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TEXTURES AND INSTABILITIES IN LIQUID CRYSTALS AND MESOMORPHIC POLYMERS

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Abstract : An aromatic polyester of monomeric units similar to PAA separated by flexible spacers show electrohydrodynamic instabilities in external electric field. As in the case of small molecule liquid crystals, conductive and dielectric modes are observed using polarizing microscopy. Slow kinetics due to the higher viscosity allow the observation of the evolution to turbulence. A new periodic texture in the dielectric domain with a frequency dependent periodicity is also observed in polymeric samples.The Freedericksz transition in the case of homeotropic anchorage is discussed.

INTRODUCTION

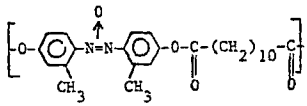
Electrohydrodynamic instabilities can occur in small molecule liquid crystals in a.c. electric fields(1). Due to the large number of experimental and theoretical (2, 3, 4) studies in the last ten years, the time and spatial dependence of the first non-equilibrium state has been clarified. At low frequencies, the conduction mode appears at a threshold potential, accompanied by a periodic deformation of the director on direction of preferred orientation. A characteristic texture is observed of parallel lines of spacing of the order of the sample thickness (Williams domains) caused by convective motion of ionized impurities. At higher frequencies, a finer texture (chevrons) takes over. In this dielectric mode, no charge oscillations but time and space oscillations of the director describe the first instable mode.

Recently, it has been shown that electrohydrodynamic instabilities also occur in polymers which possess liquid crystalline phases (5,6,7). The present work has been realised with different molecular weights of a recently synthesized aromatic polyester (DDA-9) ranging from the oliogomers up to a

molecular weight of 20000. This allows a systematic comparison with small molecule liquid crystal behaviour. The problems encountered on anchoring of the director at the surfaces of the cell are examined. The numerous textures which arise on variation of the frequency or amplitude of the potential or the sample thickness are analyzed.

EXPERIMENTAL

The aromatic polyester DDA-9 was synthesized in the laboratory of Professor Blumstein and is given by the formula (8, 9,10).



The fractionated samples have a polydispersity $\leqslant 2$ and molecular weights in the range M_n = 2300 - 6300 , as well as M_n = 20000.

The critical temperatures for the anisotropic-isotropic phase transition were obtained by polarizing microscopy, upon heating at 2°C/min. In the polymeric samples, the temperature for appearance of a biphasic isotropic-anisotropic phase is determined. The electric field was applied to the cell through S_nO_2 coated glass plates, obtained from OCLI, England. Exclusively peak to peak potential values are given throughout the present paper except when otherwise indicated. The sample thickness was calibrated by mylar spacers (furnished by MICEL Cachan France). As a reference system, two monomeric liquid crystals were used. PAA was chosen for the chemical structure similar to the monomer of DDA-9. The extensively studied MBBA has a room temperature transition easily studied without need of a hot stage.

I. ANCHORAGE

The classical methods used to obtain uniform sample orientation by anchorage at the surfaces were used : rubbing by the method of Chatelain (11) or deposit of HTAB on the surface (12). A noticable effect on the textures in zero field and on the values of threshold potential was observed, but the stability of the anchorage in time on heating to the critical temperature or on application of high potentials was uncertain. Because of the SnO_2 conductive layer oblique evaporation of SiO_2 could introduce inhomogenous fields in the cells and was not attempted. The same methods were used in the polymeric and comparative MBBA and PAA studies.

In all cases, zones of different anchorage were observed. This often permitted simultanous study of instabilities in planar and homeotropic configurations (P1 c-d). Planar zones appeared on treatment with HTAB, shearing, high potential and high temperatures. In untreated samples or after rubbing by the method of Chatelain, shearing induced planar anchorage with numerous dislocation lines. Spontanous relaxation dependent on temperature to homeotropic anchorage occured. This was confirmed also in MBBA by conoscopy and has been reported previously in PAA (11). In the black homotropic zones, the characteristic dc current instability (12) was found in MBBA and in DDA-9 (M_n=2300) at 16V and 50V respectively (P1 a-b). The homeotropic zones are stable on passing to the isotropic phase and cooling. Partial inversion occured only on strong shearing or on application of high ac potentials of the order of 100 V.

