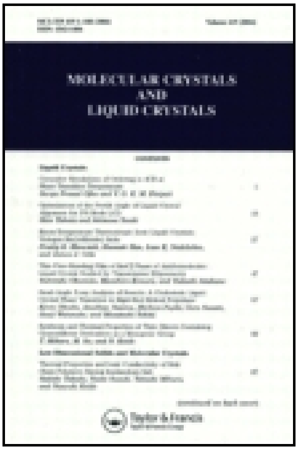

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Electric Field-Induced Flow Instabilities in Low Molecular Weight and Polymeric Nematics

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We compare the electrohydrodynamic instabilities in the thermotropic nematic phases of T2/60, a co[poly-(ethylene terephthalate)-1,4-benzoate] containing 60 mole % of *p*-oxybenzoyl groups, and in *p*-azoxyanisole (PAA). Due to the difference in their viscosities, the formation time of Williams domains in a d.c. field is on the order of an hour for the polymer, as compared to tenths or hundredths of a second for PAA. With a.c. at frequencies below 10 Hz., the threshold voltage for both materials falls significantly below the d.c. threshold value. Application of a d.c. voltage to very thin samples of both materials produces the variable grating mode pattern parallel to the rubbing direction. A similar pattern forms in PAA with low frequency a.c., but at 3 kHz the pattern changes to chevron-like domains perpendicular to the rubbing direction, and at 5 kHz dark snake-like regions move laterally across the field of view.

1 INTRODUCTION

Williams[1] was the first to study electrohydrodynamic instabilities in low molecular weight thermotropic nematic liquids, and Heilmeyer, Zanoni, and Barton[2] pointed out the potential applications of this effect to display devices. Theoretical treatments of Carr,[3] Helfrich,[4] and Dubois-Violette, de Gennes and Parodi[5] indicate that one should expect a conduction regime below a critical frequency, f_c, and a dielectric instability above this frequency. Different patterns of instability are recognized by their characteristic appearance under the polarizing microscope. Whereas Williams domain

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and the dynamic scattering mode[2] appear only below f_c, the chevron pattern exists in both regimes.

There have been a number of experimental studies of electric field-induced instabilities in low molecular weight nematics. We have recently completed an investigation[6] of electrohydrodynamic effects in the thermotropic nematic polymer T2/60 prepared by Tennessee Eastman, a co[poly-(ethylene terephthalate)-1,4-benzoate] containing 60 mole percent *p*-oxybenzoyl groups. The cell used in that study was of the familiar "sandwich" design with microscopic observations performed parallel to the direction of the electric field. We were able to observe Williams domains in this polymeric nematic, but not the dynamic scattering mode or the chevron pattern. Analogs of the variable grating mode,[7,8] and of high field turbulence,[9] both reported for low molecular weight nematics, were also seen in T2/60. A typical low molecular weight nematogen, *p*-azoxyanisole (PAA), was examined for comparison with the results obtained for T2/60. In this paper we will report some further observations for T2/60, as well as some results obtained for PAA which we believe have not been reported previously.

2 EXPERIMENTAL

Tin oxide coated slides separated by Mylar or mica spacers formed a sample cell which was heated using a Thomas hot stage. A Model 110 Wavetek generator was used to generate sinusoidal a.c., and the wave form and peak to peak voltage, V_p, was monitored using a Type 503 Tektronix oscilloscope. The rms voltage was determined from $V = V_p/2^{1/2}$. A 7 V power supply was used for the d.c. experiments. The sample was viewed along the field direction using a Bausch and Lomb polarizing microscope, and photomicrographs at a magnification of 75X were taken using a Bausch and Lomb eyepiece camera.

The *p*-azoxyanisole sample was obtained from Aldrich Chemical Company, while the T2/60 copolyester was kindly supplied by the Tennessee Eastman Company. Both were used without further purification.

3 RESULTS

A Williams domains in T2/60 using D.C.

The viscosity of a polymer such as T2/60, when compared to that of a low molecular weight nematogen, is much larger in magnitude, is much more strongly temperature dependent, and is shear rate dependent. One would expect that, due to the increased viscosity, the time required for the formation of a flow pattern in a polymeric nematic would be considerably longer. This, in fact, is the case. One can work with thinner samples, since the formation time of Williams domains varies as the square of the sample thickness due to a reduction of the bend relaxation time as sample thickness is decreased. However, there is a lower limit to the thickness which can be used to study phenomena in the conduction regime, since theory indicates the conduction regime will vanish when the bend relaxation time becomes equal to the dielectric relaxation time. We have found that a 10-μm thickness represents a good compromise, and this sample thickness has been used unless otherwise indicated.

