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INFLUENCE OF DEGREE OF POLYMERIZATION ON PHASE SEPARATION AND RHEOLOGY OF A THERMOTROPIC LIQUID CRYSTAL POLYMER

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ABSTRACT Dynamic rheometry and both high-temperature and solution NMR spectroscopy measurements were carried out on a series of thermotropic liquid crystal copolymers of 60 mole percent hydroxybenzoic acid and 40 mole percent poly (ethylene terephthalate); the members of the series differed only in the extent of solid phase polymerization. The viscosity decreased with increasing degree of polymerization, reaching a broad minimum after about five hours of solid phase polymerization. Solution NMR spectra showed only a slight deviation from chain randomness. Wide-line NMR spectra at 210° and 265°C showed that all members of the series contained both isotropic and nematic phases, with the nematic fraction increasing with polymerization time.

INTRODUCTION

The development of macroscopic structure during the processing of thermotropic liquid crystal polymers is influenced by the unique microstructure of these materials. Some liquid crystal polymers exhibit time scales for orientation development and relaxation that are very long relative to the times associated with the response of flexible-chain polymers; Moore and Denn¹, for example, observed characteristic times for the relaxation of orientation on the order of ten minutes following alignment

in a magnetic field. The orientation development and its manifestation through the macroscopic rheology is undoubtedly associated in part with the "inter-domain" material; that is, the material in regions below the level of resolution of optical microscopy where the transition between the optically-observable regions of high local orientation occurs.

It is believed that some thermotropic liquid crystalline polymers are biphasic in the melt, and that one of these phases is isotropic. Nicely and coworkers² have recently reported on the use of proton wide-line NMR spectra to show evidence of the existence of an isotropic phase in copolymers of hydroxybenzoic acid and poly(ethylene terephthalate). We summarize here rheological and NMR experiments on a series of 60 mole percent HBA/40 mole percent PET copolymers having a range of molecular weights. The viscosity of this series shows an initial decrease as a function of molecular weight, suggesting the presence of two phases. This is confirmed using proton wide-line NMR at high temperatures, which indicates both an isotropic and a nematic phase, with the nematic fraction increasing with increasing molecular weight. Proton NMR spectra of solutions show little change in the chain sequencing with molecular weight.

PREPARATION

A copolymer of 60 mole percent hydroxybenzoic acid and 40 mole percent poly(ethylene terephthalate) was synthesized by the reaction of poly(ethylene terephthalate) and p-acetoxybenzoic acid at 275°C according to the preparation method described by Jackson and Kuhfuss.³ Samples were then polymerized in the solid phase at 210°C under reduced pressure (less than 1 mm Hg) for times ranging up to 36 hours. The synthesis was repeated three times; the observations reported here are for the third batch synthesized, in which solid phase polymerization was carried out for up to 12 hours.

The inherent viscosity was measured in a solution of 60 volume percent phenol/40 volume percent tetrachloroethane at concentrations of approximately 0.60 gm/100 ml. The inherent viscosity is shown in Figure 1 as a function of time of solid phase polymerization. The inherent viscosity of the earlier batches was uniformly lower, but showed the same increase with time of solid phase polymerization.

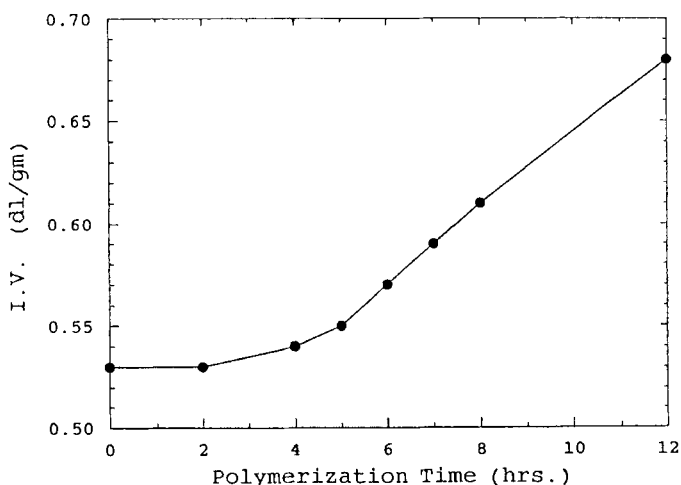


FIGURE 1. Inherent viscosity as a function of solid phase polymerization time.

