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ELECTRO-HYDRODYNAMIC INSTABILITIES IN MAIN CHAIN THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS

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ABSTRACT

We have investigated the response behavior of the thermotropic nematic polymer, DDA-9, in an electric field. DDA-9 is composed of regularly alternating moieties and flexible spacers. At a critical threshold voltage, dependent on molar mass, these polymers show the onset of instability. The appearance of a (non-fluctuating) striped pattern (Williams domains) is shown and the time of formation and relaxation of these patterns is investigated as a function of applied voltage.

Since the early studies of Williams (1), the effect of an electric field on liquid crystals of low molar mass has been investigated in detail (2,3,4,5). These studies have found important application in electro-optical liquid crystal display devices (6).

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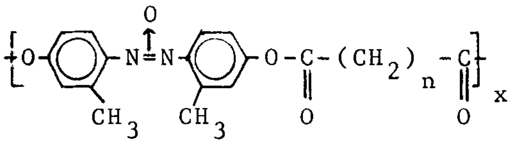
New effects could be expected in liquid crystalline polymers on application of an external electric field, but as yet few results for either side chain polymers (7) or semi-rigid main chain polymers (8,9,10,11) have been reported. The effects of molar mass, temperature, viscosity and other polymer characteristics have not been fully explored.

In a recent publication (12), we have reported on electric field effects in cybotactic nematic and ordinary nematic polyesters based on the 4,4'-dioxy-2,2'-dimethylazoxybenzene mesogenic moiety, represented by the formula:



$$\left[-O-C_6H_3(CH_3)-\overset{O}{\overset{\uparrow}{N}}=N-C_6H_3(CH_3)-O-\underset{\|}{\overset{}{C}}(=O)-(CH_2)_n-C(=O)- \right]_x$$

for n=7 (HEPTA-9, non-cybotactic); n=10 (DDA-9, cybotactic); and x=4-6. Williams domains (WD) and dynamic scattering modes (DSM) were observed in all cases.

In this work we report on the influence of molar mass on electrohydrodynamic instabilities in the polyester with n=10 (DDA-9). This polymer contains regularly alternating rigid and flexible units and its synthesis and liquid crystalline behavior have been previously described (13,14,15). The role of the molar mass for well-fractionated samples of DDA-9 in the formation and relaxation of Williams domains is reported below.

EXPERIMENTAL

The sample was placed between conducting SnO_2-coated glass plates. The sample thickness (between 10 and 30 μm) was adjusted by calibrated wedges.

In some cases a thermostable polymer film of 25 μm was used. A Mettler hot stage was used, and the observation of textures through a polarizing microscope was supplemented by measurements of transmitted light-intensity (by means of a photocell). All studies were made in polychromatic light.

It is necessary to point out that the characteristic values of threshold voltages and relaxation times, due to uncertainties related to polymeric samples (degree of ionic purity, fluctuations in homogeneity, thickness and molar mass), can only be reported semi-quantitatively. Typical threshold voltages are between 7 and 40 V. for the range of molar masses investigated. Nevertheless, one can firmly describe the trends of the phenomena investigated.

The electric field was applied perpendicularly to the sample at a reduced temperature of 0.85 or 0.95. A sinusoidal AC field was obtained from a BF generator subsequently amplified.

Surface orientation using the method of Chatelain (16) was tried, but precautions are necessary to avoid deterioration of the conductive SnO_2 layer.

Transition temperatures (T_C) were determined in the absence of electric field by hot stage polarizing microscopy at slow heating rates. The beginning of the decline of the intensity of transmitted light (on heating) corresponding to the onset of the biphase was taken as T_C (located some 4-5° below the transition N⟶I determined by DSC). Transition temperatures for various fractions are given in Table I.

TABLE I TRANSITION TEMPERATURES FOR FRACTIONS OF DDA-9

Fraction°	$\overline{M}_n$	T_{KN}	T_{NI} (DSC)	T_C °C (Microscopy)
10	2,300	---	123	119
9	2,500	91	126	120.7
8	3,400	102	132	128
7	4,000	108	141	---
6	6,300	116	154	148
5	8,000	118	161	---
4	10,000	118	162	---
9-DDA-9(model)	---	---	(100)	---

RESULTS

1. Textures in the applied electric field

Above the threshold voltage, striped patterns of alternating bright and dark regions are obtained. Figures 1 and 2 show the effects of molar mass under not too different temperatures and frequencies of the field. The black spots in Figure 1 correspond to air bubbles. In Figure 2, we note that the spacing between the bright and dark lines is not uniform.

