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Electrohydrodynamic Instabilities in Thermotropic Nematic Polymers

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ABSTRACT: Electric field induced flow instabilities in a polymeric nematic phase were investigated. The two polymers were T2/60 and T2/30, co[poly(ethylene terephthalate)–1,4-benzoate] containing 60 and 30 mol % of *p*-oxybenzoyl units, respectively. Instabilities were observed in the thermotropic nematic phase of the former, and none were seen in the isotropic phase of the latter. Williams domains formed most readily in T2/60, using dc voltage and a higher temperature, but the formation time was hours as compared to tenths or hundredths of a second for *p*-azoxyanisole. No dynamic scattering mode or chevron pattern was observed for T2/60. Analogues of the variable grating mode and high field turbulence reported for low molecular weight nematics are observed for T2/60. Since the formation time of the latter is of the order of a minute, this may provide a convenient confirmatory test for a thermotropic nematic phase in polymers.

As more types of polymers are developed which exhibit liquid crystalline behavior, there is a growing need for tests which confirm the presence of a polymeric nematic phase. For low molecular weight materials, the microscopic observation of dark "threads" representing disclination lines is taken as characteristic of the nematic phase. Indeed, the word nematic is derived from the Greek *nematos*, meaning threadlike. Although "threads" have been observed in polymeric nematics on occasion, their formation is not spontaneous, but may require a particular treatment of the sample.[1,2]

Schaefgen, Pletcher, and Kleinschuster[3] proposed that the behavior of the birefringence during heating to a thermotropic nematic phase is characteristic of that phase. Our experience,[4] however, has demonstrated that one can be deceived by the appearance of a sample in the polarizing microscope, particularly for those polymers which exhibit multiple melting peaks. McFarlane, Nicely, and Davis[5] have examined the effect of magnetically ordering a thermotropic nematic by observing changes in the NMR spectra of the ordered mesophase or the ordered solid state. The alignment in a magnetic field seems capable of providing a definitive test of a nematic phase; however, the NMR technique requires special equipment which may not be readily available. In addition, it requires about 1 h to align the molecules. We have investigated the effects observed with electric fields in the belief that these might provide a more convenient test of nematic character. Since polymer chemists may not be familiar with the literature of liquid crystals, a survey of the effect of electric fields on low molecular weight thermotropic nematics is given in the next section.

Background

Molecules capable of forming a nematic phase are characterized by asymmetrical shapes, such as a rod or thin disk, and for this reason would be expected to have anisotropic magnetic susceptibilities and dielectric constants. There should be a slight tendency for such molecules to become aligned when placed in a magnetic or electric field. Thus in the nematic phase, with suitable initial boundary conditions, application of a magnetic or electric field should result in a second-order transition (Frederiks transition) involving a cooperative alignment of the molecules. The expected behavior was observed in the case of magnetic fields,[6] but early investigations of the effect of electric fields led to divergent results, as reviewed by Gray[7] in 1962. Subsequent work has demonstrated that an electric field can induce hydrodynamic flow in a nematic liquid crystal and that flow instabilities can lead to certain definite flow patterns. Further, it was observed that the result obtained upon application of an electric field depends upon the signs of the dielectric and conductivity anisotropies of the material, and also upon the orientation of the molecules in the nematic sample prior to application of the field.

Electrohydrodynamic instabilities were first reported for low molecular weight thermotropic nematic liquids by Williams,[8] and the potential applications of this effect to display devices were explored by Heilmeyer, Zanoni, and Barton.[9] The typical experimental arrangement consists of a sandwich cell in which the sample is placed between glass slides separated by a spacer of appropriate dimensions. The slides are coated with a transparent, electrically-conducting layer of tin oxide, for example. A material such as *p*-azoxyanisole, for which the dielectric anisotropy, $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$, is negative and the conductivity anisotropy, $\sigma_a = \sigma_\parallel - \sigma_\perp$, is positive, should optimally have an initial homogenous alignment which is "planar". A uniform initial alignment of the director (a unit vector representing the preferred orientation of the molecules within a small volume element) is obtained by suitable surface treatment. This may involve a noncovalent attachment of the molecule to the substrate surface, a process referred to as "anchoring". To facilitate the subsequent discussion, we will adopt a Cartesian coordinate system with the surfaces of the glass slides parallel to the xy plane and stipulate that the electric field is applied (and microscopic observations are made) along the z direction, while the molecules are initially aligned along the x direction.