RHEOLOGY

The rheological properties of the polymers were measured at 265°C using a Rheometrics Mechanical Spectrometer model 705M in the parallel plate arrangement at 5 percent strain. All samples were dried for 21 hours under vacuum at 120°C, and then loaded into the rheometer at the temperature of the experiment under a dry nitrogen atmosphere. Each sample was allowed 20 minutes to come to thermal equilibrium, during which time the gap was set at 1 mm. Frequency sweeps were carried out over the range 0.1 rad/sec to 100 rad/sec, and the complex viscosity (η^*) and dynamic moduli (G' , G'') were measured.

Full frequency sweeps are shown in Figure 2 for the lowest and highest molecular weight polymer samples of the third batch. Data at selected frequencies are plotted as a function of solid phase polymerization time in Figure 3. The open symbols are data from replicate runs and represent the range of samples taken from the same batch, while the lines connect the average values; there is substantial variation within the batch, but the variation is less than the overall change with increasing inherent viscosity. The greatest change occurs over the first few hours of solid phase polymerization, during which time there is little

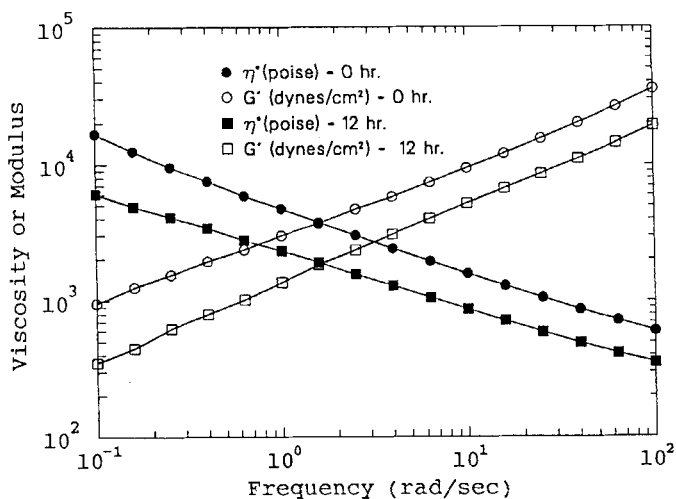


FIGURE 2. Complex viscosity (η^*) and storage modulus (G') for zero- and twelve-hour solid phase polymerization.

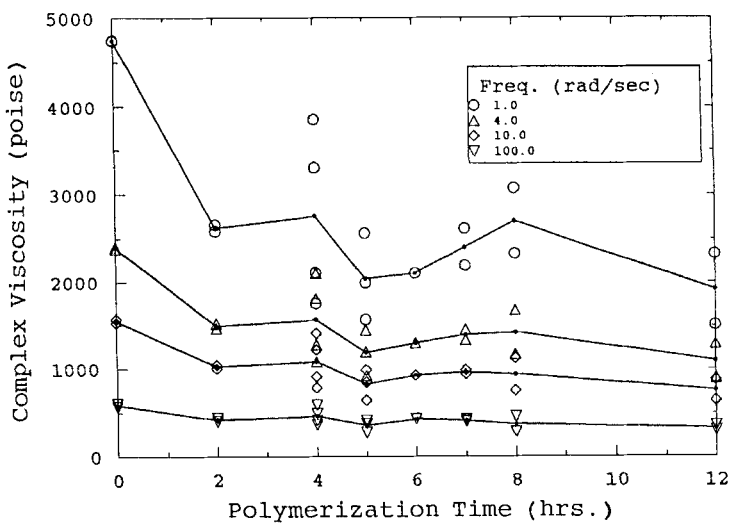


FIGURE 3. Complex viscosity at selected frequencies as a function of time of solid phase polymerization.

change in inherent viscosity. There is an apparent minimum in the viscosity at all frequencies at about 5 hours of solid phase polymerization. (A more pronounced minimum was observed at about the same polymerization time with the first two series that were synthesized, where polymerization was carried out to thirty-six hours). The molecular weight dependence of viscosity differs from that reported by Fujiwara and coworkers⁴ on a series of molecular weights of the same composition.

