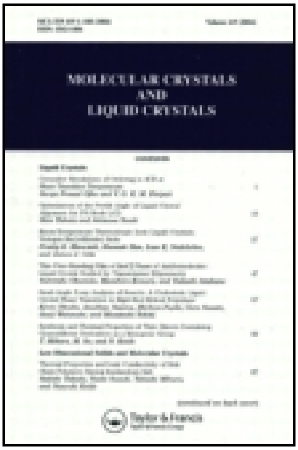


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Electrooptical Effects in the Nematic Polymer—PET/PHBA

A. Zheliaskova [a], H. P. Hinov [a], A. Derzhanski [a], K. Goranov [b] & S. Fakirov [b]

[a] Institute of Solid State Physics, 72 Lenin Blvd., 1784, Sofia, Bulgaria

[b] Laboratory of Structure and Properties of Polymers, Sofia University, 1 A. Ivanov Blvd., 1126, Sofia, Bulgaria

Version of record first published: 24 Sep 2006.

To cite this article: A. Zheliaskova , H. P. Hinov , A. Derzhanski , K. Goranov & S. Fakirov (1991): Electrooptical Effects in the Nematic Polymer—PET/PHBA, Molecular Crystals and Liquid Crystals, 195:1, 65-76

To link to this article: http://dx.doi.org/10.1080/00268949108030891

Mol. Cryst. Liq. Cryst., 1991, Vol. 195, pp. 65–76
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Electrooptical Effects in the Nematic Polymer—PET/PHBA†

A. ZHELIASKOVA, H. P. HINOV and A. DERZHANSKI
Institute of Solid State Physics, 72 Lenin Blvd., 1784 Sofia, Bulgaria

and

K. GORANOV and S. FAKIROV
Laboratory of Structure and Properties of Polymers, Sofia University, 1 A. Ivanov Blvd., 1126 Sofia, Bulgaria

(*Received September, 1989; in final form July 12, 1990*)

The influence of DC and AC electric fields on a melt of copolymer based on poly(ethylene terephthalate) (PET) and p-hydroxybenzoic acid (PHBA) were investigated. Spherulite domains or large-scale schlieren textures have been observed under an AC voltage with an above threshold amplitude depending on the initial state of the LC polymer being partly oriented or strongly scattering small-scale schlieren texture, respectively. The raise times of the texture changes were recorded to be in the range of several hours. The change of the direction of the electric field from normal to transversal using transversal geometry, confirmed the reorientation action of the AC electric field on the nematic director accompanied with the creation of band domains perpendicular to the electric field direction. All textures and light transmission curves obtained with the two geometries clearly indicated the negative value of the dielectric anisotropy of the nematic polymer which is in agreement with other investigations.

INTRODUCTION

Nowadays ever increasing interest is being paid to polymers with liquid crystal properties. Their broad practical application in is the reason for their intensive investigation. Use is made of the influence of the electric field on the low-molecular liquid crystals for liquid crystal displays,[1] in optoelectronics[2] etc. Under the influence of an electric field liquid crystal polymers also change their orientation, thus enabling scientists to get a record of information (the so-called thermorecord),[3] and also to apply them in optoelectronics.[4] A great advantage of these polymers is the possibility to control their physical properties through variation of their molecular weight. Another advantage is their stability at large temperature intervals and longer life span in comparison with the low-molecular liquid crystals. In ad-

---

†Part of this paper has been presented in the VI. European Liquid Crystal Winter Conference, Schladming, Austria (1989).

dition, the liquid crystal polymers retain their arrangement when cooled below the melting transition temperature avoiding crystallization unlike the low-molecular liquid crystals. As a result, the electric field can orient the former in a larger temperature interval. The field's electric or magnetic influence is relatively easier on the side chain liquid crystal polymers.[5-7] The main chain liquid crystal polymers interact with magnetic[8] or electric[9,10] fields less easily, since the mesogenic groups are incorporated in the main chain. Krigbaum *et al.*[11,12] have investigated the behaviour of the main chain nematic polymer containing p-oxybenzoyl units under the influence of an electric field and have observed various domains similar to those already discovered in the low-molecular nematics. Gilli *et al.*[13-15] have investigated the influence of the molecular weight (2000–7000) of the main chain nematic polymer (DDA-9) on the electrohydrodynamic instabilities and considered the memory of the domains in the frozen-in glass nematic state.