The observations for ac fields, as indicated schematically by Dubois-Violette et al.,[10] are shown in Figure 1. Beginning with a low voltage at a frequency such as 50 Hz, upon increasing the voltage to a threshold value, V_t, one sees the Williams domain pattern of striations, parallel to the y axis, with occasional bends. The threshold voltage is independent of the sample thickness above 10 μm and, as shown by the Orsay Liquid Crystal Group,[11] it remains unchanged if the sample is insulated from the conducting tin oxide layer by Teflon shields. The domain pattern arises from the organization of hydrodynamic flow into an ordered pattern of cylindrical vortices. One is reminded of the Bênard effect,[12,13] a convective instability which arises when a layer of isotropic liquid is heated from below. Markers, such as dust particles, move in spiral paths within a cylinder, progressing along the $+y$ or $-y$ direction in

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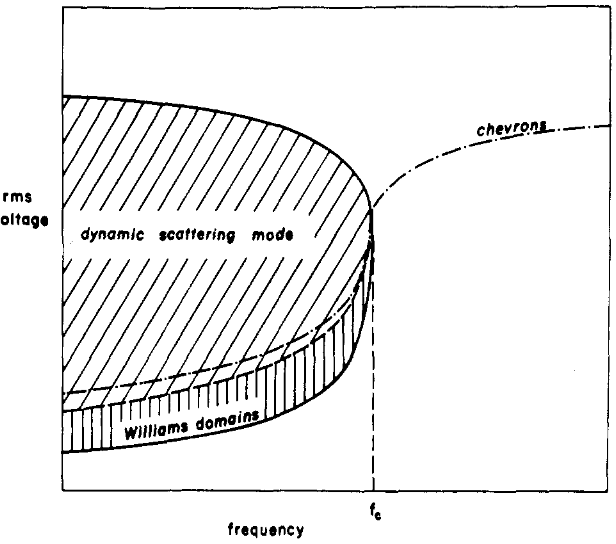

Figure 1. Regions of different types of hydrodynamic instability shown on a voltage vs. frequency diagram (ref 10).

adjacent domains. The domain pattern disappears for light polarized along the y direction, indicating that the molecules are aligned preferentially in the xz plane. There are upper and lower focal distances for the pattern due to the fact the domains act as an array of cylindrical lenses giving rise to real and virtual images, respectively. These observations are well explained by the domain model developed by Penz.[14]

As the voltage is increased above V_t, the Williams domains became more mobile and eventually a state of disordered motion, the dynamic scattering mode (DSM), is obtained. If the same observations are repeated at higher frequencies, V_t is found to increase with frequency. This increase is slow at first but becomes progressively more rapid until a critical frequency, f_c, is reached. Above f_c the Williams domains and the DSM no longer exist, but we can observe a second instability pattern, descriptively termed chevrons, which exhibits a critical field strength dependence. The chevron pattern also extends below the critical frequency, f_c but at voltages above the threshold for the formation of Williams domains.

Theoretical treatments of these electric field induced flow instabilities have been given by Carr,[15] Helfrich,[16] and Dubois-Violette, de Gennes, and Parodi.[17] Small amplitude bend oscillations in the director alignments lead to the build up of space charges due to the anisotropies of the conductivity and dielectric constant. These space charges create a transverse field along x which tilts the resultant electric field and causes a hydrodynamic flow. If the initial molecular alignment is optimally chosen, both the dielectric and viscous torques tend to increase the bend distortion angle, and this may ultimately lead to a roll instability. The solution of the resulting system of coupled equations can be obtained in two distinct branches. Let τ be the dielectric relaxation time, T the bend damping time, and ω the angular frequency. (a) If $\tau \ll T$ and $\omega\tau \ll 1$, the conduction regime is formed and Williams domains appear. The bend pattern is stationary and the space charges oscillate in sign with the applied field. The onset of the conduction instability is predicted to be voltage dependent. (b) If $\tau \gg T$ and $\omega\tau \gg 1$, the dielectric regime characterized by chevrons exists. Here the space charges do not oscillate, but shear flow occurs parallel to the y axis in the region of bending of the directors. The onset is predicted to be electric field dependent. Actually, it is only somewhat above the critical field where a combination of bend and splay distortions gives rise to the typical chevron pattern. Thus, as the frequency is increased beyond a critical value, ω_c, the system changes from the conduction regime to the dielectric regime. Even for frequencies less than ω_c, the conduction instability can be quenched by increasing the electric field, which reduces the bend relaxation time T. This can be accomplished, for example, by reducing the thickness of the sample.

