed by the multiple integer peak spacing shown in the SAXS spectrum.

The microphase order–disorder transition temperature (T_{ODT}) can be quantified by the simultaneous disappearance of higher order peaks and a dramatic decrease in the intensity of the primary peak of the azimuthally integrated SAXS images. The discontinuity in the primary peak intensity is apparent when the inverse primary peak intensity is plotted vs inverse temperature. Disordered block copolymers are expected to produce a weak primary peak due to correlations caused by joining two distinct polymer chains to form a block copolymer; however, this block copolymer system has very low chemical contrast so the intensity of the primary peak above the ODT quickly is overwhelmed by noise limiting the number of points above the ODT.[17] For the block copolymer used in these studies, the simultaneous T_{ODT} and T_{SN} were measured to be 115 ± 2 °C using SAXS, and the nematic–isotropic transition temperature (T_{NI}) was measured to be 140 ± 5 °C using polarized optical microscopy.

After purification, polymer samples were prepared for X-ray analysis by placing polymer within an aluminum washer and then sealing between two Kapton windows. As shown in Figure 2, the sample stage was designed so that in all experiments the magnetic field was applied perpendicular to the X-ray axis. Synchrotron small-angle X-ray scattering (SAXS) measurements were performed at the DUBBLE BM26B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).[20] At ESRF, *in situ* SAXS was performed within a 7 T split coil magnet allowing for real-time understanding of order transitions.[21] A separate set of samples were aligned within a 2 T permanent magnet using *in situ* SAXS at beamline 7.3.3 at the Advanced Light Source (ALS, Berkeley, CA).[22] Prior to data analysis, background scattering was subtracted from the data and normalized to account for variations in the beam intensity.

To determine the T_{ODT} in the presence of a magnetic field, polymer samples were sealed and placed within a home-built

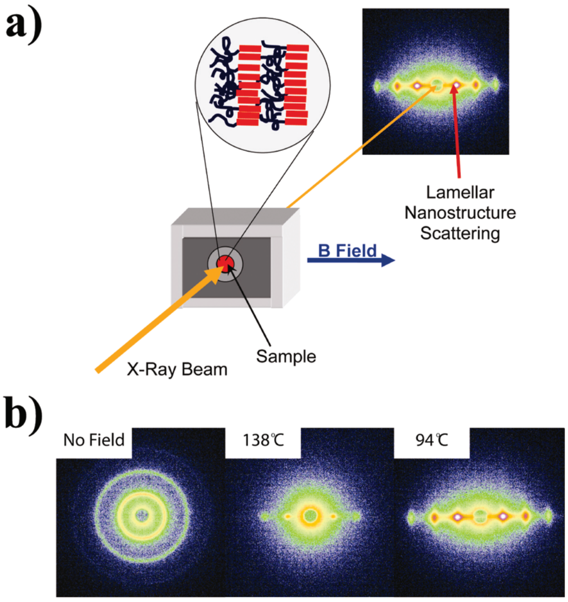

Figure 2. (a) In the presence of a magnetic field the lamellar structure of a main chain liquid crystalline block copolymer will align perpendicular to the field as the conjugated polymer lie parallel to the field. (b) The 2D SAXS images taken using a 7 T magnetic field show a high degree of alignment indicated by the sharp peaks parallel to the applied field.

sample holder which was continuously purged with nitrogen. These sample stages were thoroughly tested prior to use to confirm uniform and accurate heating. They utilize type T thermocouples which produced no measurable deviation in the temperature as a function of magnetic field strength confirmed by observing a constant temperature upon insertion into a magnetic field. Finally, the stages were further validated by confirming the zero-field T_{ODT} when the polymer was heated above 115 °C outside of a magnetic field. Samples were annealed at 140 °C (above the zero field T_{ODT} and T_{NI}) outside of the magnetic field so that initially each sample was unaligned. The samples were then cooled and inserted into the magnetic field. The temperature of the sample was then increased stepwise and held at each temperature for at least 10 min to ensure thermal equilibrium was reached. After the T_{ODT} was reached, the sample was cooled and held for at least 10 min at each temperature step. The temperature scans were repeated multiple times, and for a fixed magnetic field strength, the T_{ODT} stayed constant upon heating or cooling for all heating scans. No difference in the T_{ODT} was observed whether the sample was initially aligned or unaligned before the temperature scan. These results indicate that any change in the transition temperature is not controlled by kinetic factors and is not the result of radiation damage.