2. Formation of instability

Viewed in the polarizing microscope, the average intensity of transmitted light through a given region of the sample, on application of a sufficiently high field, varies. Typical intensity curves are given in Figure 3a and 3b. In general, an increase of intensity between two plateaux is observed (Figure 3a) and once the higher plateau is reached, no further evolution of the striped pattern instability occurs. At higher than the initial electric field, the intensity can pass through a maximum before decreasing (Figure 3b). The times for the formation

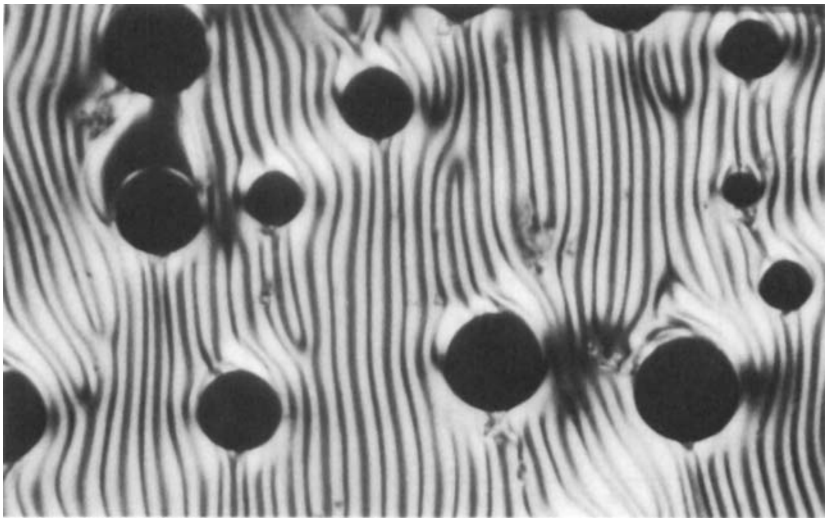


FIGURE 1 Williams domains observed for DDA-9 $\bar{M}n$=4,000; e=12 µm; 120°C; V=30v (crest to crest) at 120 Hz.
See Color Plate III, Volume 102, issue 10.

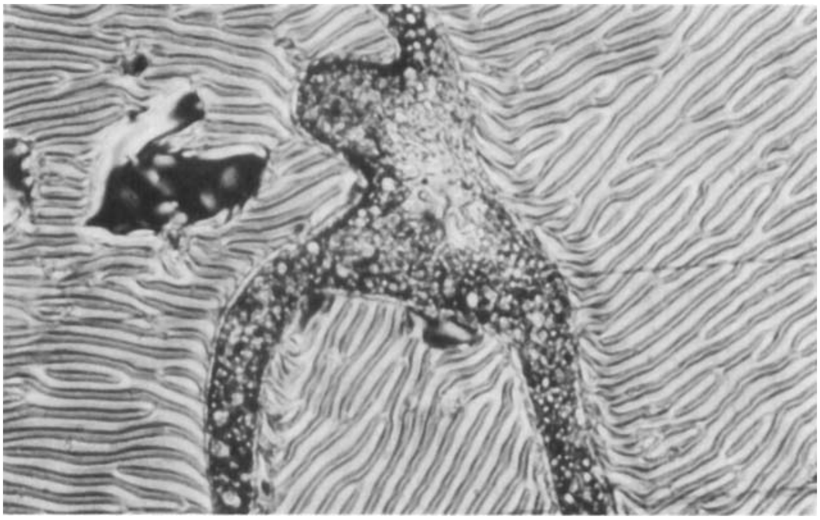
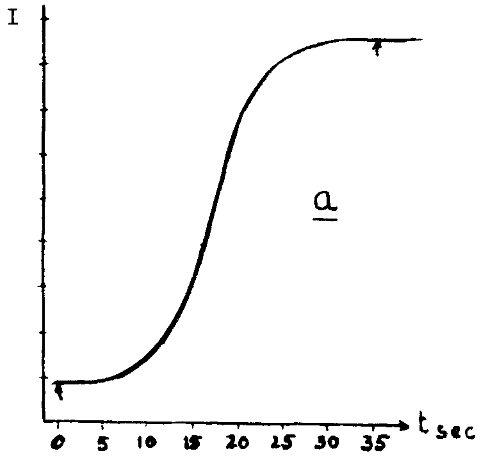
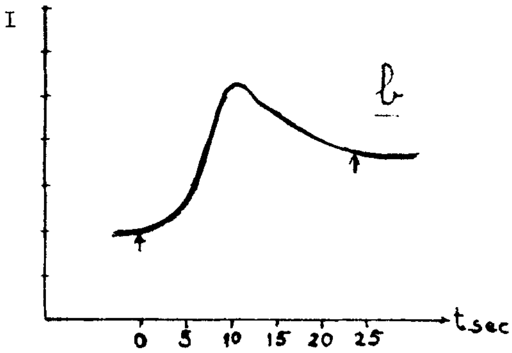


