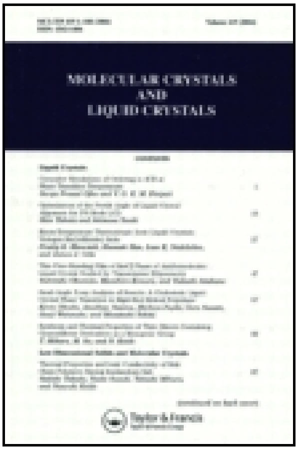

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Electrohydrodynamic Instabilities in a Nematic Aromatic Polyester in Solution and in the Melt

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Electrohydrodynamic Instabilities in a Nematic Aromatic Polyester in Solution and in the Melt

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Electrohydrodynamic instabilities have been studied in an aromatic polyester. Several modes are observed as a function of several parameters such as the frequency of the applied field and the type of surface anchorage. Although similarities to the behaviour of small molecule liquid crystals were found, there are new effects associated with the high viscosity of polymeric samples. The influences of the molecular weight and of the concentration in the polymer liquid crystal/conventional liquid crystal solution are discussed.

Les instabilités électrohydrodynamiques obtenues dans un polyester aromatique sont étudiées. Différents modes sont mis en évidence lors d'une étude en fonction de divers paramètres tels la fréquence du champ appliqué ou la configuration d'ancrage. De nombreuses analogies avec les cristaux liquides de petites molécules sont relevées ainsi que des différences liées à la viscosité élevée, aux modifications des constantes élastiques ou de l'anisotropie de conductivité avec la température ou la masse moléculaire de nos échantillons.

INTRODUCTION

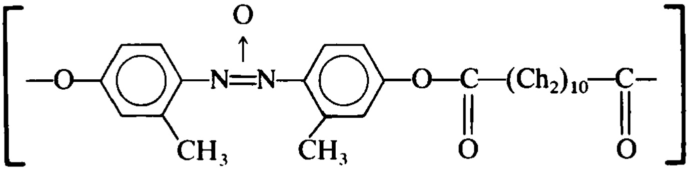
Studies of the behaviour of small molecule liquid crystalline materials (such as MBBA or PAA) in an electric field have demonstrated the existence of two main types of textures for sufficiently thick samples. Above a threshold voltage, V_s, and at low frequencies, typical Williams domains occur. These are characterized by a periodic deformation of the director and a convective motion of ionic impurities. At higher frequencies, the ions can not move fast enough for this effect to occur and a different type of regime appears in which there is a periodic oscillation of the local nematic director. In addition to these two main types of texture, a large variety of others can be observed such as broad domains and bidimensional patterns.

Recent work has shown that in systems containing semi-flexible polymeric chains with mesomorphic character, electrohydrodynamic instabilities also occur.[1]

The present work concerns the recently synthesized aromatic polyester DDA-9. We have explored analogies with small molecule liquid crystals systems and investigated the effect of the degree of polymerization. Solutions of DDA-9 in a similar liquid crystalline host were also studied.

EXPERIMENTAL

Fractionated samples of an aromatic polyester, DDA-9 (2, 3, 4)† were used with molecular weights M_n = 2300, 2500, 3400, 6300, and 20000. The monomer of DDA-9 is



The commercial samples of PAA were obtained from Eastman. The critical temperature was above 135°C and the samples were used without further purification.

The MBBA sample was synthesized at the laboratories of "Physique des Solides" of Orsay.‡

The textures and transition temperature were studied with a polarizing microscope equipped with a hot stage. The critical transition temperatures for the anisotropic → isotropic phase transition, in the case of the small molecule liquid crystals (SMLC) and for the appearance of the biphasic zones in the polymer liquid crystal were measured at a heating rate of 2°/min.

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†The DDA-9 samples were furnished by Prof. Blumstein (Dept. of Chemistry of Lowell, Mass. 01854) whom we wish to thank.

‡We thank Dr. Pieranski, Orsay for furnishing the sample of MBBA.

The electric fields were applied to the samples by use of transparent S_nO_2 coated glass plates. The sample thickness ranged from 5 to 50 μm and were calibrated by Mylar spacers.

The surfaces were treated using the method of Chatelain[7] for planar anchorage and by deposition of cetyltrimethylammonium bromide[8] dissolved in warm toluene for homeotropic anchorage.

The cells were filled, either by deposition, melting and squeezing the isotropic phase between the glass plates, or by capillarity.

The sinusoidal fields were obtained with a Hewlett Packard 203 A generator and a d.c. amplifier. The voltages quoted are peak to peak values.

RESULTS

I. Textures in a Sinusoidal Field, Low Frequency

I.1. Williams Domains (planar anchorage)

The textures described by Williams[9] arising from a periodic deformation of the director and a convective motion of the ionic impurities (followed by the dust movement) were clearly observed in the polymer samples with a molecular weight between 2300 and 6300.[4,5,6] They were also found for all solutions of the polymer with these molecular weights in a SMLC of similar chemical structure, namely PAA ($\Delta\epsilon < 0$, $\Delta\sigma > 0$) and for a solution of 20% (by weight) DDA-9 of high molecular weight (20000) in PAA.