Figures 1–3 illustrate the development of the Williams domain pattern in a 10-μm sample of T2/60 at 275°C under 6.4 V d.c. All of the photomicrographs were taken under cross polaroids using an original magnification of 75X. After 30 minutes, very careful scrutiny is required to detect even short segments of the Williams domains. The pattern is more clearly seen in Figure 2 taken after 1 hr, and Figure 3 illustrates a fully developed pattern after 3 hrs. The basic feature is a light area bordered on each side by a pair

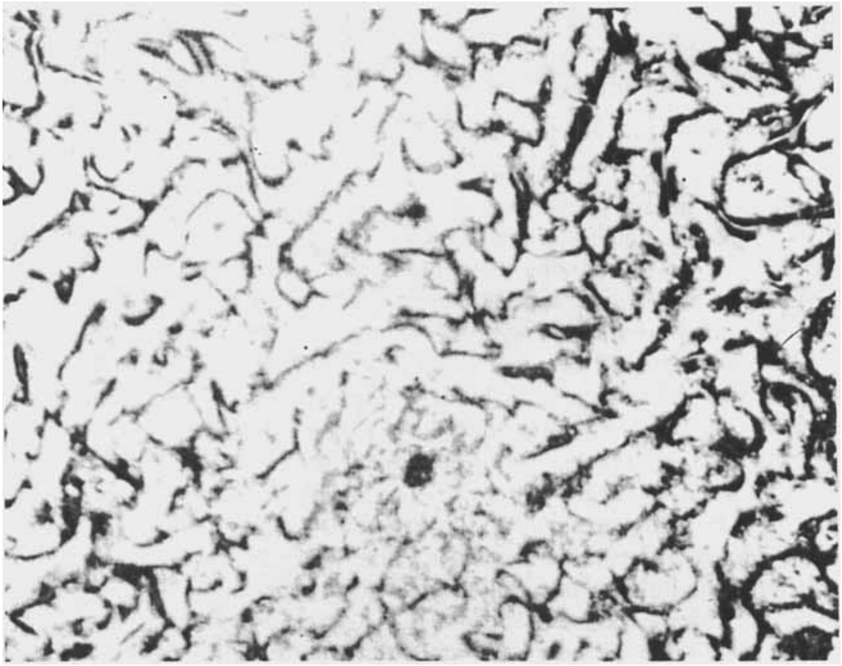

FIGURE 1 Onset of the Williams domain pattern in a 10 μm sample of nematic polymer, T2/60, at 276°C after 30 min. under a d.c. field of 6.4 V. (Photomicrograph taken with crossed polars using an initial magnification of 75X).

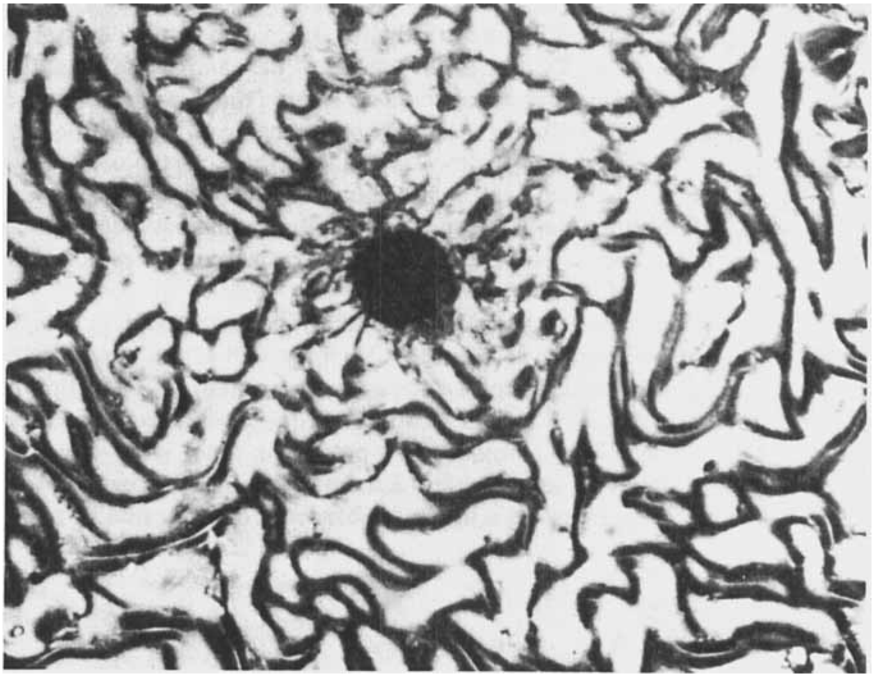

FIGURE 2 Further development of the pattern shown in Figure 1 after 1 hr.