II. TEXTURES IN SINUSOIDAL FIELDS AND PLANAR ORIENTATION

II.1. Williams Domains (WD)

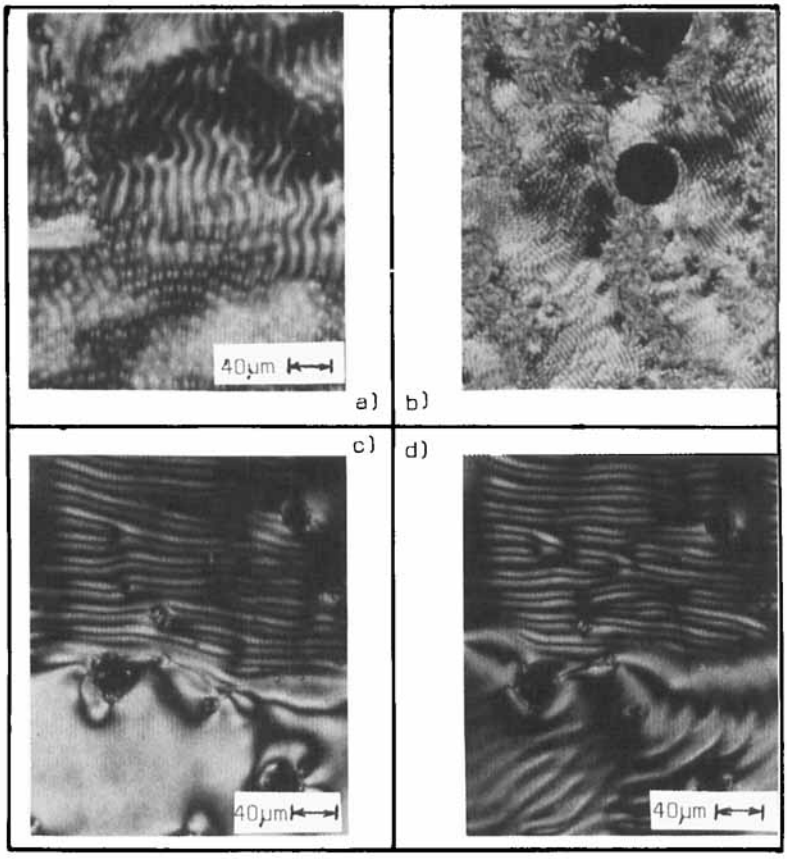
As in small molecule liquid crystals at low frequencies, in the low molecular weight samples a WD - type texture is observed. For the molecular weights studies (2300, 2500, 3400, 6300) the threshold potential varied between a few volts to tens of volts.

For a given molecular weight, the threshold potential increases slowly with the frequency of the applied field until the vicinity of the cutoff frequency F_c. Appearance times (fig.1) are of the order of minutes as in other nematic polymers (5,6,7).

II.2. Effect of sample thickness

WD are characterized by the invariance of the spatial periodicity determined by the sample width (photos P 2b and 2c) correspond to samples of different molecular weight but constant thickness d = 12μm. Both present the same periodicity of around 20 μm corresponding to the association of two convective rolls of different sense of rotation. The WD in PAA at equal thickness are comparable as seen in P2a. In P3b, the same Mn as in P3a is shown for a thickness of 4μm, clearly demonstrating the corresponding decrease in periodicity.

The dark areas in P3b are homeotropic zones, not to be confused with round dark air bubbles also present. The different aspects of the WD in the preceeding photos arise from different focalization of the microscope (P2b and P3a).