I.1.a.) Threshold potential for Williams domains

An expression of the threshold potential, V_s for the Williams domains has been calculated as:[10,11]

$$V_S^2 = \frac{V_a^2\,(1 + \omega^2\zeta^2)}{\xi^2 - (1 + \omega^2\zeta^2)} \tag{1}$$

ω is the frequency of the applied field, ζ the ionic relaxation time:

$$\zeta^{-1} = 4\pi\left[\frac{\sigma_\parallel}{\epsilon_\parallel} + \frac{\sigma_\perp}{\epsilon_\perp}\right] \tag{2}$$

$\epsilon_{\parallel,\perp}$ and $\sigma_{\parallel,\perp}$ are the dielectric constants and conductivities parallel and perpendicular to the molecular axis. ξ is the Helfrich parameter V_a is the Helfrich potential discussed in more detail in the next paragraph.

The cut-off frequency fc is defined using the symbols in formula (1) as:

$$fc = \frac{(\xi^2 - 1)}{2\pi\zeta} \tag{3}$$

In Figure (1), $Ln\, fc$ is plotted against $1/T$. The activation energy of the ions ΔE is obtained from the slope of this plot. In effect fc is dominated by ζ and therefore by $\sigma_{\parallel}$,[12,13,14] and thus

$$\sigma_{\parallel} = \frac{A}{T} \exp\left(\frac{-\Delta E}{\kappa T}\right) \tag{4}$$

Effect of degree of polymerization

The variation of the threshold frequency with molecular weight can be related to two main factors: the first being the Helfrich voltage;

$$V_a^2 = -\left(\frac{16\pi^3 \epsilon_{\parallel}}{\epsilon_a \epsilon_{\parallel}}\right) \cdot \left(\frac{2\eta_2}{\gamma_1 + 2\eta_2}\right) \cdot K_{33} \tag{5}$$

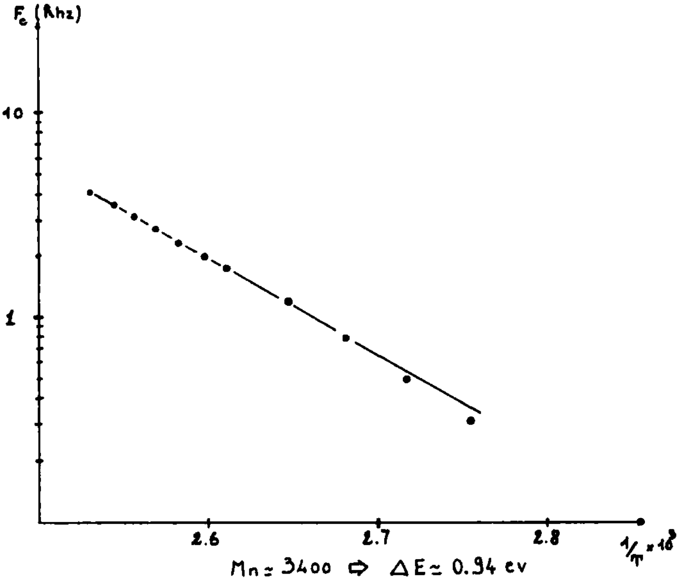


FIGURE 1 Variation of the cutoff frequency $Ln(f_c)$ as a function of the inverse temperature for the pure polymer (M_n = 3400).

TABLE I

Threshold potential for the appearance of the Williams domains far from the cutoff frequency f_c for DDA-9 samples of different molecular weights and two reduced temperatures *T*/*TC* (Kelvin).

M_n / T	2300	2500	3400	6300	50% 3400 in PAA (g/g)
$0.95T_c$	10V	13V	22V	27V	
$0.98T_c$	9V	12V	18V	28V	10V

(where K_{33} is the bend elastic constant, η_2, γ_1 are viscosity coefficents, ϵ_d is anisotropic dielectric constant) appears to increase slowly with degree of polymerization (DP). This is possibly due to an increase of K_{33} with DP which has also been observed in the magnetic Freedericksz transition.[15] This effect on the threshold voltage can be seen at low frequency $\omega < fc$, as indicated in Table I and Figure 2, 3, for the DDA-9 samples of molecular weight ranging from that of the monomer (PAA) to 6300.