of thin dark lines. The distance between the two focal points in samples of this polymer is generally small, perhaps due in part to the fact that the applied voltage exceeds the threshold value. The d.c. threshold voltage for T2/60 is estimated to be approximately 2 V. Since it required 4 hrs to detect Williams domains at 270°C with this voltage, this estimate may be somewhat too low due to partial decomposition of the sample during this time.

For low molecular weight nematics the domain size is approximately equal to the sample thickness, and the domains form more slowly in thicker samples. Our observation for T2/60 indicate that polymeric nematics follow the same behavior. Figures 4 and 5 illustrate the Williams domains formed at 270°C in T2/60 samples of thickness 10 μm and 28 μm, respectively. While our measurements showed a rather broad dispersion, the average values for the domain size, 10 μm and 26 μm, corresponded to the sample thickness within experimental error.

Our previous work[6] demonstrated that the formation time of Williams domains was substantially increased by reducing the temperature only a few degrees. This can be attributed to the very large temperature coefficient of the melt viscosity expected in this temperature region. The long relaxation time

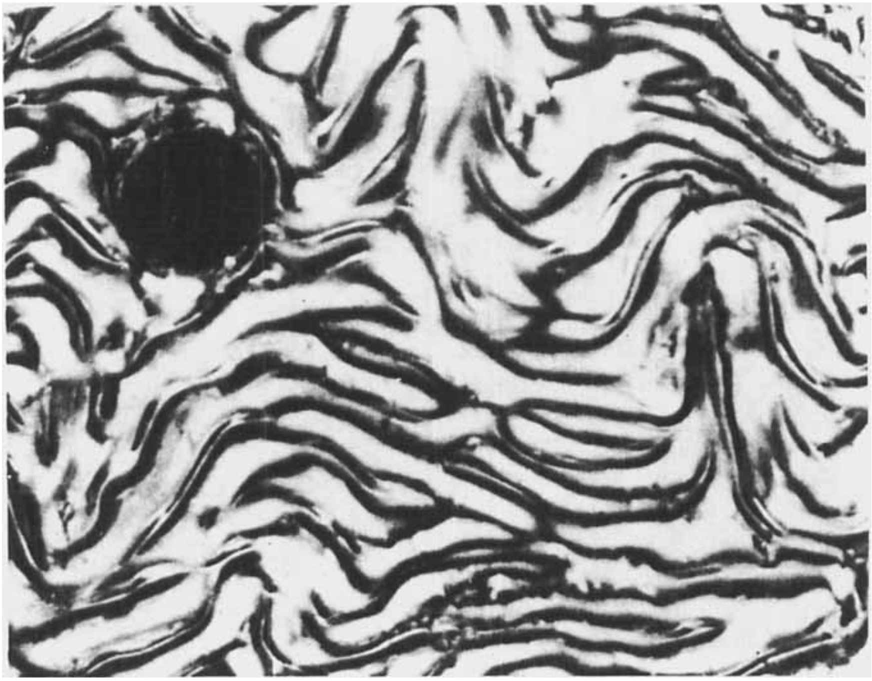

FIGURE 3 Essentially "mature" Williams domain pattern formed in the T2/60 sample of Figure 1 after 4 hr.

is a disadvantage in domain formation, but it does permit the domain structure to be retained in supercooled samples. The photomicrograph appearing in Figure 6 was taken of a 10 μm sample at 25°C. The sample had been maintained at 275°C for 4 hrs with 6.4 V applied, and the voltage was switched off before cooling the sample. The domain pattern in Figure 6 is still quite evident despite crystallization of the sample, although not as sharp as it was at 275°C. Low molecular weight nematogens do not afford this possibility to supercool a domain structure.

We were able to observe the formation of Williams domains in a d.c. field at temperatures as low as 265°C, but not below. It was previously shown[6] the the nematic phase of T2/60 exhibits local turbulence under a high electric field, and this effect vanished at 265°C. These observations are concordant with the *DSC* scan of this polymer, which indicates that melting of the crystalline regions is complete at 265°C.