FIGURE 2 Williams domains observed for DDA-9 $\bar{M}n$=2,500; e=12 µm; 114.7°C; V=20v (crest to crest) at 60 Hz.
See Color Plate IV, Volume 102, Issue 10.



a) V=11v; frequency=60 Hz; $\overline{M}n$=3,400
121.6°C=0.95T_C



b) V=15v; frequency=60 Hz; $\overline{M}n$=3,400
121.6°C=0.95 T_C

FIGURE 3 INTENSITY OF TRANSMITTED LIGHT AS A FUNCTION OF TIME--I=Intensity in arbitrary units; t=unit is 5 seconds of Williams domains are determined by the separation between the two plateaux as indicated by arrows in Figures 3a and 3b, and are given in Figure 4. Times of formation of Williams domains increase with the decrease of the applied potential, with the molar mass and with the decrease of temperature.

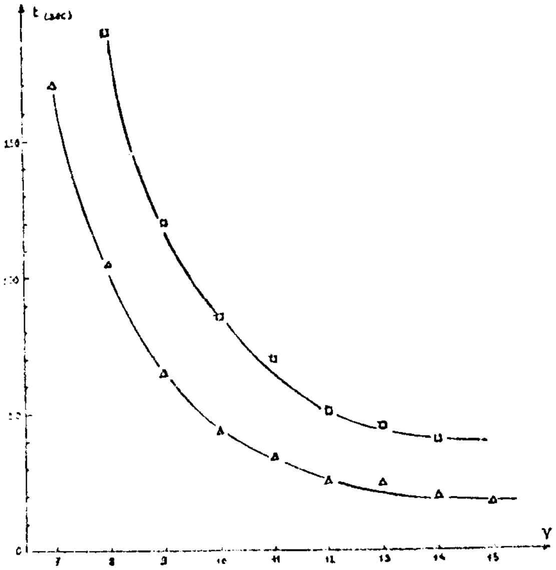


FIGURE 4 FORMATION TIME OF WILLIAMS DOMAINS AS A FUNCTION OF APPLIED VOLTAGE--
$\overline{M}n$=3,400; e=12μm; 60 Hz; 126.6°C=0.95T_C
$\overline{M}n$=3,400; e=12μm; 60 Hz; 113°C=0.84T_C

For a given molar mass and a given temperature, the relaxation times (T_{relax}) do not depend on the value of the applied field (or on the time of formation of Williams domains), as shown in Table 2. They still depend on molar mass and temperature in the same way as the formation times. A precision not exceeding 10% for the time measurements cannot be expected because of experimental uncertainties of the method.

TABLE II

	f=60 Hz M_n=2,300; 113°C	f=60 Hz M_n=3,400; 126.6°C	f=60 Hz M_n=3,400; 113°C
T_{relax}	20 sec	35 sec	40 sec

3. Threshold potentials.

The threshold potential for the formation time of 0-4 minutes was measured at the frequency of 60 Hz In Figure 5, the threshold voltage for appearance of Williams domains is given as a function of molar mass at the temperature of 0.95 T_C and for the formation time of about 3 minutes.