The second factor arises from the cut-off frequency, *fc*. If the number of conducting ions does not change appreciably in the samples of different molecular weights, then a variation in the activation energy ΔE (Table II, Figure 1) would be sufficient to explain the decrease in cut-off frequency as the DP of the polymer is increased

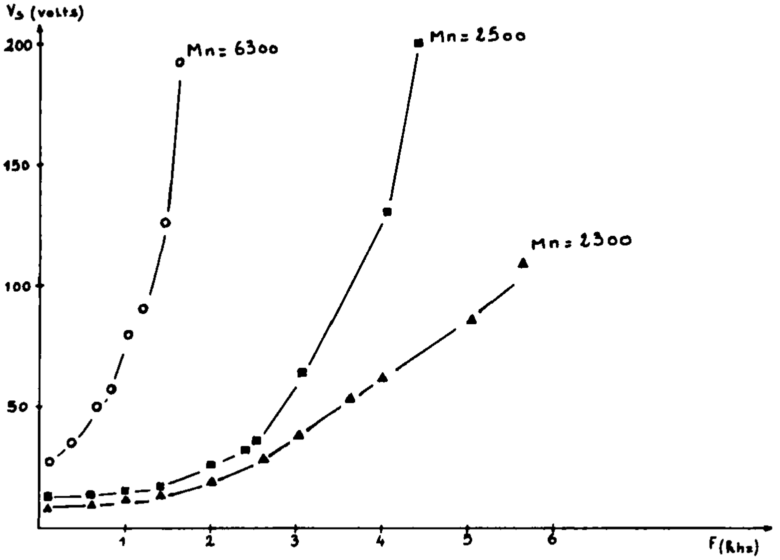


FIGURE 2 Variation of the Williams domain threshold as a function of frequency for a temperature T = 0,98 Tc and three different degrees of polymerization.

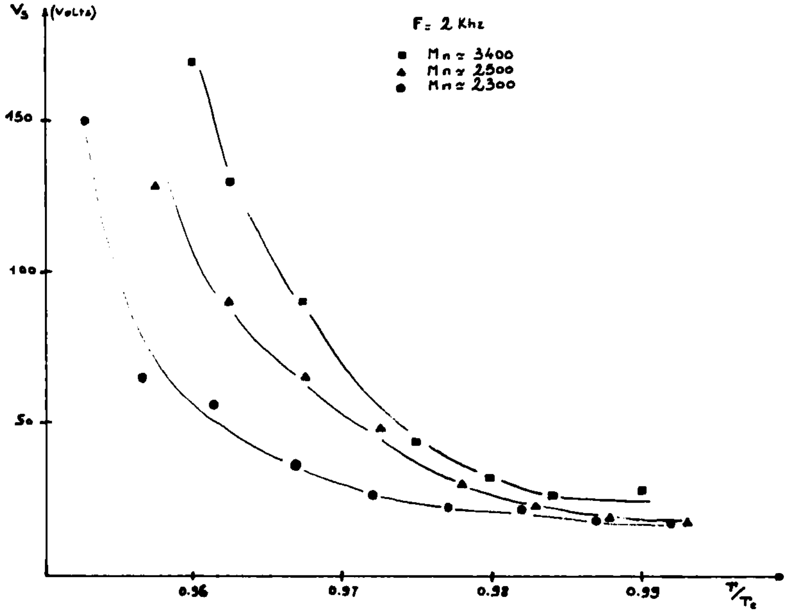


FIGURE 3 Variation of the Williams domain threshold as a function of reduced temperature for three sample of different molecular weight. The frequency is 2000 Hz.

(Figure 2). The apparent decrease of ΔE for $Mn = 6300$ could be due to imprecision in the value of V_s caused by the high viscosity of this sample. Another contribution is the different average temperature used for the measurement of ΔE compared with the other samples.

Effect of the polymer concentration

The increase in V_a and decrease in f_c can also be obtained by increasing the polymer concentration in a PAA solution. Again, an increase in K_{33} and in ΔE would be expected.

TABLE II

Activation energies calculated from the slope of the plot of $Ln(f_c)$ against $1/T$. T_c is the temperature at which biphasic separation occurs and T_{av} the average temperature used for the measurement.

Mn	PAA	2300	2500	3400	6300
$\Delta E_{(ev)}$	0.6	0.73	0.89	0.93	0.74
$T_{av.}^{(°C)}$	115°	107°	109°	115°	132°
$T_c^{(°C)}$	135°	119°	120.7°	128°	148°

I.2. Homeotropic anchorage

I.2.a. Pure polymer Mn = 4000

In zero field, zones anchored perpendicular to the surface appear black under the polarizing microscope. A Freedericksz transition is observed around 10 V (Figure 4), over the entire frequency range. The tilting of the director leads to Newton colors for white light corresponding to a progressive increase in birefringence.[16,17] On further increasing the potential at frequencies $\omega < fc$, a WD-type instability appears. A large part of the sample is now oriented parallel to the surface (Figure 4). The threshold for the WD is somewhat higher than in the planar case and the direction of the convective roll less regular because of the presence of numerous domains of different orientations. At higher frequencies the "broad domain" instability observed, occurs once the director is tilted parallel to the surface. This instability occurs chiefly with samples with a planar anchorage.