B Williams domains formed using A.C.

Williams domains were observed in nematic T2/60 using a.c. at frequencies up to 100 Hz; however, more distinct domain patterns and shorter formation

FIGURE 4 Williams domains formed after 6 hrs. in a 10 μm sample of T2/60 at 268°C with 6.4 V. d.c.

times were found at frequencies of 1 Hz and below. Figure 7 illustrates the pattern which appeared in a 10 μm sample at 278°C after 1 hr using 1.4 V and 1 Hz. The more finely structured feature of Figure 7, as compared with the d.c. domains shown in Figure 2, is typical of the a.c. pattern. It should be noted that this a.c. voltage, although not a threshold value, is still below the d.c. threshold of 2 V. We had anticipated that the a.c. threshold voltages would decrease smoothly toward the d.c. value as the frequency was reduced. The Orsay Liquid Crystal Group[10] has given a theoretical relation for the a.c. threshold voltage, V_t, in terms of the d.c. threshold, V_0:

$$V_t^2 = V_0^2\left\{\frac{1 + (\zeta - 1)(f/f_c)^2}{1 - (f/f_c)^2}\right\} \tag{1}$$

where f_c is the critical frequency separating the conduction and dielectric regime and the Helfrich parameter, ζ, exceeds unity if instabilities are observed. Clearly this relation predicts $V_t > V_0$ for any finite frequency f, and that V_t should extrapolate smoothly to V_0 as the a.c. frequency approaches zero.

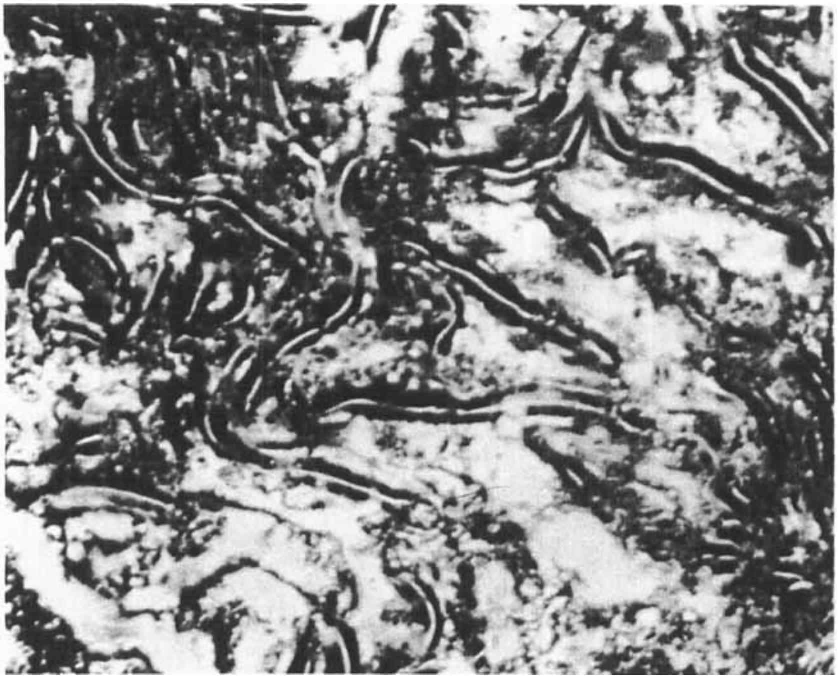

FIGURE 5 Williams domain pattern formed after 7.5 hrs. in a 28 μm sample of T2/60 at 270°C using 6.4 V. d.c.

We therefore investigated the a.c. threshold voltage for nematic T2/60 as a function of frequency. These measurements proved to be time consuming and rather imprecise at frequencies above 20 Hz. Figure 8 shows these experimental threshold voltage values, as measured for a 10 μm sample of T2/60 at 271°C, plotted against frequency. V_t decreases rather abruptly below 10 Hz and falls to 0.7 V at 1.0 Hz, a value significantly below the 2 V d.c. threshold.

The behavior of the threshold voltage at low frequencies might arise as a result of the polymeric nature of T2/60, or it may represent a general behavior of nematics at low frequencies. To resolve this question, we investigated the a.c. threshold voltage of PAA in the low frequency range. It was found that a Williams domain pattern could be formed in a 10 μm sample of PAA at 0.17 V and 0.5 Hz, as shown in Figure 9. We note that this voltage is well below the d.c. threshold value of 6 V. This sample had been ordered by the Chatelain rubbing technique.[11] Twice during each cycle the domains form perpendicular to the rubbing direction and disappear. The photomicrograph appearing in Figure 9 was taken at approximately peak voltage.