P1. a) Instability at d.c. voltage 16 V in MBBA, homéotropic orientation, sample thickness 12 µm, T = 22°C. b) Instability in "black zones" in DDA-9, M_n = 3900, seconds after application of d.c. voltage 50 V, sample thickness e = 5 µm , T = 120°C. c) Comparison of instabilities obtained in planar (upper) and homeotropic (lower) orientation in DDA-9 sample of M_n = 2300, 3 minutes after application of a sinusoidal potential (3000 Hz, 22 V), e = 12 µm , T = 113°C. d) Same as in c) at 35V, 5000 Hz (See Color Plate I)

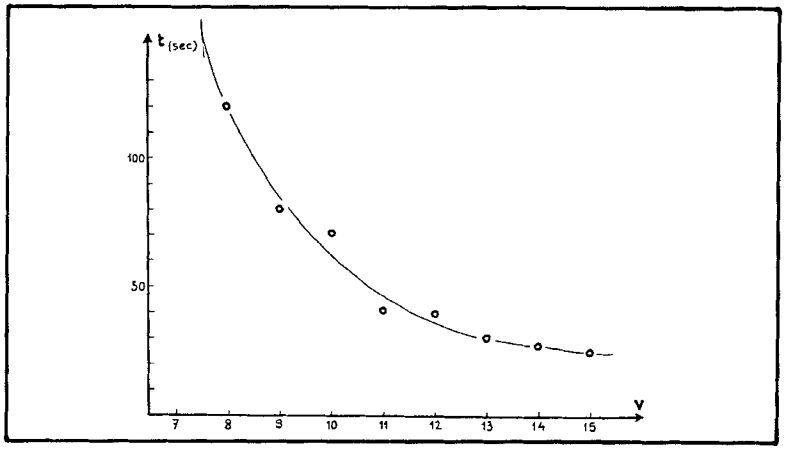


FIGURE 1. Formation times for Williams domains as function of applied voltage in DDA-9 sample. M_n = 2300, T = 113°C (0.95T_c) sample width e = 12 μm.

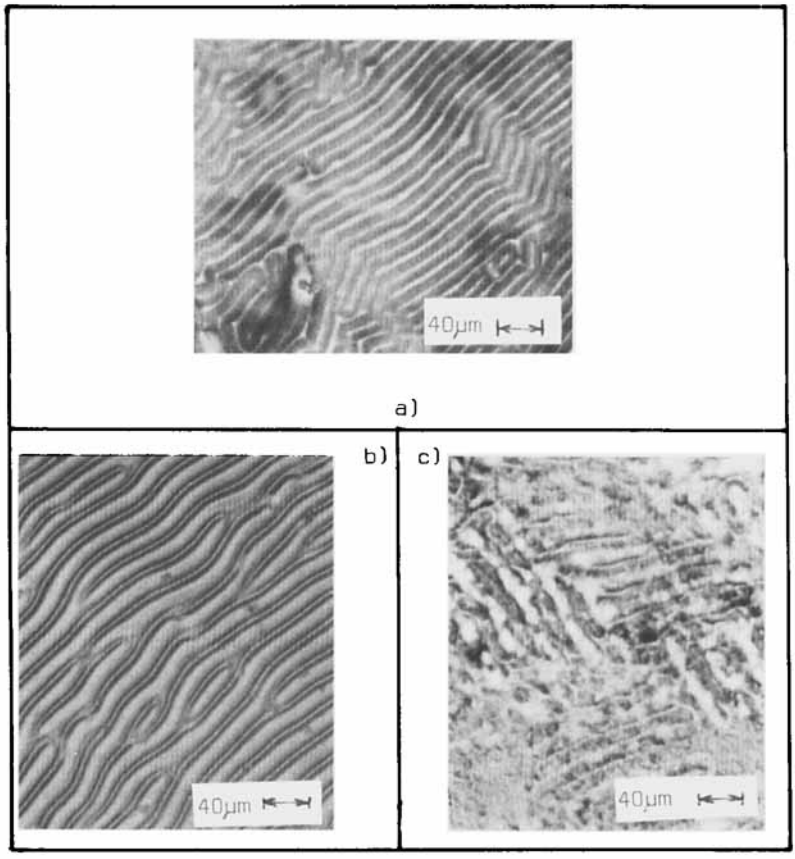
It has been shown that a virtual image can be observed below the sample (14, 15, 16, 17).