This paper deals with the behaviour of a high molecular weight main chain nematic copolyester under the influence of AC and DC electric fields in two geometries.

MATERIALS AND EXPERIMENT

The object of our investigation is the liquid crystal copolymer PET/PHBA based on poly(ethylene terephthalate) (PET) and p-hydroxybenzoic acid (PHBA) containing 50 mole % oxybenzoic units with a molecular weight about 15000 according to viscosimetric data (intrinsic viscosity of 0.56 in phenol/tetrachloroethane mixture). This copolymer was obtained by transesterification in the melt of PET with p-acetoxybenzoic acid.[16] The thermal transitions, wide-angle X-ray scattering patterns, the effect of different lengths of oxybenzoate blocks and optical microscopy observations have already been studied.[17] In this paper the investigation has been carried out with planar and transversal configurations of the samples. The planar configuration was of the sandwich cell (type A): two slides covered by a thin semitransparent conductive coating of a tin oxide (SnO_2) and a silizium monooxide (SiO) serving as an orienting layer (Figure 1a). The thickness of the cell was about 10 microns determined by the polymer layer, which also served as a spacer. The electric field was applied along the optical axis, perpendicular to the polymer layer. The cells with transversally applied electric field (type B) were prepared by glass slides, with aluminum folio electrodes with thickness of $d = 20$ microns between them (Figure 1b). The cells were heated by a calibrated Mettler hot stage. A polarizing microscope PZO supplied with a photoattachment was used for the optical observations. A photomultiplier with a recorder was used to registrate the intensity of the transmitted light. The power source was Model GZ-109 voltage generator. A Tektronix oscilloscope was used to control the shape and size of the applied voltage. The examined polymer—in both types of cells—was placed on one of the glass slides, the temperature was increased up to 260°C and the polymer was melted. The cell was obtained through pressing and fixing of the second slide against the first one. The measurements were carried out at temperature from 240°C to 280°C.

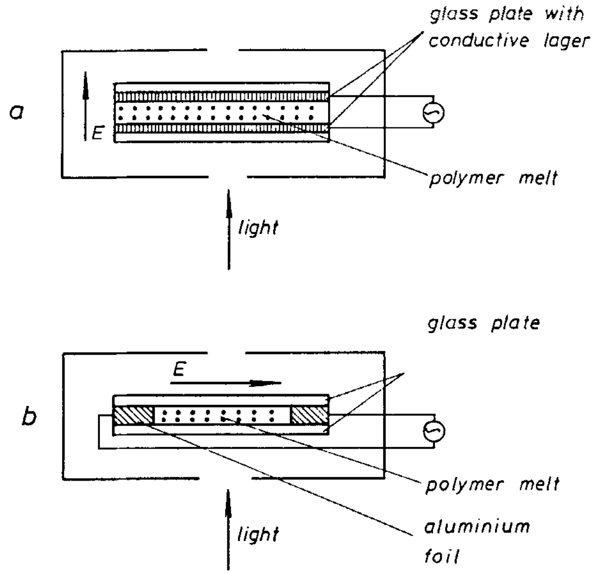


FIGURE 1 A scheme of the experimental cells (a) with electric field parallel to the direction of the light (type A) (b) with electric field transversal to the direction of the light (type B).

RESULTS

A DC voltage was applied on a cell type A (Figure 1a) from $U_{=} = 20$ V to $U_{=} = 100$ V. The dynamic scattering of the light was observed in the dark area of the optical picture (Figure 2) at $U_{=} = 50$ V, which is similar to the dynamic scattering in the low-molecular liquid crystals. The increase of the voltage to $U_{=} = 100$ V did not change the texture shown in Figure 2.

Various initial textures of the polymer appear (Figure 3a and Figure 4a), due to the different manner of preparing the cells.

One of the initial textures is obtained when the nematic director—showing the average orientation of the polymer molecules—was planar-oriented by means of slipping of the slides against each other and by the orientation effect of the substrates (Figure 3a). The other initial texture shown in Figure 4a, is a manifestation of the free planar arrangement of the nematic director between both slides. The primary arrangement of the polymer causes light dispersion of the transmitted light in all directions. Then the obtained texture is relatively dark with a fine structure, which is known in the literature as small-scale schlieren texture (Figure 4a).