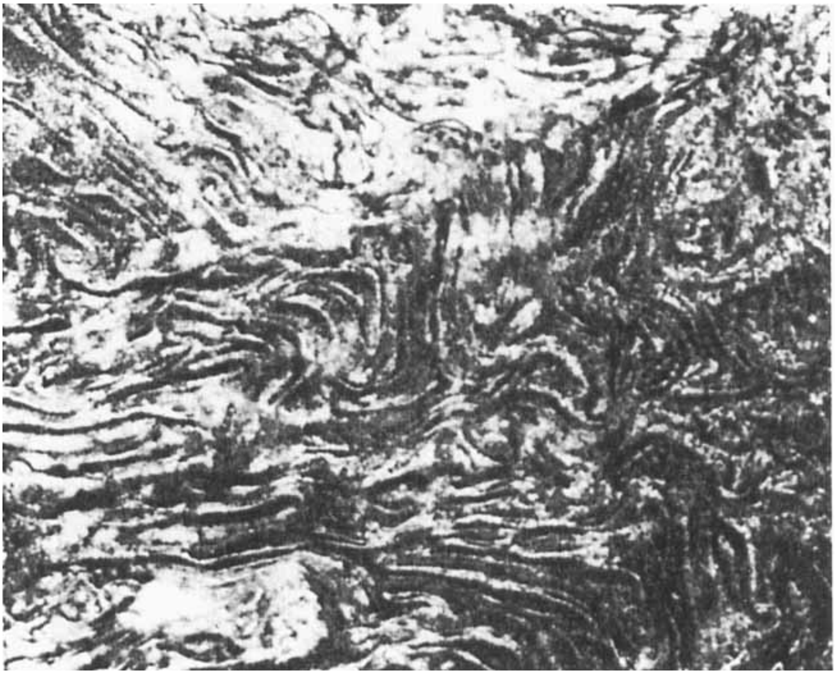

FIGURE 6 Domain pattern retained at 25°C after cooling a 10 μm sample of T2/60 held 4 hrs. at 275°C with 6.4 V.

Threshold voltages measured at different frequencies for a 30 μm sample of anchored PAA at 131°C are shown in Figure 10. The inset to this figure shows the frequency dependence of the threshold voltage for the formation of Williams domains. This is similar to that shown for T2/60 in Figure 8, indicating that the behavior observed at low frequencies for T2/60 is typical of nematic materials of this type. The remainder of Figure 10 illustrates threshold voltages for three types of instability in PAA plotted against frequency on a logarithmic scale. The open circles refer to Williams domains and the filled circles to the dynamic scattering mode (DSM). The latter exhibit a similar decrease in the low frequency range and, below 5 Hz, V_t for the DSM barely exceeds that required for the formation of Williams domains. The triangles in Figure 10 indicate threshold voltages for the chevron pattern in PAA above 100 Hz. We were unable to observe the chevron pattern in this sample at lower frequencies. However, for a much thinner sample obtained using no spacer it was possible to follow the frequency dependence of V_t for the chevron pattern down to 0.5 Hz. These data (not shown) revealed a similar decrease of V_t below 10 Hz.

