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Structural Studies of HIQ-40 Using Small and Wide Angle X-ray Scattering

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Introduction: We discuss the study of a thermotropic liquid crystalline polymer, through simultaneous small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS), optical ellipsometry, and differential scanning calorimetry (DSC), for the study of its phase transformation kinetics. The material selected for study was HIQ-40 with composition: 40 mol percent p-hydroxybenzoic acid (HBA), 30 mol% of p-hydroquinone (HQ), and 30 mol% of isophthalic acid (IA). It is an thermotropic liquid crystalline polymer, that develops low degree of crystallinity upon thermal treatment. These materials self-organize into a hierarchy of structures that require complementary techniques for their structural analysis. The thin films used are cast from solution, because the rate of evaporation - faster than the rate of ordering in the LCP, permits formation of amorphous, transparent films.

Methods and Materials: X-ray studies allow us to follow the time-development of phase transformations either from the melt state, or the isotropic glassy state. These studies provide information about crystallization and melting of different crystallographic modifications, formation of lamellar structure, and competition between liquid crystalline and true three-dimensional crystalline phases.

For the study, the HIQ-40 samples were annealed isothermally at 150°C, 230°C or 290°C and for comparison a nonannealed sample was studied. Then changes at heating were observed through the methods mentioned above. The samples have initial crystallinity and after melting of the crystals they undergo a nematic phase transition.

The SAXS system at NSLS was equipped with a two-dimensional position sensitive detector. The sample to detector distance was 172.7 cm and the X-ray wavelength, λ , was 0.154 nm. SAXS and WAXS data were taken continuously during the heating to 375°C. Each scan was collected for 30 sec. Since the samples were isotropic, circular integration of the scattered intensity, I , was used to increase the signal to noise ratio. The following corrections were made to the SAXS raw intensity: background subtraction, sample absorption, changes in incident beam intensity, and thermal density fluctuation correction from I_s^4 vs. s^4 plot ($s=2\sin\Theta/\lambda$ where Θ is the half scattering angle) [1]. Structural parameters were determined from the one dimensional electron density correlation function, $K(z)$, obtained by discrete Fourier analysis of the Lorentz corrected intensity [2]. $K(z)$ was determined from:

$$K(z) = \sum_{j=1}^N (4\pi I_{\text{CORR}}) s^2 \omega_N^{(j-1)(z-1)} \quad (1)$$

where:

$$\omega_N = e^{-2\pi i/N} \quad (2)$$

is the N^{th} root of unity [3]. In eqn. 1, z is the direction normal to the lamellar stacks; N is the number of actual data points; and I_{CORR} is the intensity, corrected for background and thermal density fluctuations. Linear extrapolation from the beam stop region to $s=0$ was used in the summation. The long period, L , scattering invariant, Q , linear stack crystallinity, χ_C , and crystal thickness, l_C , are determined from $K(z)$ according to the method of Strobl and Schneider [2].

On the other hand, optical methods are highly sensitive to changes in the polarization state of light at early growth times. To complement the X-ray studies, we have constructed a two-dimensional, optical ellipsometer that simultaneously measures the retardation and azimuthal angle of light transmitted through the sample, at every pixel in the sample's image. The spatial resolution is similar to that of optical microscopy, and very weakly birefringent samples can be studied [4]. We compared the results obtained with this instrument to those achieved with SAXS, WAXS, and differential scanning calorimetry, and discuss the limitations and advantages of each approach for the study of polymer structure.

Results: The two peaks appear on $2\theta = 14.37$ and 23.54 degrees. This corresponds to d -spacing according to the Bragg's law of 5.344 \AA , and 3.34 \AA respectively. These peaks are almost the same as the ones reported in Cantrell et al. [5] and Blundell et al. [6], corresponding to the crystal form C, which means that the crystalline order can be attributed to the regular HQIA sequences ((HQ) - p-hydroquinone and (IA) isophthalic acid). The integrated WAXS intensity increases sharply after melting. This correlates very well with the increase of the retardance after melting, observed in the ellipsometric studies. The increase in both cases is due to developing of nematic order, which increases both the retardance, and the scattering at large angles.

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References:

- [1]. O. Glatter and O. Kratky, in "Small angle X-ray Scattering" (Academic Press Inc. , NY, 1982)
- [2]. G. R. Strobl and M. Schneider, *J. Polym. Sci., Polym. Phys. Ed.* **18** (1980) 1343.
- [3]. *Matlab Reference Guide*, The Math Works, Inc.: Natick, MA (1992) 182.
- [4]. R. Oldenbourg, G. Mei, New *Polarized light microscope with precision universal compensator*. *J. Microscopy*, **180(2)**, 140, (1995).
- [5]. G. Cantrell, C. McDowell, B. Freeman, C. Noel, *The influence of annealing on thermal transitions in a nematic copolyester*, *Journal of Polymer science: Part B Polymer Physics*, **37**, 505, (1999).
- [6]. D. Blundell et al. *High Perform Polym.*, 1, 97, (1989).