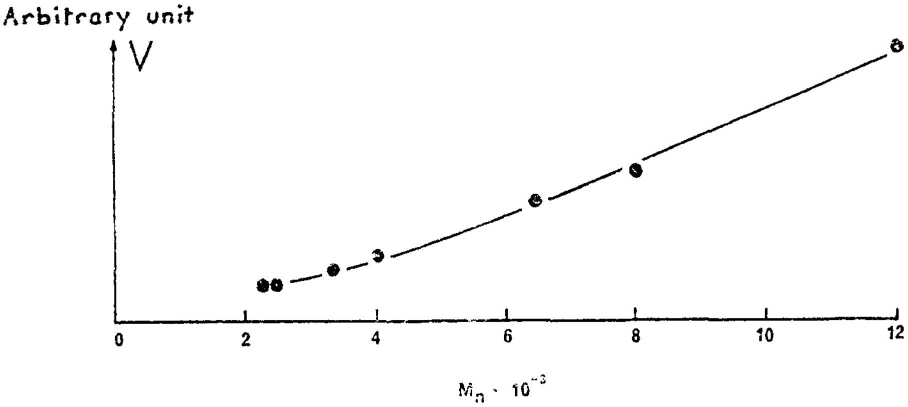


FIGURE 5 THRESHOLD VOLTAGE FOR APPEARANCE OF WILLIAMS DOMAINS INSTABILITIES AS A FUNCTION OF TIME FOR DIFFERENT MOLAR MASSES OF DDA-9.

4. Dynamic scattering mode.

Table 3 gives the onset of DSM for different molar masses. One can see the drastic influence of the molar mass on the onset of DSM.

TABLE III ONSET OF DSM FOR DIFFERENT MOLAR MASSES (at 60 Hz; T_{red}=0.88; maximum V=100 v).

	$\overline{M}_n$	Volt
Polyester DDA-9	3,300	60
" "	4,000	70
" "	6,300	no DSM
" "	8,300	no DSM
Model Compound 9-DDA-9 (monotropic)	1,200	30

CONCLUSIONS

The polymers studied display homogeneous orientation in the electric field due to the negative anisotropy of polarizability. All studied fractions up to $\overline{M}n$=10,000 form Williams domains at low voltage. With the increase in voltage, the time for the formation of Williams domains decreases. The voltage for Williams domain formation increases with molar mass of the polymer, especially in the case of molar masses exceeding 4,000 (Figure 5). The model compound 9-DDA-9 showed Williams domains formation at a voltage comparable with low molar mass fractions of the polymer.

At higher voltages, DSM was observed for fractions up to $\overline{M}n$=3,000-4,000 (applied voltage up to 100 V.). The critical voltage for DSM increases rapidly with the molar mass of DDA-9 (Table 3).

These preliminary studies demonstrate the effect of molar mass on hydrodynamic instabilities in thermotropic liquid crystalline polymers with regularly alternating mesogenic groups and flexible spacers in the main chain. A quantitative study of the frequency dependence is in progress and will be presented in a future paper.

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REFERENCES

1. R. Williams, J. Chem. Phys. 39, 384 (1963).
2. W. Helfrich, Mol. Cryst. Liq. Cryst., 21, 187 (1973).
3. G. Durand, Molecular Fluids Les Houches, 402, Plenum Press (1973).
4. E. Dubois-Violette, G. Durand, E. Guyon, P. Manneville, P. Pieranski, Solid State Physics, Suppl. 14, 147, Acad. Press (1978).
5. E.P. Raynes, Liquid Crystals of One and Two Dimensional Order, 176, Springer (1980).
6. I. Shanks, Contemp. Phys., 23, 65 (1982).
7. H. Finkelmann, Makromol. Chem., 180, 803 (1979).
8. W.R. Krigbaum, M.J. Lader, Mol. Cryst. Liq. Cryst., 62, 87 (1980).
9. W.R. Krigbaum, M.J. Lader, A. Ciferri, Macromolecules, 13, 554 (1980).
10. W.R. Krigbaum, C.E. Grantman, H. Toriumi, Macromolecules, 15, 592 (1982).
11. P. Corazza, M.L. Sartirana, B. Valenti, Macromolecules, 15, 592-96 (1982).
12. A. Blumstein, H.W. Schmidt, O. Thomas, G. Kharas R.B. Blumstein and H. Ringsdorf, Mol. Cryst. Liq Cryst. (Letters), 92, 271 (1984).
13. A. Blumstein, S. Vilasagar, S. Ponrathnam, S.B. Clough and R.B. Blumstein, J. Polym. Sci., 20, 877 (1982).
14. R.B. Blumstein, E.M. Stickles, and A. Blumstein, Mol. Cryst., Liq. Cryst., 82, 205 (1982).
15. G. Maret and A. Blumstein, Mol. Cryst. Liq. Cryst., 88, 195 (1982).
16. P. Chatelain, Acta Crystallograph., 1, 315 (1948