SOLUTION NMR

Solution NMR provides information about chain sequencing. Polymer samples from the third batch were dissolved in a 3-to-1 deuterated chloroform/trifluoroacetic acid solution (3 wt%). Proton spectra were obtained on a Bruker AM-500 500 MHz spectrometer. Peak assignments were reported previously by Nicely et al.² Peak areas were determined by fitting of the spectra to a theoretical lineshape. Each peak was modeled as a Lorentzian-convoluted Gaussian; the Lorentzian character accounts for the homogeneous linewidth and the Gaussian character accounts for the inhomogeneous (i.e., chemical shift) broadening of each peak. The relevant portion of a typical proton spectrum and an optimal fit is shown in Figure 4.

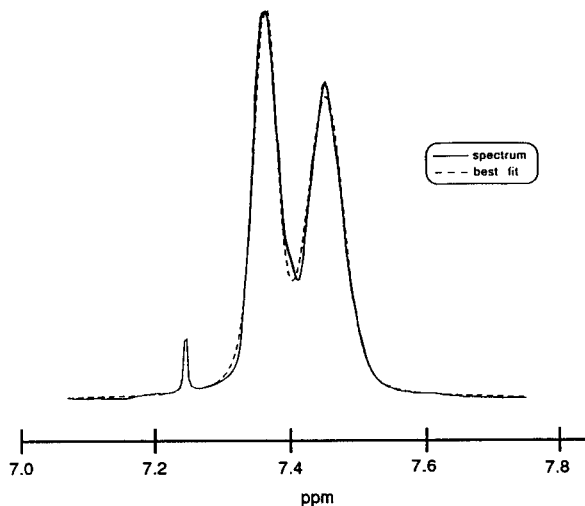


FIGURE 4. Solution proton spectrum for a sample with seven hours of solid phase polymerization.

The preference factor measured for a sample of 60 percent HBA / 40 percent PET supplied by Eastman was 1.27, which is close to the "best fit" value of 1.3 reported by Nicely and coworkers² for a series of Eastman polymers with monomer compositions ranging from 20 to 80 mole percent HBA. (A preference factor of unity indicates a random sequencing of monomers.) The preference factors for various times of solid phase polymerization of the third batch synthesized in this study are shown in Table 1. The proton results were corroborated for one sample using carbon-13 NMR. All values are around 1.2, indicating a small deviation from randomness.

TABLE I Preference factor from solution NMR.

Solid phase polymerization time (hours)	Preference factor
0	1.20
2	1.21
4	1.20
5	1.26
7	1.22
8	1.21
12	1.25

HIGH-TEMPERATURE NMR

Polymer samples were dried for two days in a vacuum oven at 120°C and then sealed in 5mm NMR tubes. Broadline proton spectra were obtained on a homebuilt spectrometer operating at 180 MHz with a 4.3 Tesla superconducting solenoid. A polymer sample which had experienced no solid phase polymerization was held at 210°C in the spectrometer and exposed to a continuously purged nitrogen atmosphere for 27 hours, simulating the usual conditions for solid phase polymerization; proton spectra were recorded at various times. Proton spectra were also recorded at 265°C for samples which had undergone solid phase polymerization for periods ranging from zero to twelve hours, as described above; spectra for these samples were recorded at 10 and 18 minutes after reaching 265°C.