Thus far we have described only the behavior of (ϵ_a^-, σ_a^+) materials. The appropriate initial alignment and type of instability patterns for other combinations of signs of these anisotropies have been discussed by Dubois-Violette et al.[10]

Turning to polymeric thermotropic nematics, the effect of electric fields has been reported by Finkelmann, Naegle, and Ringsdorf[18] for copolymers having nematogenic groups attached, through aliphatic chain spacers, to the backbone of a poly(methyl methacrylate) chain. They investigated alignment by an electric field to form a homotropic texture (molecules aligned along the z direction). The initial state of their samples was unoriented. The time required to achieve orientation decreased as the voltage was increased above a threshold value. The authors give a relaxation time (after switching off the field) of ca. 5 s and speculate that a lower value would be expected if defined boundary conditions had been used. Hence, the behavior of their polymeric nematics is rather similar to that observed for low molecular weight materials. The relaxation time for this polymeric system is somewhat longer, but not by more than one order of magnitude. Although these authors mention some type of turbulent flow, it was not their objective to study this phenomenon.

There have been no reports concerning the observations of Williams domains, or studies of any other type of electric field induced instabilities in thermotropic nematic polymers. We will demonstrate that domain patterns can, in fact, exist in a copolyester which has been characterized as nematic, using NMR techniques.[5] Moreover, it will be shown that the observation of electrohydrodynamic instabilities is rather easy and does not require sophisticated instrumentation. These advantages make it particularly convenient for the characterization of thermotropic nematic polymers.

Experimental Section

The conventional arrangement[6] was used for observing electro-optical effects in both low molecular weight and polymeric liquid crystals. Tin oxide coated slides (Practical Products Co., Cincinnati, Ohio) were arranged as a sandwich cell containing the liquid crystalline material. Mylar films or mica spacers were used to fix the cell thickness unless otherwise noted. Orientation was attempted with the use of a cotton swab by the Chatelain rubbing technique.[19] This cell was heated with the use of a calibrated Thomas hot stage (Philadelphia, Pa.). The sample was viewed along the electric field direction, using a Bausch and Lomb polarizing microscope (Rochester, N.Y.), and the visual observations were recorded with the use of a Model N eyepiece camera with cone attachment (Bausch and Lomb). All photomicrographs were taken with a magnification of 75×.

A Model 110 Wavetek generator (San Diego, Calif.) was used to generate sine waves whose amplitude range from 0.07 V at 0.05 Hz to 10 V between 25 and 105 Hz. For frequencies above approximately 50 Hz, an audio amplifier yielded up to 200 V without appreciable distortion of the wave form. A Type 503 Tektronix Oscilloscope (Portland, Oregon) was used to monitor the wave form and measure the peak-to-peak voltage, V_p. The rms voltage, V, was obtained from $V = V_p/2^{3/2}$. A 7 V power source was used for the dc experiments.

The p-azoxyanisole (PAA) sample was obtained from Aldrich Chemical Co. (Milwaukee, Wis.) and used without further purification, while the two copolymers, co[poly(ethylene terephthalate)-1,4-benzoate], containing 30 and 60 mol % p-oxybenzoyl units were kindly supplied by the Tennessee Eastman Co. (Kingsport, Tenn.). These copolymers will be referred to below

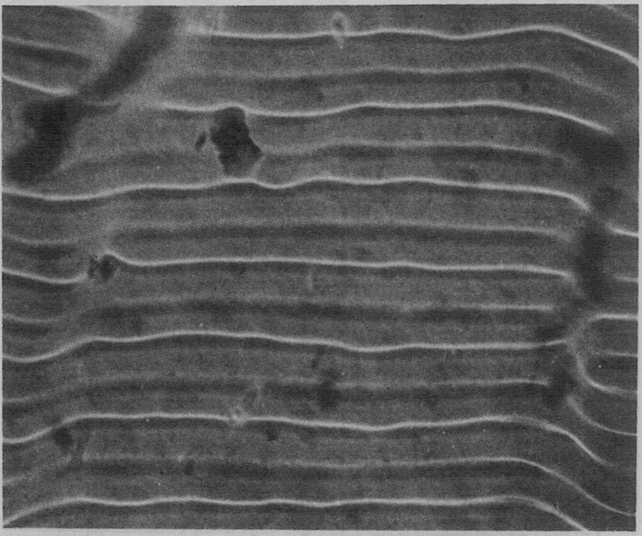

Figure 2. Photomicrograph (original magnification 78×) of Williams domains observed in a sample of *p*-azoxyanisole (PAA), having "planar" alignment (rubbing direction vertical).