II.3. Anchorage

Rubbing by the method of Chatelain was used in the DDA-9 samples in the vertical direction. It is known that a uniform planar anchorage is more difficult to obtain in polymers with flexible chains and high viscosity. Furthermore, the numerous impurities and air bubbles present in DDA-9 perturb considerably the organization by reducing the effective surface (18). Finally, the slow appearance time of the WD textures causes imprecision in the threshold potential V_S and for $V > V_S$ a subsequent bidimensional non-equilibrium state occurs.

II.4. Transition to turbulence

Compared to small molecule liquid crystals (19) the relaxation to the higher bidimensional mode is slow. A spatial modulation of the convective rolls and an increase in the number of defects and ramifications (P4a) preceed the regular "stair case" structures seen in P4b.

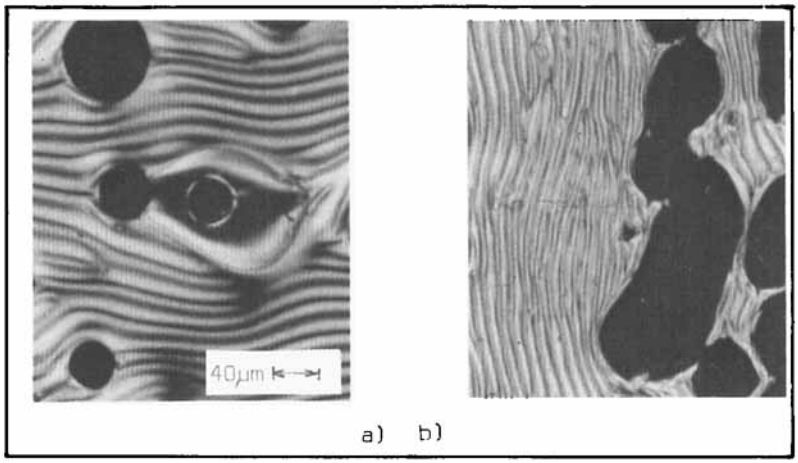


P2 : a) Williams domains in purified PAA (T_c = 132°C), 200 Hz, 20 V, 100°C, 12 µm. b) Williams domains in DOA-9. M_n = 3400, 2 minutes after application of potential, 60 Hz, 11 V, 121.6°C , 12 µm. c) Williams domains in DOA-9. M_n = 6300, 600 Hz, 55 V, 140°.6 C 12 µm. **(See Color Plate II)**

Further increase of the potential leads to the turbulent (Dynamic Scattering) Mode. (Fig. 2), accompanied by invasion by dislocation lines (20).

II.5. Dielectric mode

Photos P5 a and b give examples of the "chevron" mode in



P3 : a) Williams domains in DDA-9 . M_n = 3900, 5 min. after application of ac potential . 120Hz, 30 V, 120.5°C, 12 µm. b) as in a) for thinner sample. "Black zones" of homeotropic anchorage are visible.
(See Color Plate III)

MBBA in the dielectric domain (frequency 380 Hz). The finely spaced lines of the dielectric mode are barely visible but increasing the potential (21,22,13) sharpens the chevron structure and increases the periodicity possibly by coupling with other hydrodynamic instabilities (23,24)(fig.3) for example, the conduction mode. The observed texture consists then of long, often moving (snake-like) lines with striated chevrons, both periods being larger than in the pure dielectric mode. Similar effects occur in the DDA-9 samples near the cutoff frequency (P5c, d). The pure dielectric mode is not observed, probably due to a low contrast, extremely fine periodic structure in the high viscosity polymer sample.