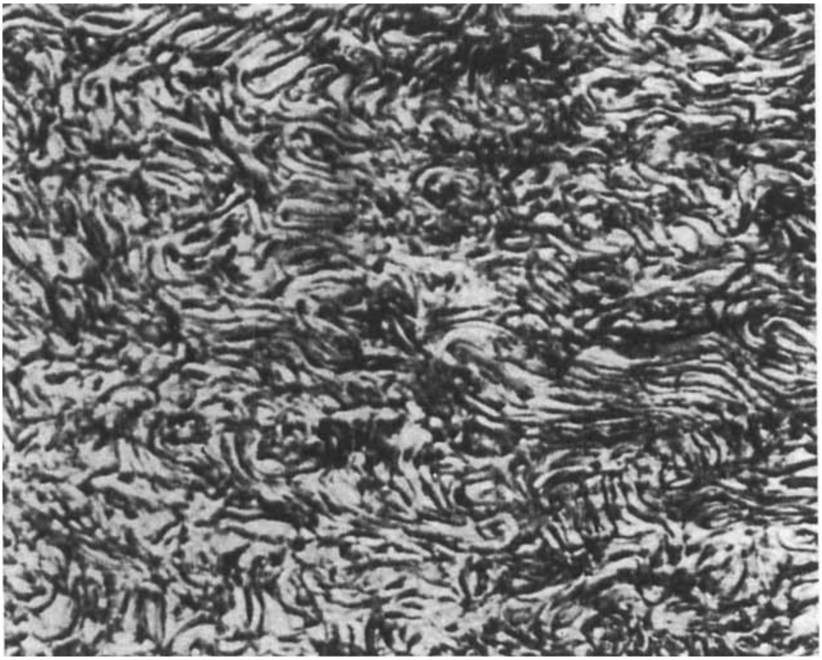

FIGURE 7 Onset of the Williams domain pattern in a 10 μm sample of T2/60 maintained at 278°C 1 hr. with an applied a.c. voltage of 1.4 V and 1.0 Hz.

The foregoing points to a difference in the process leading to instabilities for low frequency a.c. as compared to d.c. The literature suggests the possibility of anomalous behavior under both conditions. For example, de Gennes[9] has suggested that more readily interpretable results are expected from the use of a.c., rather than d.c., since a.c. should avoid complicating electrode effects. On the other hand, the Orsay Liquid Crystal Group[10] has found that experimentally determined values of Helfrich parameter ζ for 4-methoxybenzylidene-4′-butylaniline (MBBA) appear to decrease with decreasing sample thickness, d. They suggest that the results obtained for thin samples may be affected by spurious charge injection when the transit time of an ion, $d^2/\mu V$, becomes less than $1/2f$, where μ is the ionic mobility. This would lead to the expectation that, for a fixed sample thickness, V should vary linearly with f. This relation appears to describe the behavior shown in Figures 8 and 10 at very low frequency. On the other hand, a discontinuity in behavior between very low frequency a.c. and d.c. might be explained in terms of surface field effects.[12] The distribution of charge depends upon the electric field, the ionic mobility, and the dielectric con-

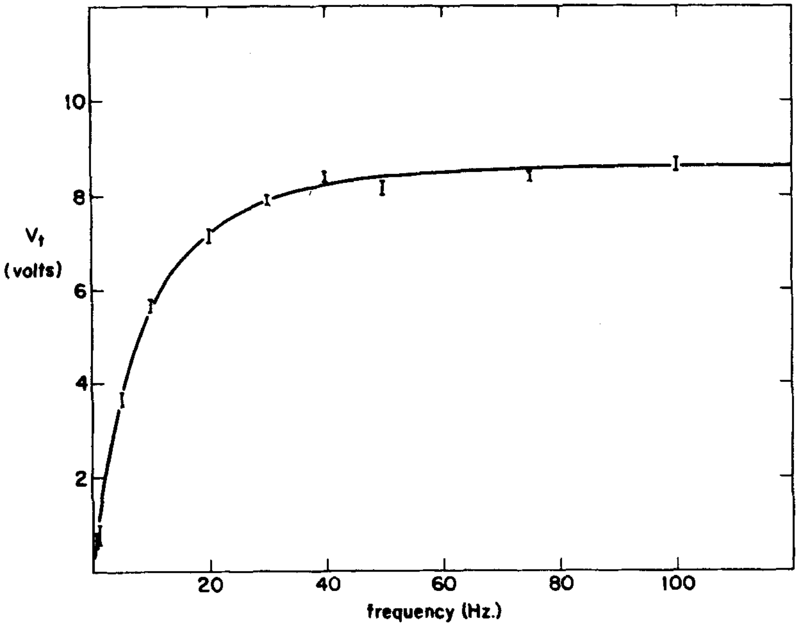

FIGURE 8 Frequency dependence of the threshold voltage, V_t, for the formation of Williams domains as observed at low frequencies for T2/60 at 271°C.