Figure 3. Williams domains as formed in an unoriented sample of PAA.

as T2/30 and T2/60, respectively. Only the latter forms a thermotropic nematic phase.

Results and Discussion

The first region of voltage and frequency examined was that in which Williams domains would be expected to appear. We have used PAA throughout as a low molecular weight reference material for comparison with the observations made for polymeric T2/60. Figure 2 illustrates the typical appearance of Williams domains in a PAA sample which has been given a "planar" alignment by the Chatelain rubbing technique. This photomicrograph was taken at the upper focus of the domain pattern, using 75× magnification. The temperature was 122 °C, and 8 V at 250 Hz was applied across the 30 μm thick sample. The pattern is a system of parallel bright lines oriented perpendicular to the rubbing direction. Alternate lines are somewhat broader, and the pattern spacing is approximately equal to the sample thickness. Figure 3 illustrates the appearance of Williams domains in an unoriented (and presumably unanchored) sample of PAA. This photo was taken of a 10 μm thick sample at 134 °C, using 6 V dc. In this case the domains are arranged in a random fashion.

We anticipated that, due to the high viscosity and long relaxation time of the polymer relative to low molecular weight materials, considerable time might be required for the formation of Williams domains in polymers which exhibit a nematic phase by virtue of their high chain extension. The domain pattern is formed more rapidly in thinner samples due to the reduction of the bend relaxation time. However, when the latter becomes equal to the dielectric relaxation time, instabilities associated with the conduction regime vanish. From these considerations we selected 10 μm as a compromise sample thickness. Figure 4 exemplifies Williams domains as seen in an unoriented sample of T2/60 at 275 °C after 3 h in a dc field of 6.4 V. One sees a more or less random arrangement of a feature consisting of a thin bright line bounded by two dark lines, the dimension of the total being about 10 μm. Initially, only very short segments of this feature became visible, and the pattern developed slowly with time. The general electro-optical features shown in Figure 4 for T2/60 are consistent with those observed in Figure 3 for PAA. For either unanchored sample, curved thin bright lines are bounded on either side by broad dark lines. The similarity of these features provides evidence that Williams domains are indeed formed in the thermotropic polymer examined here. We were unsuccessful in obtaining an anchored sample of T2/60 analogous to that shown for PAA in Figure 2.

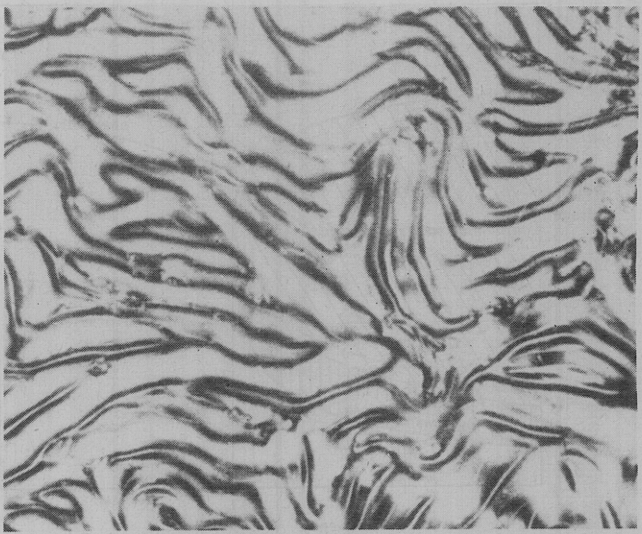

Figure 4. Williams domains formed after 3 h in a nematic copolymer T2/60 at 275 °C (6.4 V dc).