I.2.b. Polymer in liquid crystal solution

Different behaviour is observed for solutions consisting of the polymer with a M_n of less than 20,000 and a SMLC. Below 20% (by weight) a "grid pattern" type instability appears prior to the Freedericksz transition on increasing the electric field and in a frequency range comparable to that of the planar WD.

It is possible that this two dimensional pattern corresponds to a splay type instability[11] for which anchorage symmetry no longer allows the monodimensional form of the planar case to occur.[18] The threshold potential V_s^2 for the homeotropic electrohydrodynamic instability is dependent on K_{11} as well as on the ratio $\sigma_{\|}/\sigma_{\perp}$, whereas the Freedericksz transition depends only on K_{33} with this geometry. The relative magnitude of these quantities determines which of the instabilities will occur first (Figure 4) at a given molecular weight or for a given solution.

The temperature is also important. The homeotropic conductive instability is often only observed near the critical aniso-iso temperature, possibly due to the rapid variation of the cutoff frequency for this mode, or of rapid increase of α_3/α_2near Tc.

The bidimensional texture is stabilized with $Mn = 20000$ polymer solutions and an increase in electric field modifies the aspect (Ph1).

I.3. Isotropic instabilities

At low frequencies and in d.c. fields, a "convective torus" instability occurs with homeotropic anchorage. This instability does not vanish at the isotropic transition and was observed in all the cases

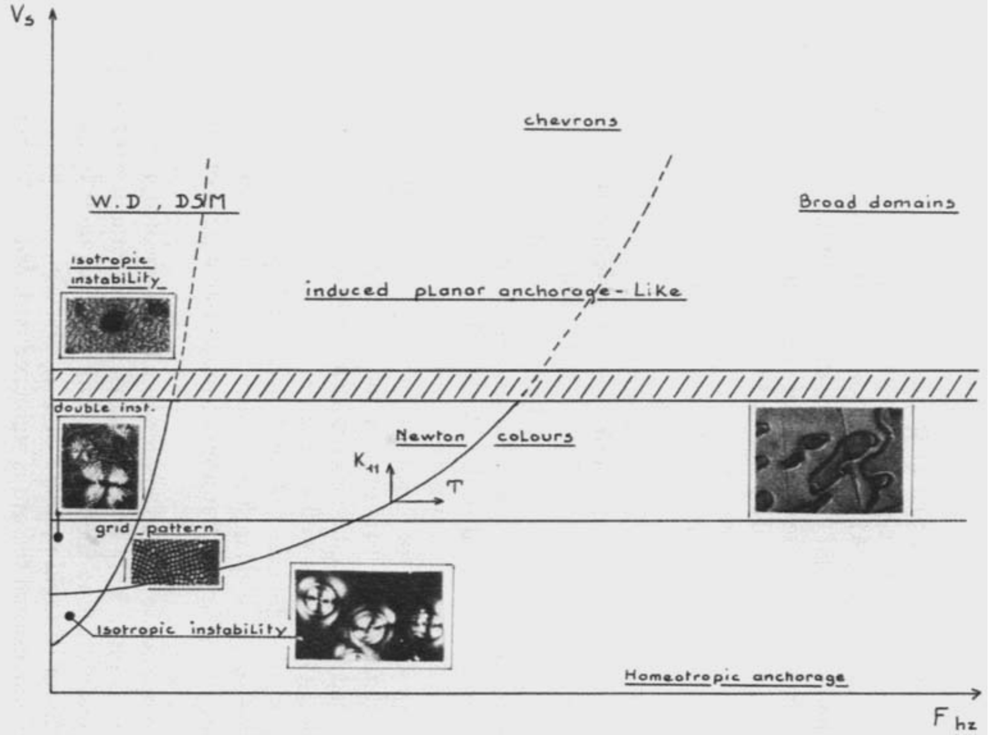


FIGURE 4 Variation of the threshold potential as a function of the frequency of the applied field for the different types of electrohydrodynamic instabilities and for the Freedericksz transition in homeotropic anchorage.

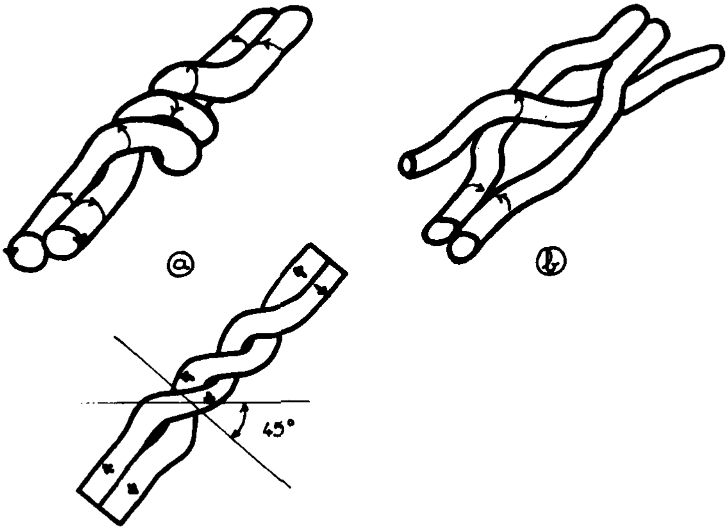


FIGURE 5 Defects obtained in the photo ph2E. The rolls of the Williams domain structure become thinner and entangle, DDA-9, Mn = 3900, 0.1 Hz 20 V, 120°C, (d = 12 μm).