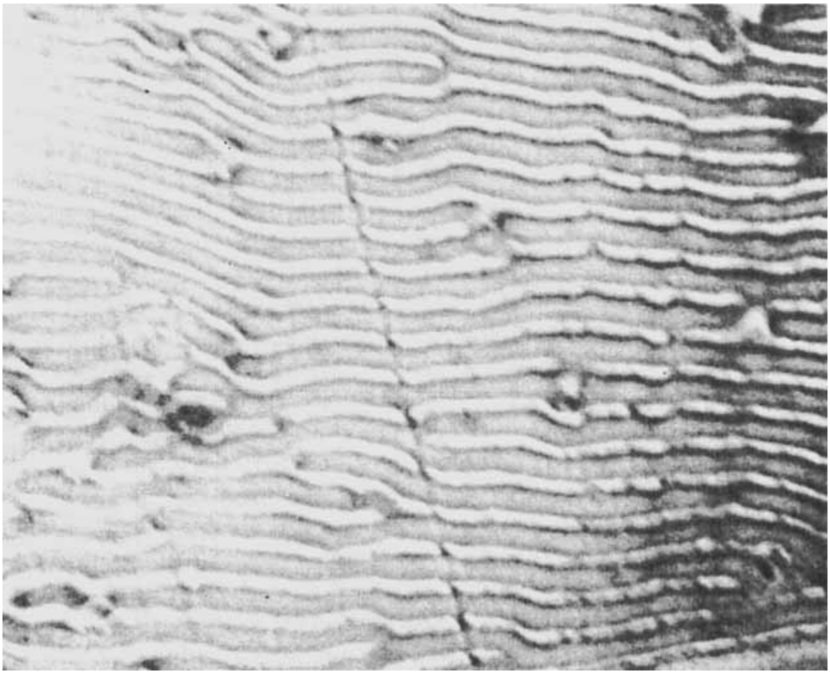

FIGURE 9 Williams doamin pattern formed in an anchored 10 μm sample of PAA at 133°C with low frequency a.c. (0.17 V and 0.5 Hz). Rubbing direction vertical.

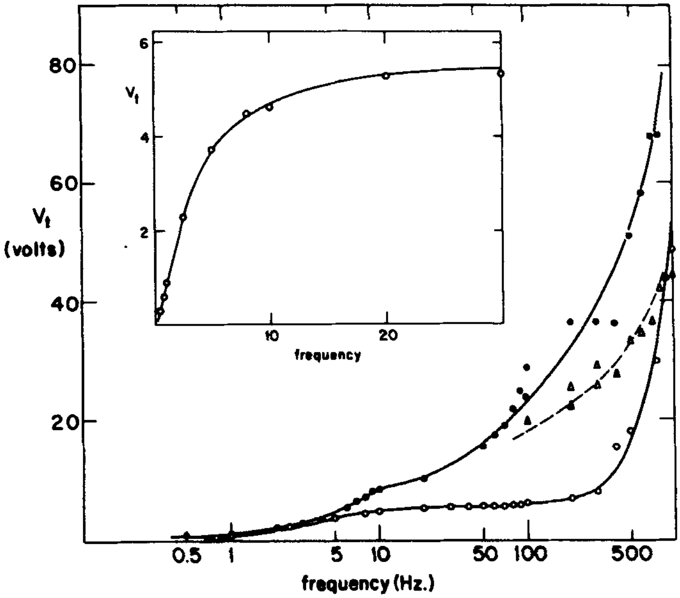

FIGURE 10 Frequency dependence of the threshold voltages V_t, shown as V_t vs. log frequency, for a 30 μm anchored sample of PAA at 131°C. Threshold voltages indicated for Williams domains O, the DSM ●, and chevrons ▲. Inset shows V_t vs. *f* for the formation of Williams domains at low frequencies.

stant of the medium. Since the dielectric constant is not only anisotropic, but also depends upon the electric field, these non-linear effects, through coupling of the space charge and surface field, may result in a large enhancement of the surface field for low frequency a.c. which would not occur for d.c.

C Observations for very thin PAA samples

Reduction of sample thickness leads to a shorter bend relaxation time, and the disappearance of the conduction regime. Hence, Williams domains and the DSM are no longer seen. In their place one finds a different domain pattern having a periodicity which decreases with increasing voltage. This is termed the variable grating mode (VGM). The VGM pattern has been reported for low molecular weight nematics by Vistin'[7] and by Greubel and Wolff.[8] Vistin' examined PAA, *p*-azoxyethoxybenzene, and mixtures of these two nematogens, and reported VGM domains formed *parallel* to the rubbing direction. Derzhanski, Petrov, Khinov, and Markovski[13] suggested that the VGM instability arises from flexoelectric coupling, a concept first introduced by Meyer.[14] This suggestion was subsequently confirmed by

FIGURE 11 VGM pattern observed in a very thin, anchored sample of PAA at 133°C with an a.c. field of 0.05 V and 0.05 Hz (rubbing direction vertical).