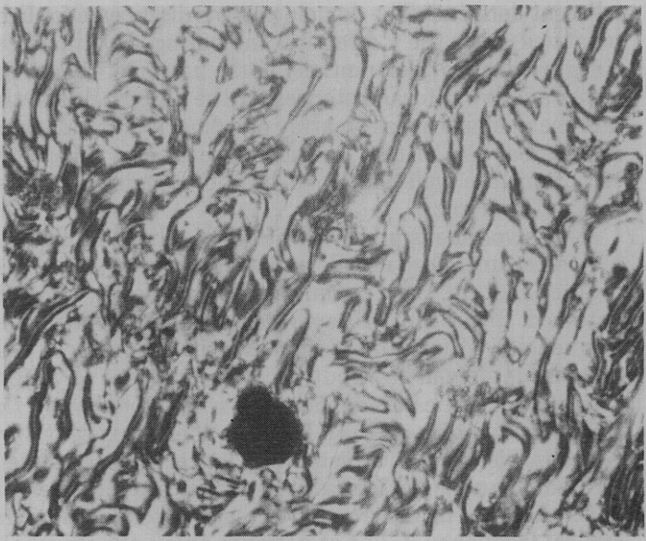

Figure 5. Domain pattern formed after 6 h at 268 °C and 6.4 V dc.

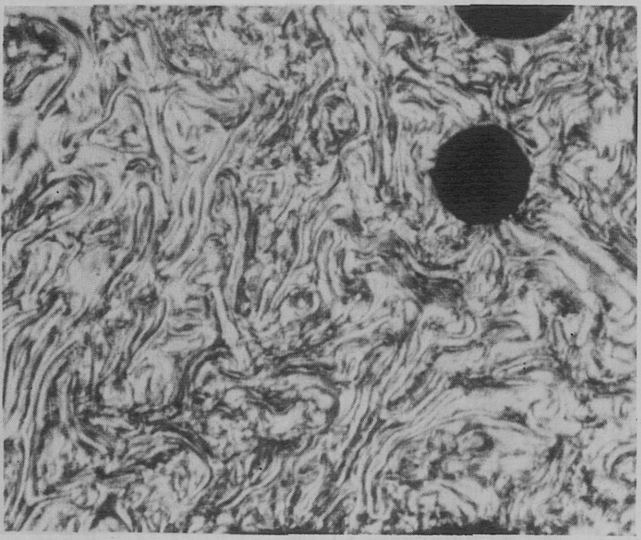

Figure 6. Domain pattern after 3 h at 276 °C under an ac field of 0.7 V at 0.5 Hz.

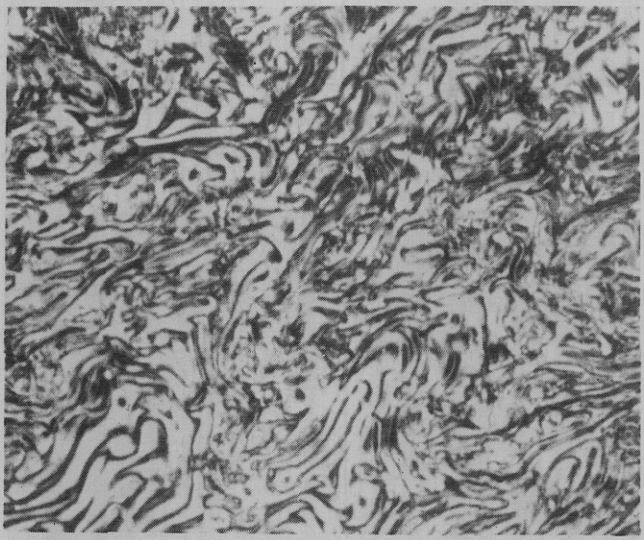

Figure 7. Same as Figure 6, but after 4 h and 10 min at 268 °C.

As might be expected, the development occurred more slowly at lower temperatures. In Figure 5 we show the domains formed at 268 °C after 6 h with the same voltage. The dark lines are more numerous, and the individual bright regions are of smaller area than those of Figure 4. The distance between two focal points was small for the polymer sample. The views seen from the two focal positions differed by a displacement of the bright line, and in some areas of the sample both bright lines were visible simultaneously. According to theory,[14] the separation of the two focal points decreases as the voltage is increased beyond V_t. This may offer an explanation for our observation concerning T2/60.