studied. For 20% (by weight) DDA-9 of M_n = 20000 in PAA, this mode appears at around 1 volt, the threshold increasing rapidly with frequency (Ph. 1). In the range 1 Hz–100 Hz, a coupling to the homeotropic instability occurs (Ph 1). Beyond 100 Hz the threshold for the grid pattern instability is lower than that of the convective one but the latter can still be observed at high electric fields above 100 V. In pure DDA-9 of M_n = 20000 a well-defined anchorage could not be obtained and the convective instability was the only one observed.

I.4. Evolution toward turbulence

Above the threshold of the WD, an increase in the applied field causes a transition to turbulent behaviour (DSM). The high viscosity of the DDA-9 samples slows down the kinetics and allows for detailed observation of the various steps. After the WD, a two dimensional pattern first appears (Ph2)[18] in the convective rolls due to a spatial modulation which finally forms a regular square grid consisting of mini-rolls. At low frequencies various other patterns are observed. For example, the Williams convective rolls oscillate in time and space and can become tilted at 45° angles, due to characteristic defects (Figure 5, ph. 2).

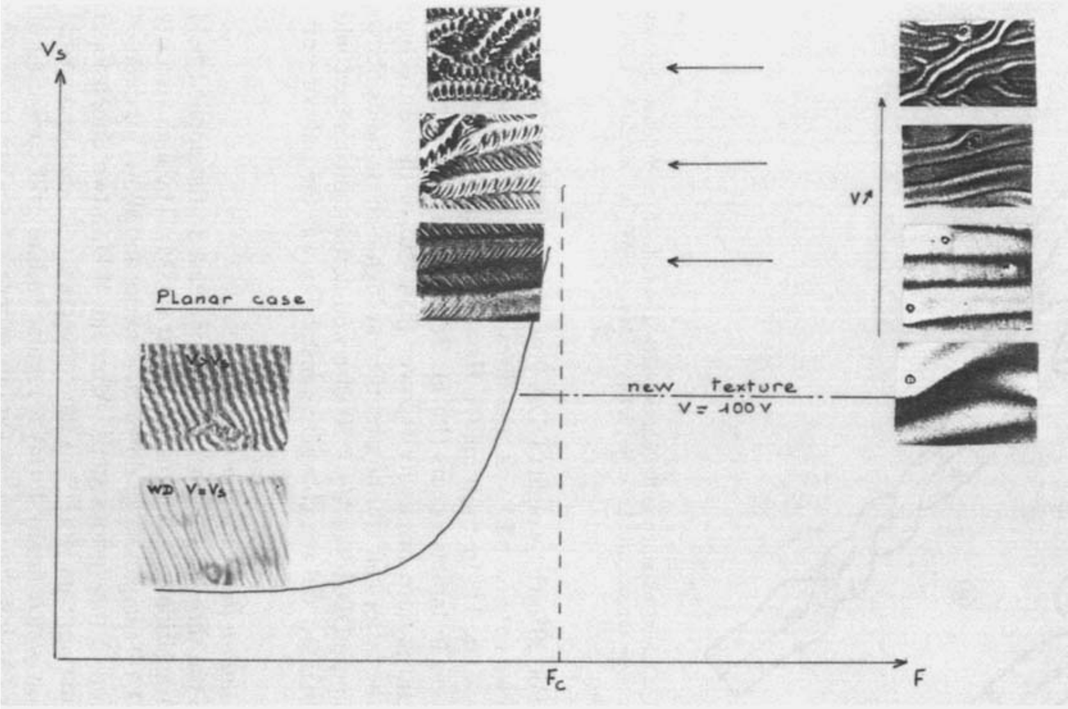
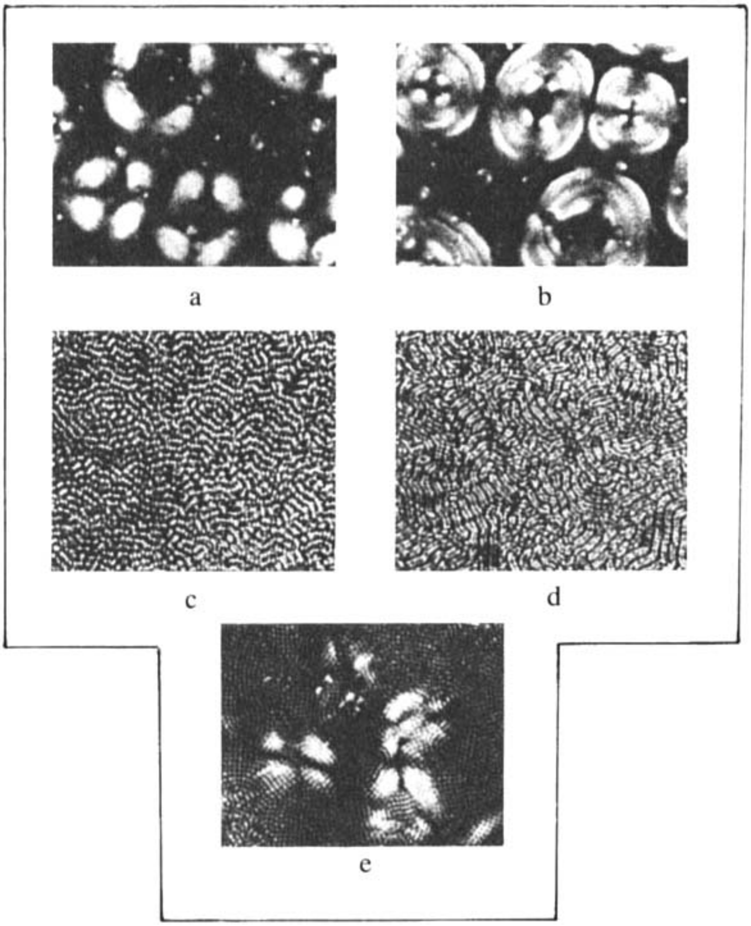