Russian workers.[15,16] A different behavior of the VGM was reported by Greubel and Wolff,[8] who found the domains aligned *perpendicular* to the rubbing direction for MBBA.

As indicated in our earlier study,[6] we were able to observe, in a 4 μm sample of T2/60 at 270°C, a pattern which appeared to exhibit some orientation parallel to the rubbing direction, and which we believe represents the VGM in this polymeric nematic. In the course of that study, we conducted a parallel investigation of the behavior of thin samples of PAA which will be reported here.

Figure 11 shows a photomicrograph of the VGM pattern formed in a very thin (no spacer) sample of PAA at 133°C using an a.c. voltage of 0.05 V at 0.05 Hz. The sample had been anchored by rubbing, and under these conditions the VGM pattern is parallel to the rubbing direction in agreement with the report of Vistin'.[7] However, upon increasing the frequency and voltage the pattern begins to change into one aligned perpendicular to the rubbing direction. The domain pattern observed for the same PAA sample at 19.8 V and 3 kHz appears in Figure 12. This pattern resembles that seen

FIGURE 12 Chevron-like pattern formed in the PAA sample of Figure 11 at 19.8 V and 3 kHz (rubbing direction vertical).

at the onset of chevron formation. The darker features barely visible in Figure 12 become more distinct as the frequency is further increased. Figure 13 shows the pattern seen in the microscope under crossed polars at 14.8 V and 5 kHz. The dark "snakes" move laterally across the chevron-like pattern with an undulating motion. Although the chevron-like pattern is not seen in Figure 13, it was still visible in other portions of the slide.

In conclusion, comparison of T2/30 and PAA has shown that Williams domains can be formed in polymeric, as well as in low molecular weight, thermotropic nematic phases. In both cases the sample thickness determines the domain size but, for a given thickness, the formation time is much longer for the polymeric nematogen due to its larger melt viscosity. One can take advantage of this longer relaxation time to prepare supercooled polymer samples which retain the domain structure at room temperature. For a.c. at frequencies below 10 Hz, both PAA and T2/60 exhibit threshold voltages for Williams domains which are significantly smaller than the d.c. threshold values. A similar threshold behavior at low frequencies is observed for chevrons and the dynamic scattering mode in PAA. Finally, a snake-like

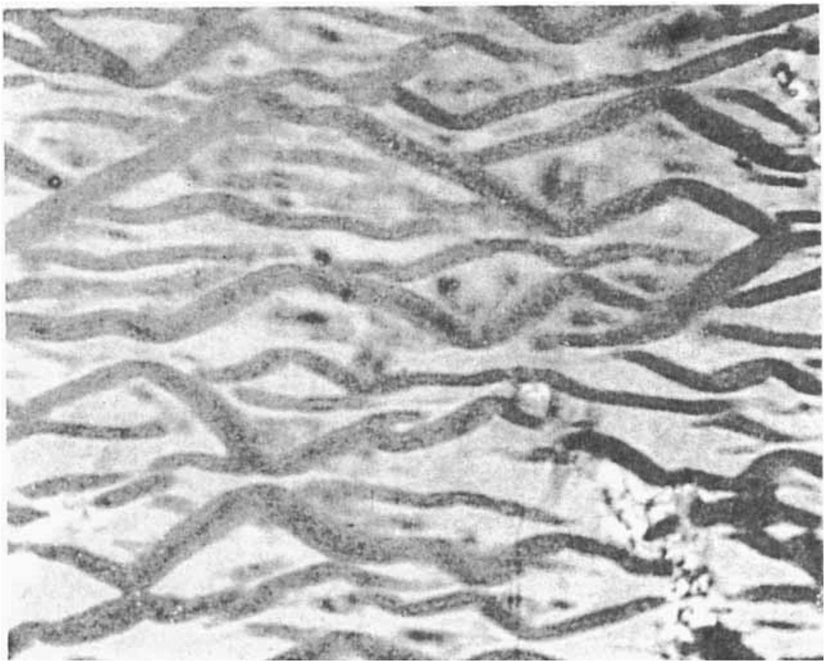

FIGURE 13 Pattern of undulating domains observed in the sample of Figure 12, but at 14.8 V and 5 kHz.

instability pattern, occurring over a wide frequency range in very thin samples of PAA, has not been previously reported.

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