II.6. High frequency, low potential mode

For frequencies above the cutoff, a new texture (25) was found (P6a and c). These textures were also observed in conventional liquid crystals (24). The threshold potential is less than 100 V and does not vary with applied frequency. The wide spacing of the texture is larger than the sample thickness and in the vicinity of the cutoff frequency, chevrons appear inside the dark lines. (P6b). The appearance

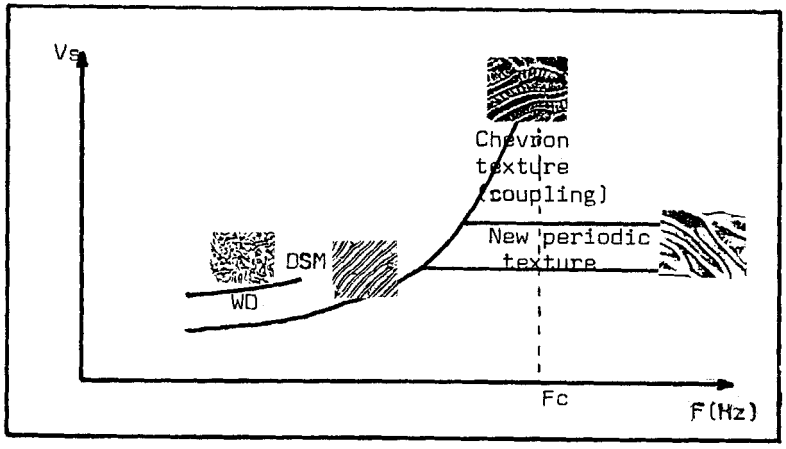


Fig. 2 : Threshold voltage for appearance of instabilities as function of frequency. The domains giving the appearance of broad domain texture as well as the organization in chevrons inside this texture are shown.

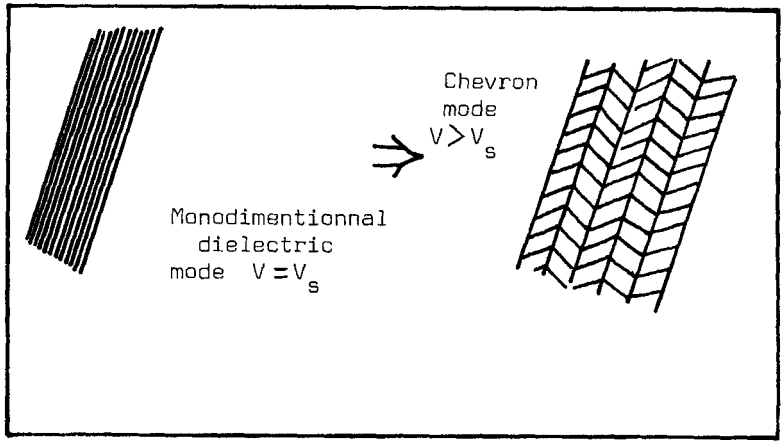
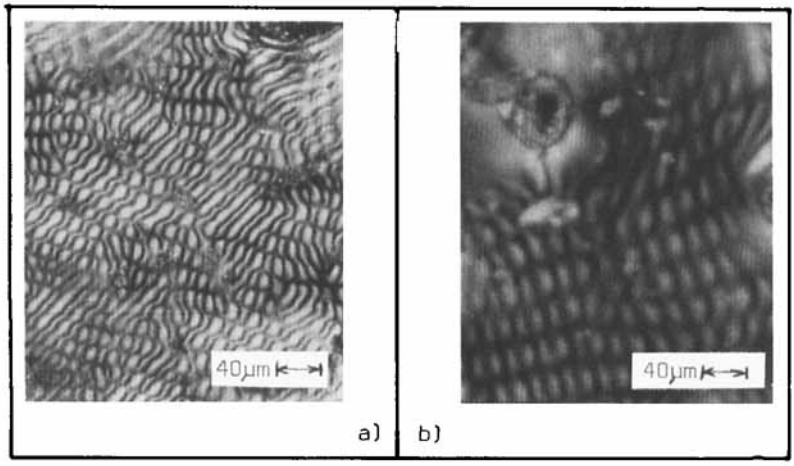


Fig. 3 : Evolution in MBBA illustrating chevron textures given in P5 a) and b).