FIGURE 6 Variation of the Williams domain and broad domain threshold in planar anchorage as a function of frequency. The pictures of these instabilities show the reduction of the periodicity of the broad domains with an increase in potential, and the appearance of chevrons in the vicinity of the cutoff frequency of the Williams domains. Samples: 10% of DDA-9 M_n = 3400 in PAA (d = 24 μm).



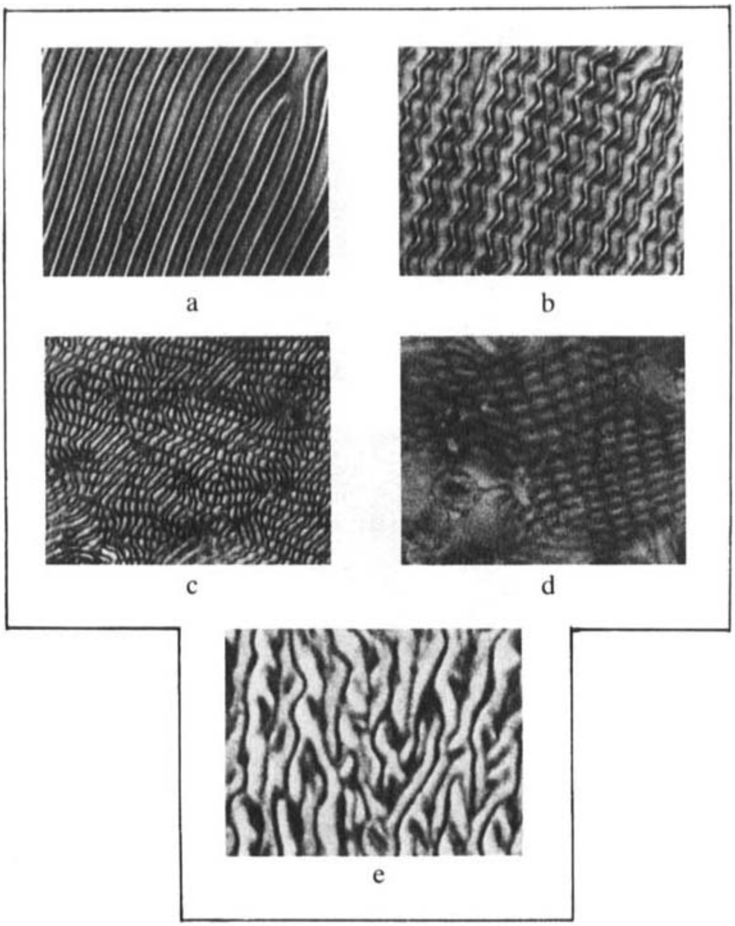
Ph 1
Sample 20% DDA 9 20000 (g/g) in PAA, thickness d = 23 μm Temperature T = 130°C homeotropic anchorage.