Typical spectra at 210° and 265°C are shown in Figure 5. Both narrow and broad peaks can be observed in each case. The narrow peak is associated with protons in regions of the sample that experience rapid isotropic motion. This peak sharpens continuously in passing from 210° to 265°, which is consistent with increasing molecular motion; it can be resolved at 265°C into two peaks separated by 3.25 ppm, associated with aliphatic and aromatic protons. The broad peak is associated with protons which experience anisotropic motion. The lineshape at 210°C indicates no preferred orientation, but at 265° the broad lineshape appears as a symmetric pair of peaks, indicating alignment of the nematic phase with the external magnetic field. The fraction of isotropic phase was determined by integration of the spectrum. The isotropic fraction for the 60 percent HBA / 40 percent PET sample supplied by Eastman was 0.22; this is smaller than the value of 0.38 for this composition and temperature read from the graph in Nicely et al.²

The isotropic fraction at 210°C is shown as a function of the time under nitrogen purging in the spectrometer in Figure 6. There is a monotonic decrease in the amount of the isotropic component with time. The isotropic fraction at 265°C is shown in Figure 7 as a function of the time of solid phase polymerization. These results show a similar decrease, particularly over the interval from two to seven hours of polymerization, but there is considerable scatter. Experiments on other polymer batches lead us to conclude that the overall trend is correct, and that the experimental scatter is due largely to sample variability within the batch. (This was obviously not an issue for the experiment at 210°C, since all data were from the same sample.)

The second moments of the melt spectra, divided by the nematic fraction, are plotted in Fig. 8 as a function of the isotropic fraction. The ordinate is a measure of the average orientation of the nematic phase. The correlation is good, and suggests that the nematic orientation should also correlate with the viscosity. There is too much sample-to-sample variation to establish such a relation, however.

CONCLUSIONS:

The rheological properties of this liquid crystalline polymer, and hence the development of orientation, are sensitive to the presence of an amorphous phase in the predominantly-nematic material. The trend of the data

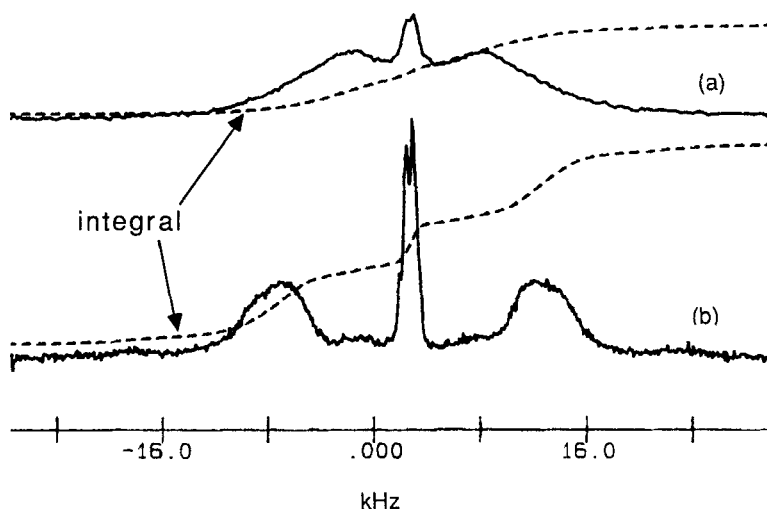


FIGURE 5. Proton spectra. (a) 210°C after eight hours in the spectrometer. (b) 265°C for a sample with eight hours of solid phase polymerization.

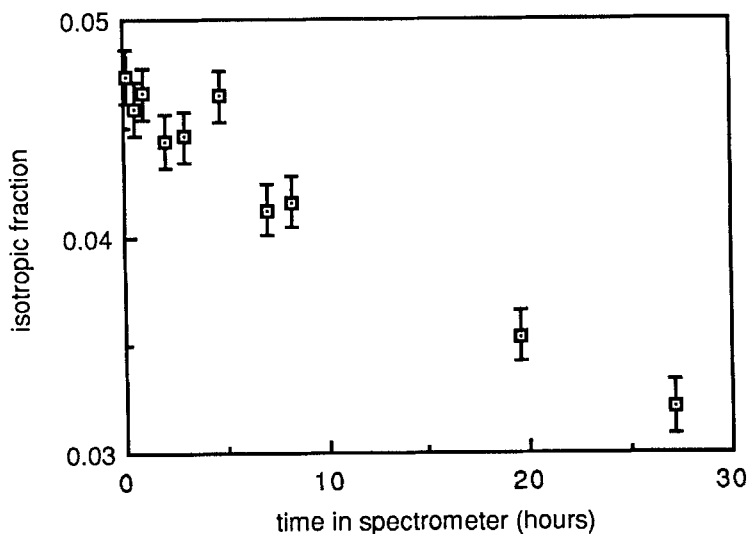


FIGURE 6. Isotropic fraction at 210°C as a function of time in the spectrometer.