P4 : a) Beginning of bidimensional organization in DDA-9 ($\overline{M_n}$ = 2500) 1200 Hz, 57 V, 12 µm, 144.7°C. b) Bidimensional organization in DDA-9 (M_n = 2300) 60 Hz, 24 V, 101.1°C, 12µm. (See Color Plate IV)

and relaxation times of this mode are long. This could be proof of convection in the vicinity of the glass surfaces.

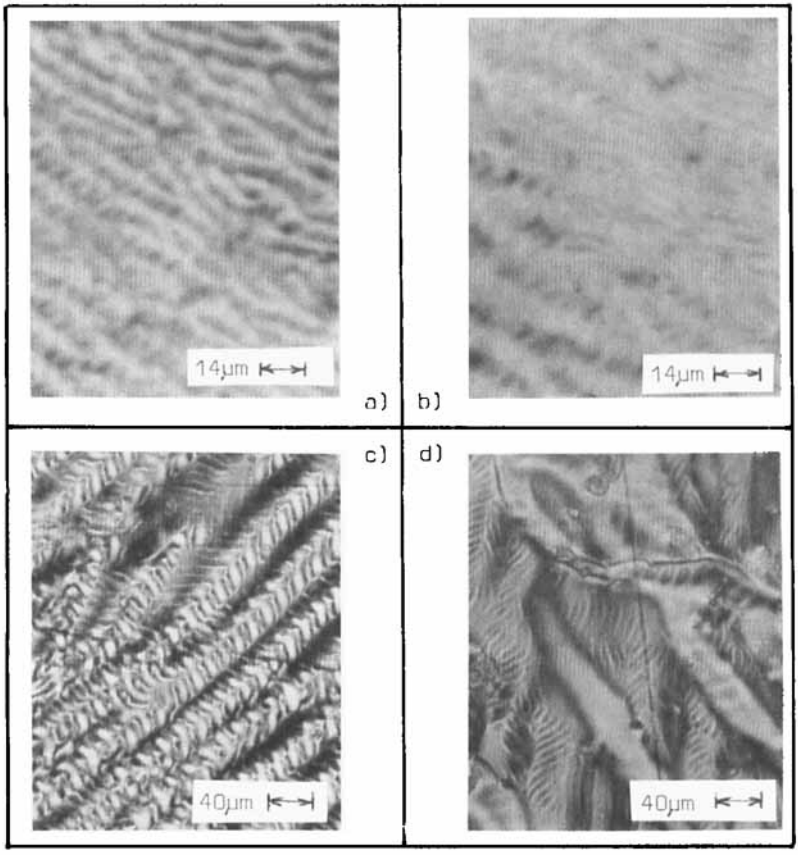
II.7. High molecular weights

For the sample of M_n =20000 no satisfactory anchorage could be achieved. The sample thickness was varied between 10 and 100 µm and the ac potential increased to 200 V. The formation of WD type instabilities could not be observed even after 24 h, as could be explained by the large viscosity of the sample (5,6). In a dc current "convective torus" instabilities were easily observed. The risk of sample degradation in these experimental conditions is high.

III. HOMEOTROPIC ORIENTATION

Low molecular weight samples (Mn = 4000) were also studied in the homeotropic configuration. In zero field the zones anchored perpendicular to the surface appeared black under the polarizing microscope.