RESULTS AND DISCUSSION

SAXS allows for the *in situ* detection of lamellar block copolymer alignment in the presence of a magnetic field and the ability to probe the effects of magnetic field perturbations on rod–coil block copolymer self-assembly. Upon heating an unoriented sample within a magnetic field to an appropriate temperature, the polymer quickly reaches a highly aligned state (Figure 2). When a 2 T magnetic field was used, the block copolymer lamellar order persists past the *ex situ* T_{ODT} of 115 ± 2 °C and disorders above 120 ± 3 °C. This deviation of the T_{ODT} appears to be field strength dependent and is significantly more dramatic at higher field, with order persisting until 147 ± 3 °C at 7 T, as shown in Figure 3. The order–disorder transition for this system is determined using the 1D azimuthally integrated SAXS profile which shows a dramatic decrease in the primary peak intensity and a loss of higher order peaks near the order–disorder transition (Figure 4). The T_{ODT} at 7 T is significantly higher than either the *ex situ* T_{ODT}/T_{SN} or T_{NI}, suggesting that the block copolymer and liquid crystalline interactions are strongly affected by the presence of the field. Since the samples heated from a highly aligned state or cooled from an unaligned state display the same T_{ODT}, it appears that the increase in T_{ODT} results from a stabilization of the lamellar morphology induced by the magnetic field, perhaps resulting from favorable enthalpic interactions created by the coupling between the aligned liquid crystalline PPV domains and the magnetic field.

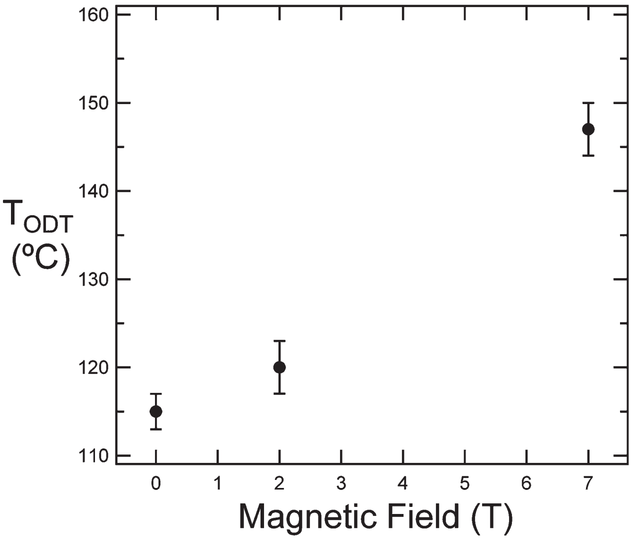

Figure 3. *In situ* small-angle X-ray scattering was used to quantify the order–disorder transition temperature (T_{ODT}) as a function of magnetic field strength. The T_{ODT} increases strongly as a function of magnetic field strength.

While magnetic fields have not been shown to affect classical coil–coil block copolymer transitions, they have been shown to alter the transition temperature of liquid crystalline systems.[23,24] Since the liquid crystalline interactions are strong in this block copolymer system compared to the Flory–Huggins block copolymer interactions,[19] the block copolymer morphology is dominated by the rod-like moiety's liquid crystalline behavior. Unfortunately, due to geometry constraints, higher angle scattering used to characterize the liquid crystalline phase transitions was inaccessible. Because of this, we are unable to determine if the smectic–nematic transition shifts with the order–disorder transition or if a new morphology is formed where the block copolymer is ordered and the liquid crystalline moieties have nematic ordering. In previous studies, an ordered block copolymer and liquid crystalline nematic morphology has not observed for this system for any molecular weight or volume fraction since the order–disorder and smectic–nematic transitions always happen simultaneously.[17−19] This suggests that the order–disorder transition of the block copolymer may in fact be dominated by the liquid crystalline smectic–nematic transition. Therefore, any increase in the liquid crystalline transitions will also likely manifest itself in an increase in the block copolymer