A 0,1 Hz 2V
B 0,1 Hz 2,2V
C 1 KHZ 38V
D 1 KHz 50V
E 50 Hz 30 V

II. High Frequency Instabilities

II.1. Dielectric mode

In a planar geometry, near and above the cutoff frequency, *fc*, the ionic charge carriers cannot relax and an oscillation of the director occurs.[11] At the threshold for this type of (dielectric) instability a typical structure consists of fine, weakly contrasted lines. It has been observed in numerous SMLC with $\Delta\epsilon < 0$, $\Delta\sigma > 0$. The focalizing effect[20] is much weaker than in the WD. On increasing the electric field, a chevron texture appears which results from the possible coupling of the focalizing effect with the conductive mode.[21] This causes an increase in the contrast and in the periodicity of the pattern. One



Ph 2

Sample 50% DDA 9 3400 (g/g) in PAA d = 12 μm T = 120°C planar

A : 10 Hz 15 V
B : 10 Hz 25 V
C : DDA 9 2300 , T = 115°C, d = 12 μm, 1200 Hz, 57 V
D DDA 9 2300 , T = 101°C, d = 12 μm, 60 Hz, 24 V
E DDA 9 3900 , T = 120°C, d = 12 μm, 0,1 Hz, 20 V

of the aspects of the observed texture consists of long moving snake-like lines,[22] with chevron stripes (Ph. 3). The periodicity of these lines and of the stripes is larger than the oscillation of the director, in the pure dielectric mode which is given by the wave vector K:

$$K_{33}\, K^2 = 2\omega\eta' \, [(\xi^2 - 2)/\xi^2] \tag{6}$$

with $\eta' = \gamma_1 + (\alpha_2/2\eta_2) \cdot (\gamma_1 - \gamma_2)$, a viscosity coefficent. The typical variation of the period with $\sqrt{\omega}$ which is found is that also found for the critical field.[11]

The dielectric mode could not be observed for the pure polymer or for concentrated polymer solutions. A possible explanation is that the wave vector is dependent on $\sqrt{\eta'}$ as shown in (6). A large increase of a factor of a 100 in the rotational viscosity, γ_1^*, has indeed been observed (for a 20% g/g solution of low molecular weight DDA-9 in PAA) by relaxation of the magnetic Freedericksz transition.[15] The reduction of the expected periodicity would already explain the non-observance of the texture at the enlargement used. In comparison, the low viscosity of PAA compared to that of MBBA, makes it possible to observe the same spatial periodicity in the former at a much higher frequency. This hypothesis could be verified by reducing the cutoff frequency by purification of the PAA-DDA-9 sample.

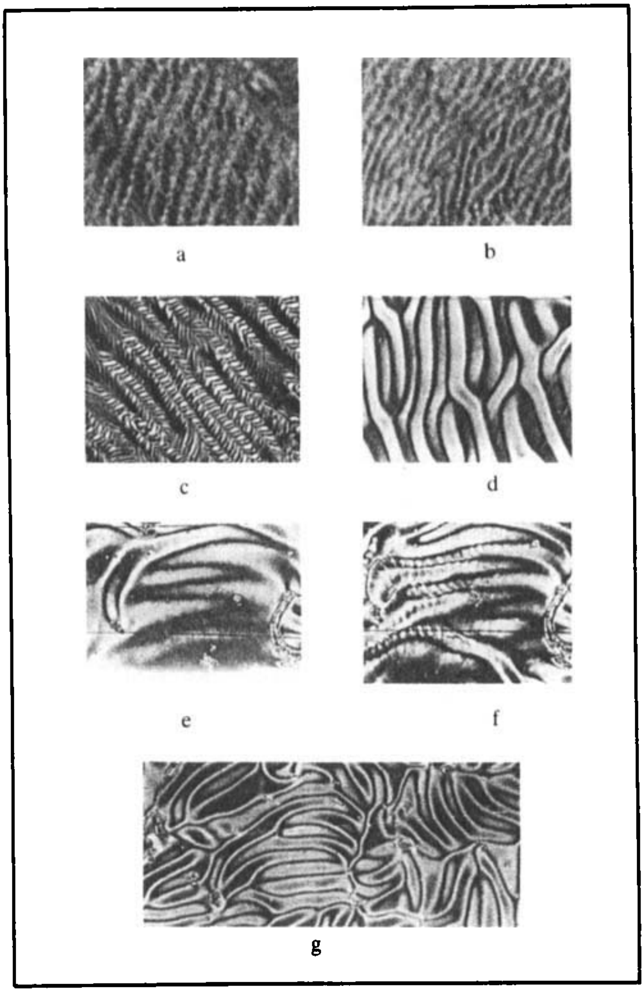
Chevron-type textures were observed in the case of a pure polymer for molecular weight < 4000 and for solutions in PAA. A coupling between three different modes: WD, dielectric and broad domains could be the cause.[18,23] (Ph 3–4, Figure 6).

II.2. High frequency mode: Broad domains

1) For a threshold voltage varying from sample to sample between 50 and 150 V, we have observed a new instability for frequencies > *fc* of the WD. Similar textures were already observed in SMLC[18,23] and were named "broad domains." A certain number of observations made in SMLC were also found for the polymeric LC.

2) The threshold potential does not show a strong dependence with the frequency or with the sample thickness (Figure 6).