Williams domains are also formed with the use of very low frequency ac, although the domain pattern develops more slowly. Figure 6 illustrates a photomicrograph of T2/60 at 276 °C which resided 3 h in an ac field of 0.7 V, 0.5 Hz. The temperature and time correspond to those in Figure 4. Again, the dark lines are more numerous and the individual bright regions are smaller in area. Figure 7 shows a T2/60 sample after 4 h and 10 min under the same ac field, but at a lower temperature of 268 °C. The predominant feature here is bright areas bounded by dark lines, and the characteristics of the Williams domain pattern are more difficult to locate in this picture. Finally, a sample of T2/60 held at 275 °C under a field of 1.4 V and a frequency of 1 Hz for 3 h is shown in Figure 8. Here the dark lines are still finer and more numerous, and segments of the typical domain pattern can only be found in isolated portions of the sample. It is evident from our study that the pattern is most clearly developed with dc and at higher temperatures. The difference in the times required for the formation or dissipation of the flow patterns of T2/60 and PAA is expected from the higher viscosity and longer relaxation time of the polymer. In fact, when one considers these differences, and the possibility of molecular entanglements in the polymer, it is somewhat surprising that the Williams domain pattern should be seen in a polymeric nematic.

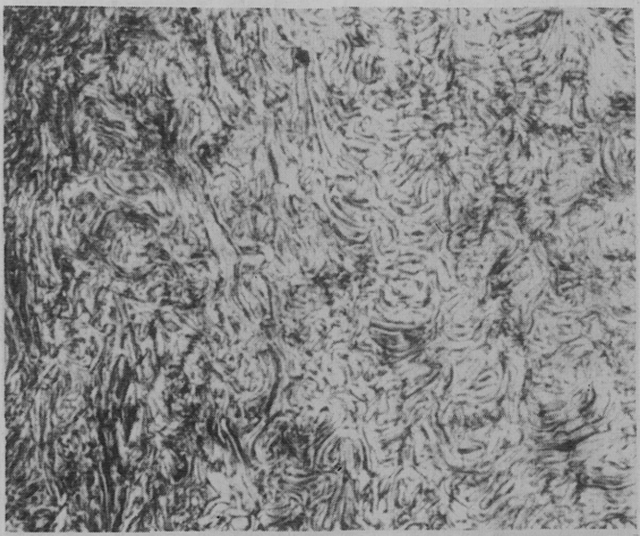

Figure 8. Same as Figure 6, but with an ac field of 1.4 V at 1.0 Hz.

We did not observe a Williams domain pattern with either dc or ac for T2/30, copolymer containing 30 mol percent oxybenzoyl units, which we believe does not exhibit a nematic phase. Hence, this domain pattern can serve as a test of nematic phase. One disadvantage is that, even under optimum conditions, considerable time is required to develop the pattern.

We next turn to flow instabilities observed at higher voltages. For low molecular weight nematics, as the voltage is increased beyond V_t, the Williams domains exhibit an oscillating motion at the bends. Further increase of voltage leads to a more violent motion and eventually to a random tumbling with many bright dots. This latter behavior is termed the dynamic scattering mode (DSM). We were unable to observe the DSM in T2/60. Gruler and Meier[20] reported, for a 100 μm sample of PAA AT 135 °C, that at still higher voltage the DSM is replaced by a pattern of dark spots showing strongly turbulent flow. Their photomicrograph, taken for a dc voltage of 62.5 V, also showed a pattern of smaller bright cells bounded by dark edges and having a dark dot in the center. We have observed both of these features with PAA in an ac field, although not simultaneously. Figure 9 illustrates the pattern of dark spots observed in a 10 μm sample of PAA at 132 °C upon applying 100 V at 750 Hz. A similar pattern was observed in polymeric T2/60 at 271 °C under a field of 150 V at 50 Hz, as shown in Figure 10. This pattern begins to form in the polymer as soon as the field is applied, but 30 s to 1 min is required for turbulent flow within the dark spots to attain its maximum intensity. The region of the voltage vs. frequency plot in which T2/60 exhibited high field turbulence is shown in Figure 11. We were unable to complete the left portion of this diagram due to the low signal output of our generator at the lower frequencies.

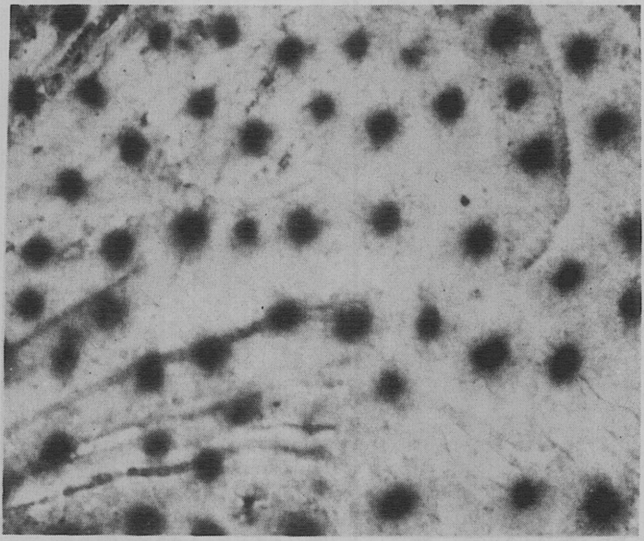

Figure 9. High-field pattern of dark, turbulent spots seen in PAA (100 V and 750 Hz).