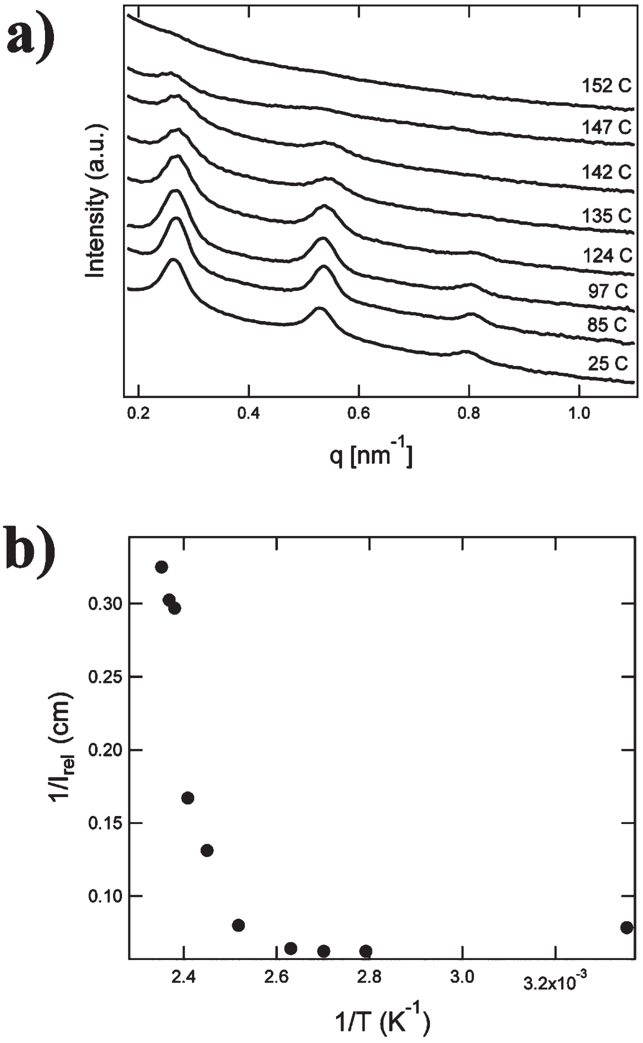

Figure 4. (a) Azimuthally integrated scattering intensity of PPV−PI under a 7 T magnetic field as a function of temperature. The integer multiples of q^* demonstrate that the block copolymer self-assembles into a lamellar morphology. (b) An order−disorder transition temperature is confirmed by plotting the inverse of the primary peak intensity versus inverse temperature and locating the discontinuity in the curve which coincides with a disappearance of the higher order reflections.

order−disorder transition because the liquid crystallinity dominates the block copolymer phase separation. The change in the transition temperature can be possibly described by accounting for the difference in the anisotropy of the magnetic susceptibility of liquid crystalline phases.[24] The deviation in the smectic−nematic transition of small molecule liquid crystals follows theoretical predictions in that it scales quadratically with magnetic field strength, leading to much larger deviations at high field strengths via the following equation

$$\Delta T_{\mathrm{ODT}} = \frac{T_{\mathrm{ODT}}(H = 0)}{2Q}(\chi_{\mathrm{S}} - \chi_{\mathrm{N}})H^2 \qquad (1)$$

where ΔT_{ODT} is the increase in the smectic−nematic transition temperature and is a function of the original smectic−nematic transition temperature with no magnetic field ($T_{\mathrm{ODT}}(H = 0)$), the difference in the anisotropy of the magnetic susceptibility between the smectic and nematic phases ($\chi_{\mathrm{S}} - \chi_{\mathrm{N}}$), the magnetic field strength (H), and the latent heat of the transition (Q). The difference between the smectic and nematic phases is positive because coupling between orientational and positional order in a smectic phase increases the liquid crystalline ordering; this results in a higher anisotropy of the magnetic susceptibility compared to the nematic phase.[25] It has been shown that the smectic−nematic transition for small molecule liquid crystals should increase slightly in the presence of a magnetic field because the absolute magnitude of magnetic susceptibility anisotropy should be higher in the more highly ordered smectic phase; however, the effect in these systems is small with the smectic−nematic transition increasing by less than 1 °C. The cause of the large increase in the T_{ODT} in our block copolymer system ($\Delta T_{\mathrm{ODT}} \sim 30$ °C) is not completely understood; however, it may result from several factors since the anisotropy of the magnetic susceptibility for each phase is not known and the latent heat of the smectic−nematic transition is too small to observe with conventional techniques.