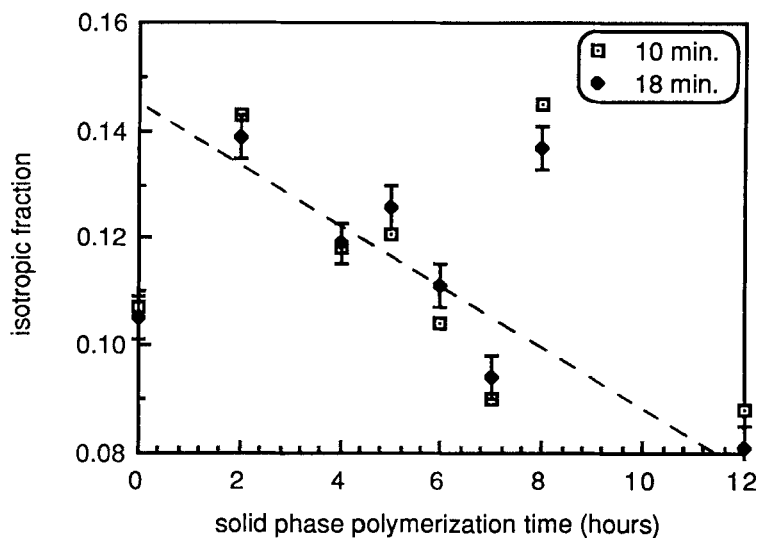


FIGURE 7. Isotropic fraction at 265°C as a function of time of solid phase polymerization. (Error bars omitted from 10 minute data for clarity.)

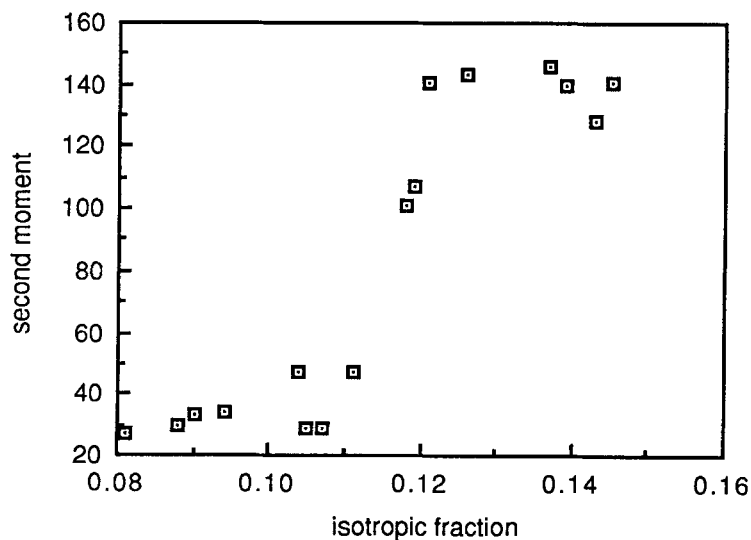


FIGURE 8. Second moments of the melt spectra at 265°C, divided by nematic fraction, as a function of isotropic fraction.

suggests that the viscosity is reduced by increasing the nematic fraction, and that the average nematic orientation is increased with increasing isotropic fraction; this would be consistent with a picture of nematic domains and isotropic material "between" these domains. Regardless of the mechanism, however, it is likely that the rheological response of thermotropic liquid crystal polymers will be significantly affected by small variations in the isotropic fraction, and sensitivity to the phase diagram can be expected to have a major influence on processing behavior.

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