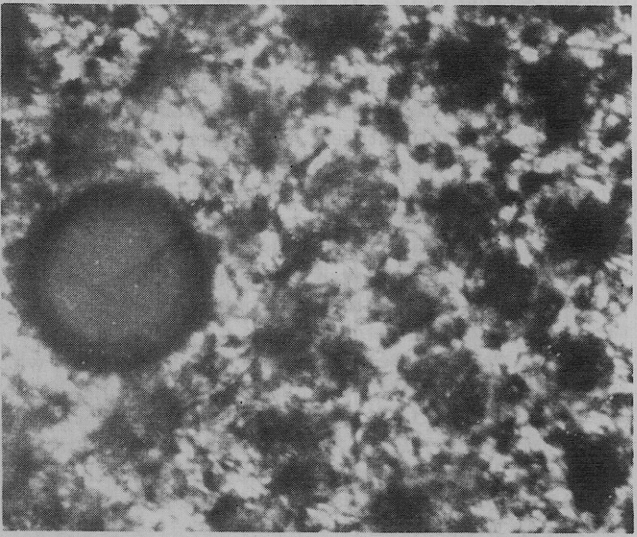

Figure 10. High-field turbulence pattern seen in polymeric T2/60 at 271 °C (150 V, 50 Hz).

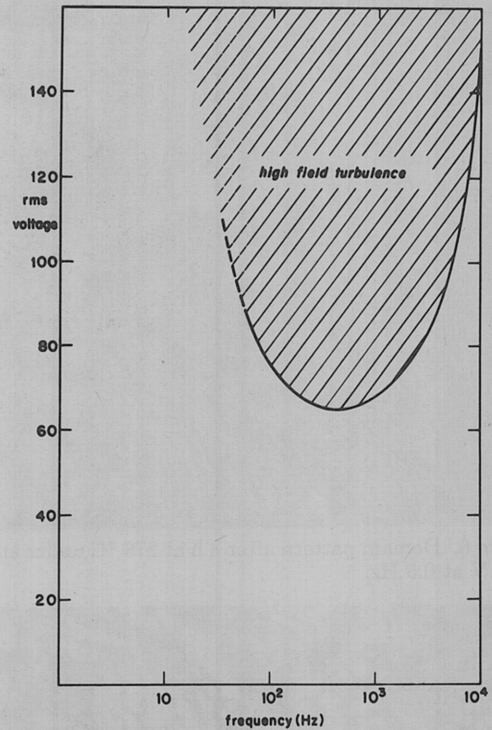

Figure 11. Region of the voltage vs. frequency diagram in which high-field turbulence was observed in T2/60

Figure 12. Variable grating mode domain pattern in a thin sample of PAA (rubbing direction vertical).

A curious observation was made concerning the effect of the electric field upon adventitious bubbles in the T2/60 sample. The area of the bubble decreased as the field strength was increased, and eventually a thin film appeared to be pulled from the walls to partially fill the cavity of the bubble. This thin layer exhibited turbulent motion.

The high field effect just described was not observed under comparable conditions for T2/30. Since the formation time for high field turbulence is short, this appears to offer a rapid test to determine whether or not a given polymer exhibits a thermotropic nematic state. It will clearly be necessary to examine a variety of polymers in this class to determine the generality of this test.