At very high magnetic fields where the sample becomes nearly fully aligned, the impact of increasing magnetic fields should slow approaching a maximum ΔT_{ODT} caused by difference in the anisotropy of the magnetic susceptibility between the smectic and nematic phases ($\chi_{\mathrm{S}} - \chi_{\mathrm{N}}$) approaching zero as both the smectic phase and nematic phase approach maximal alignment. Furthermore, at high magnetic fields, as the block copolymer alignment approaches a maximum, we would expect any contributions on the ΔT_{ODT} from the block copolymer physics would be reduced. Based on previous work, these studies are operating in magnetic field strengths where alignment of the liquid crystalline domains and block copolymer structure is still increasing with increasing magnetic field strength so we would not expect the ΔT_{ODT} to asymptote to a maximal value for these magnetic field strengths.[2]

While we do see much greater deviations in the ΔT_{ODT} at high magnetic field, the absolute change in the smectic−nematic transition of the block copolymer system is orders of magnitude higher than previously studied small molecule liquid crystals for similar field strengths. It is unlikely that differences in the anisotropy of the magnetic susceptibility or the latent heat of the transition between previously studied small molecules and this block copolymer system can fully account for the large increase in the T_{ODT}. While coil−coil block copolymer self-assembly can be accurately described by a combination of the Flory−Huggins strength of interaction (χN) and the volume fraction of each block, rod−coil block copolymers are frequently liquid crystalline, and a liquid crystalline interaction term is needed to quantify this effect. This interaction can be approximated by a Maier−Saupe parameter (μN) having a similar functional form to the Flory−Huggins interaction. In PPV−PI, the Maier−Saupe term is quite large and may dominate phase behavior.[19] In turn, when the block copolymer is exposed to a magnetic field, the field stabilizes liquid crystalline order by externally promoting alignment because there is an enthalpic gain when the liquid crystalline moieties align with the field. This influence probably dominates and is the reason that the ordered phase persists to much higher temperatures in the presence of the field. This effect is very similar to the stabilizing influence of a magnetic field on small molecule liquid crystals in which fields have been observed to alter transition temperatures.[23,24] The lamellar block copolymer morphology also improves the liquid crystalline order of the smectic phase by pinning the PPV chain ends to the block copolymer interface which further increases the difference in the magnetic susceptibility anisotropy between the smectic and nematic phases

($\chi_S - \chi_N$). Minor gains related to the loss of interfacial curvature from large, aligned grains and subtle effects on χN may also contribute, but these are likely subtle in comparison to the liquid crystalline effect. This is in contrast to classical block copolymer systems where electric fields influence alignment via a balance of surface tension and ponderomotive forces and changes in the T_{ODT} in the presence of an electric field may depend on the difference in the dielectric constant of each block.[14,26]

CONCLUSIONS

For the first time, magnetic fields have been shown to have a strong effect on the order−disorder transition temperature (T_{ODT}) of a liquid crystalline rod−coil block copolymer. The polymer thermodynamics have been studied as a function of temperature and magnetic field strength using *in situ* small-angle X-ray scattering. In a 2 T magnetic field we observe a 5 °C increase in the T_{ODT}, and for fields as high as 7 T we observe an increase in the T_{ODT} of 32 °C, showing that both the block copolymer and liquid crystalline transitions of the material are affected. The anisotropy of the magnetic susceptibility of the liquid crystalline rod-like domain leads to alignment and also causes the T_{ODT} to increase as a function of magnetic field strength. This work could be used toward understanding how to optimize alignment procedures since magnetic alignment has been shown to be extremely dependent on the processing parameters (temperature, time, etc.) and especially the location of the T_{ODT}.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Figures showing azimuthally integrated *in situ* SAXS patterns as a function of temperature for a 2 T magnetic field and the case with no magnetic field; heating and cooling SAXS patterns at each magnetic field strength; figures confirming the liquid crystalline transitions through polarized optical microscopy and birefringence. This material is available free of charge via the Internet at http://pubs.acs.org.

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