3) The instability disappears at the isotropic phase transition. The periodicity of the texture at the threshold depends linearily on the sample thickness (Ph 4 B and G). When the voltage is increased, a rapid decrease in the periodicity is observed following a law of ~ 1/V. The initial periodicities at the threshold appears to be quite large and it is possible that the actual threshold occurs at a lower value and at a periodicity too large to be observed under the microscope.



Ph 3

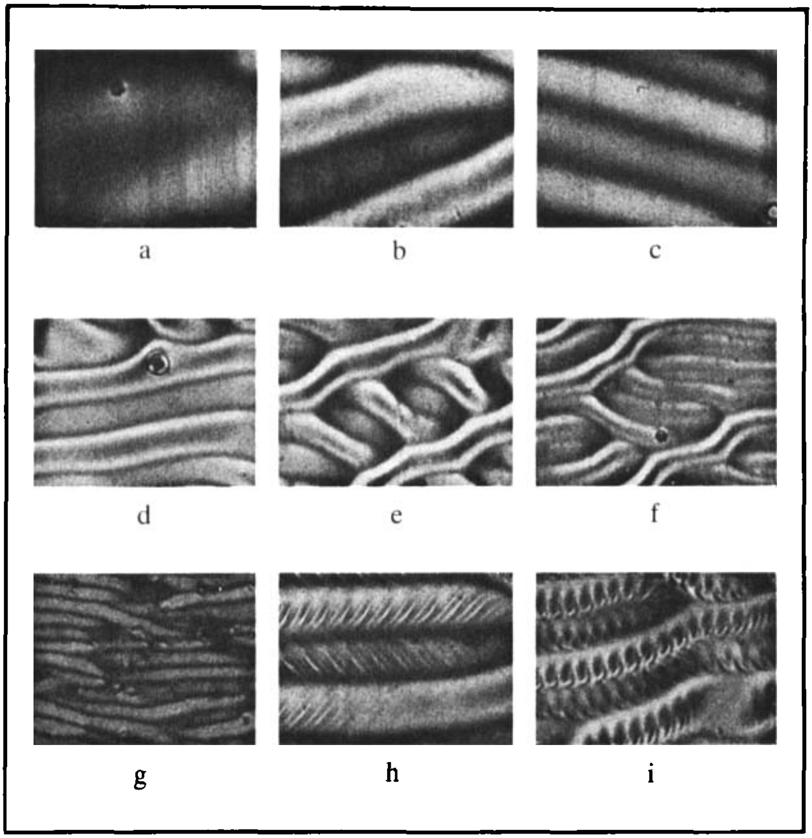
A, B : chevron and broad domain texture in MBBA T = 22°C, d = 12 μm 370 Hz, 220 V.

C : Chevron texture in DDA - 9 Mn = 2500
T = 130°C, d = 12 μm, 3000 Hz, 66 V

D : broad domains in DDA-9 3400
T = 100°C, d = 12 μm, 4000 Hz, 250 V

E, F DDA-9 Mn 2500 , T = 115°C, d = 12 μm
4000 Hz E: 120 V broad domain texture
F: 130 V chevrons

G:DDA 9 2300, d = 12 μm, 3200 Hz, 152 V



Ph 4

10% g/g DDA 9 3400 in PAA
T = 115°C, d = 24 μm (except G d = 6 μm)
100 KHz

The largest periodic structures we have observed were of the order of 200 μm (ph 4 A).

On increasing the voltage the period is reduced and a change of texture occurs (ph 4 E and F). At very high voltage, initially parallel domains become oriented at 45°C angles and a pattern of entangled lines takes over.

Flow is easily observed due to the presence of dust particles in the low viscosity PAA solutions. The particles follow the lines defined by the texture, parallel to the surface and the velocity increases with increasing voltage.

If the frequency is reduced, near to the vicinity of the *fc* of the WD, stripes at 45° angles in the form of chevrons and probably consisting of mini-WD appear inside the lines (Figure 6, Ph 4 H and I). This would seem to demonstrate a spatial oscillation of the director parallel to the sample surface. The flow of matter can also be observed in this case. A constant displacement of neighbouring stripes in opposite directions can be associated with the tilt of the chevrons in the observed line.

CONCLUSIONS

We have presented the analogies between low molecular weight polymer nematics and comparable small molecule liquid crystals with $\Delta\epsilon \leqslant 0$, $\Delta\sigma > 0$. Similar electrohydrodynamic instabilities are observed in the various modes for both high and low frequencies of the applied field: comparable textures, threshold voltages and an evolution to the dynamic scattering mode occur in both cases. On the other hand, new polymeric effects have also been demonstrated. The increase in times for the appearance of certain textures and for the transition to turbulence, makes a detailed study of these phenomena possible. The role of the degree of polymerization has also been mentioned. Ideas on the modification of the viscosity coefficients, the conductivity and the Franck elastic coefficients with chain length have been formulated. These ideas deserve further investigation, and measurements, which are presently in progress.

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