Williams domains are characterized by their appearance at a threshold voltage, V_t, by orientation of the cylindrical vortices perpendicular to the rubbing direction, and by the fact that the periodicity of the spacing is nearly independent of the applied voltage for $V > V_t$. As indicated above, reduction of the sample thickness should lead to the disappearance of the conduction regime. Vistin'[21] and Greubel and Wolff[22] have reported another domain pattern for thin samples of low molecular weight thermotropic nematics. The spatial periodicity of this domain pattern decreases with increasing voltage, so this has been termed the variable grating mode (VGM). Vistin' examined a mixture of 62 mol % PAA and 38 mol % *p*-azoxyethoxybenzene, as well as the two separate nematogens. In all three cases he observed VGM domains *parallel* to the rubbing direction whereas Greubel Wolff found the VGM domains to be perpendicular to the rubbing direction for *p*-methoxy-*p*-*n*-butylazoxybenzene. Meyer[23] has introduced the concept of flexoelectricity, or curvature electricity, as the liquid crystal analogue of piezoelectricity in solids. Derzhanski et al.[24] have suggested that the VGM instability arises from flexoelectric coupling, and this suggestion was subsequently confirmed by Russian workers.[25,26]

Figure 12 illustrates the domains formed parallel to the rubbing direction in a sample of PAA at 133 °C at a dc voltage of 6.4 V. In this case no spacer was used, so we can only estimate that the sample thickness was below 6 μm. The domain structure formed after 1 h in T2/60 at

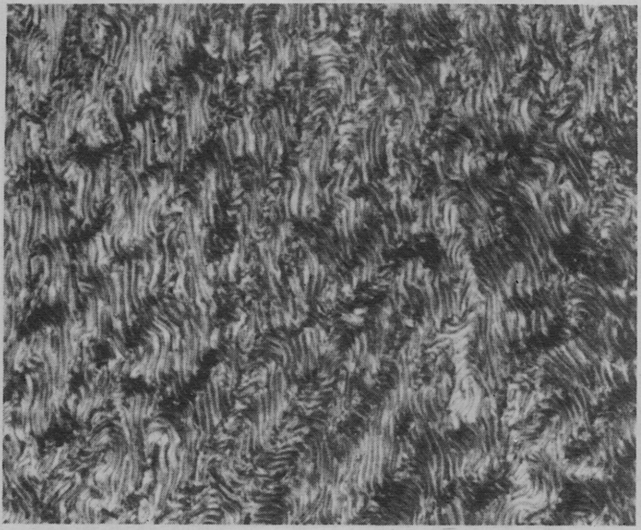

Figure 13. Domain pattern in a 4 μm sample of T2/60 at 270 °C (rubbing direction vertical).

270 °C and for a comparable voltage is exhibited in Figure 13. A 4-μm spacer was used for this sample. There may be a suggestion of polymer alignment parallel to the rubbing direction, but only over short distances and in some areas of the sample. According to the theory of flow instabilities mentioned above, the conduction regime (and Williams domains) would not be expected for samples as thin as those shown for PAA and T2/60 in Figures 12 and 13, respectively.

Conclusions

Two copolyesters were investigated in this study. T2/60, having 60 mol % oxybenzoyl units, forms a nematic phase upon melting, while T2/30 melts to an isotropic liquid. The classical low molecular weight nematogen, *p*-azoxyanisole, was utilized throughout for comparison with the behavior of nematic T2/60 under electric fields. The pattern of flow instabilities was examined with the use of 75× magnification with a polarizing microscope, and the thickness of the polymeric samples in the sandwich cell was generally 10 μm.

The Williams domain pattern was formed in the polymer most clearly at higher temperatures, and with dc voltages. Complete formation of the pattern in T2/60 required hours (as compared with a fraction of a second for PAA), although short segments of Williams domains in the polymer could be discerned earlier. Decreasing the temperature, or use of low-frequency ac, results in a finer structure of the dark lines, and slower development of the domains. The difference in formation time for T2/60 and PAA is due to the much higher viscosity of the polymer. No Williams domain pattern was found for T2/30 under comparable conditions, as expected.

We were unable to observe the dynamic scattering mode or chevrons in T2/60. At high fields a pattern of dark, turbulent regions forms in both PAA and T2/60, but not in T2/30. Since the high-field pattern forms in the polymer in a minute or less, this may provide a convenient test for a thermotropic nematic phase in polymers.

For very thin samples the variable grating mode pattern was observed for an oriented sample of PAA, and a somewhat similar pattern was observed for T2/60. However, in the latter case orientation, if any, was achieved over only small regions of the sample.

We believe this represents the first study of electric field induced flow instabilities in a thermotropic nematic polymer. This work needs to be extended to other polymers of this type to determine whether the effects observed for T2/60 are specific to that polymer or general for this class. Finally, this study points to the importance of determining the Ericksen-Leslie constants for at least one polymeric nematogen of this type, since theory would be a much more useful guide to future experiments if even order of magnitude estimates of these phenomenological constants were available for polymers.

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