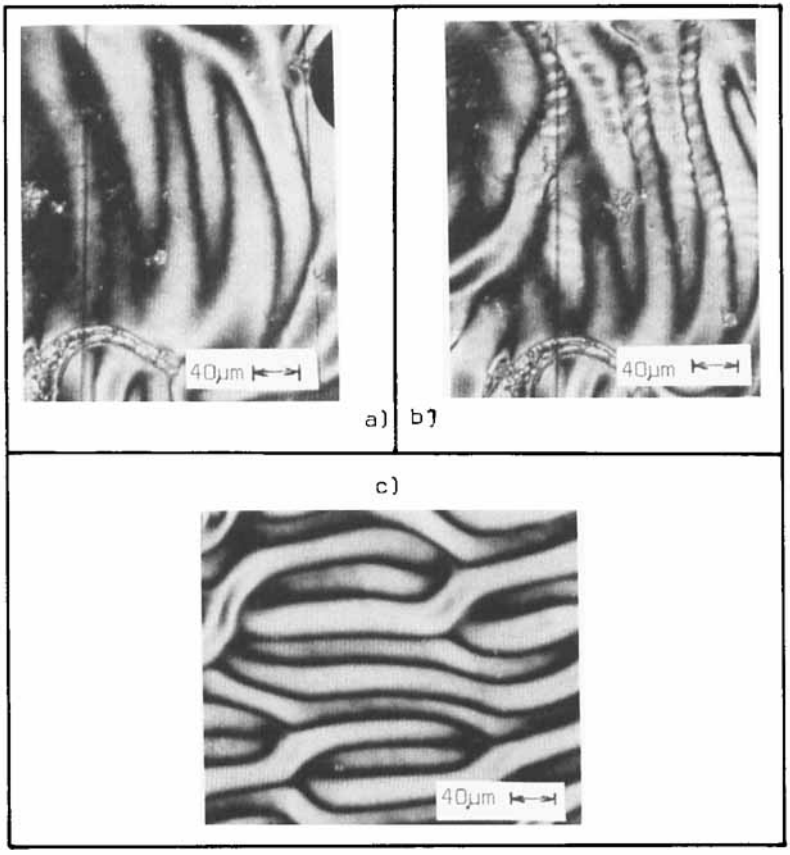
In the entire range of frequences an electric Frede-



P5 : a) Chevron texture in MBBA (T_c = 45°C) at 370 Hz, 220 V, 22°C, 12 µm. b) as in a) at 250 V (At lower potential a finer texture corresponding to monodimensional dielectric mode is observed). c) Chevron texture in DDA-9 (M_n = 2500) 3000 Hz, 66 V, 102,6°C (0.85 Tc), 12 µm. d) Chevron texture in DDA-9 (Mn = 2300) 2800 Hz, 130 V, T = 101,1°C (0,85 Tc) e = 12 µm (two minutes after application of field). **(See Color Plate V)**

ricksz transition was observed for a constant potential around 10 V. The flipping over of the director leads to an increase in birefringence and progressive coloring (4,26).

In small molecule liquid crystals the Fredericksz transition can be masked by the splay WD instability at lower



P6 : a) Texture obtained in DDA-9 (M_n = 2500), 4000 Hz, 120 V, 114,7°C = 0.95 T_c , 12 µm. b) as in a) at 130 V. c) Texture obtained in DDA-9 (M_n = 3400) 4100Hz 250 V, 12µm, two minutes after application of field. (See Color Plate VI)

threshold (27). In polymers, the splay elastic constant is expected to increase rapidly with molecular weight (28), with a corresponding increase in the splay WD threshold. On further increasing the potential above the Fredericksz transition at low frequency $F < F_c$, a WD - type instability occurs (P1d). The threshold potential is somewhat higher than in the planar configuration, and the organization less regular.

At high frequency no new effects due to the original homeotropic orientation are found above the Fredericksz transition.

CONCLUSION

We were able to demonstrate in this paper the many analogies between the polymeric nematic DDA-9 at low molecular weights with comparable ($\Delta\varepsilon < 0$, $\Delta\sigma > 0$) conventional liquid crystals. For exemple, evidence was given for the existence of both conduction and dielectric modes, for a possible coupling between conductive and dielectric modes, for a turbulent DSM.

Typical polymeric effects were analyzed. The problem of sample anchorage at high molecular weights requires development of new methods. A new high frequency broad domain texture was observed, as well as a homeotropic Fredericksz transition.

The onset of turbulence in these anisotropic materials merits further investigation. Slow relaxation times due to high viscosity should allow a detailed study of the transition mechanisms involved.

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