In Figure 3a regions with more oriented polymer are also shown. We suppose that the polymer molecules in these regions are tilted to the slides. The applied alternating electric field 100 V, $f = 50$ Hz at temperature 250°C changes the texture. Probably the electric field tends to straighten the nematic director. The optical picture changes and the three-dimensional spherulite domains—appear (Figure 3b). After the change of the microscope focus the domains were also observed in

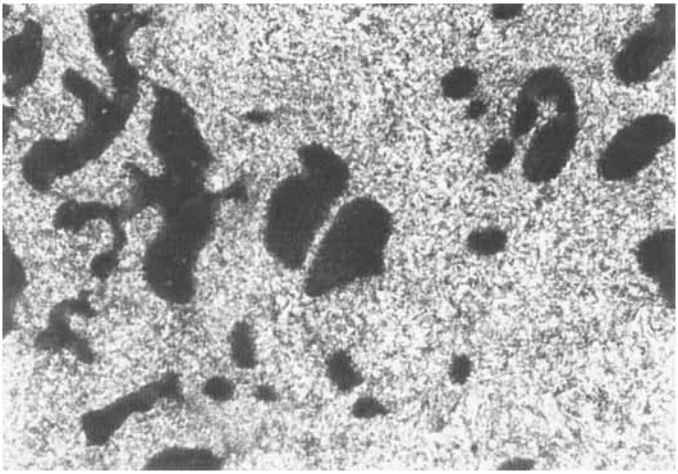
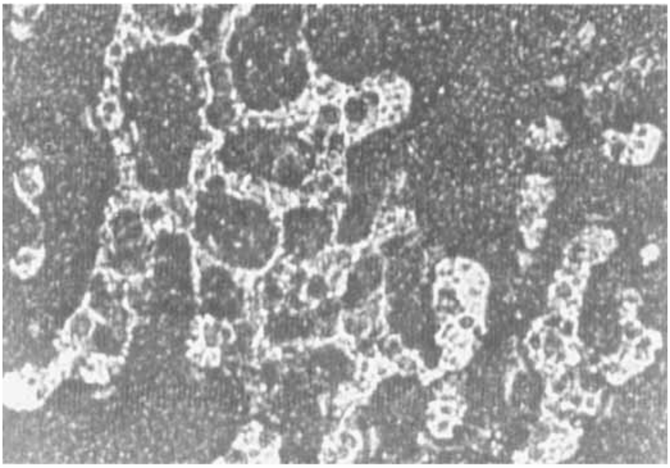


FIGURE 2 A dynamic scattering in the dark areas of a PET/60 PHBA cell, type A, obtained at 240°C, $U = 100$ V, P I A, magnification 100×.

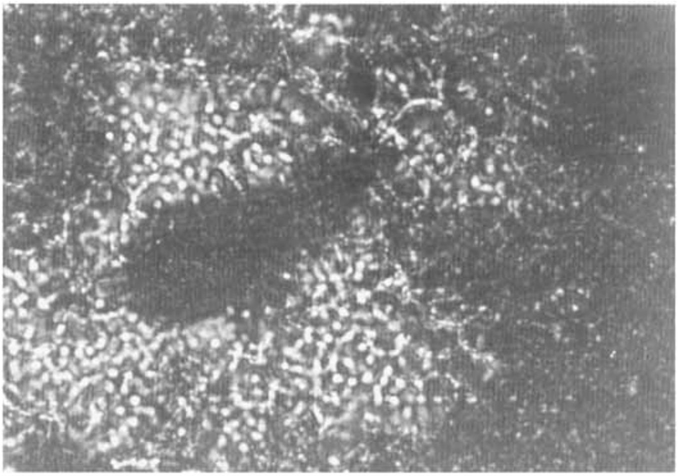
depth (Figure 3c), which shows the existence of the domains in the bulk. They need about two hours to appear—and in the course of time they become clearer. After the electric field was turned off the spherulite domains were still existing at the same temperature.

On the sandwich cell type A with initial small-scale schlieren texture (Figure 4a) alternating voltage of 180 V, $f = 50$ Hz, was applied at 250°C. The texture did

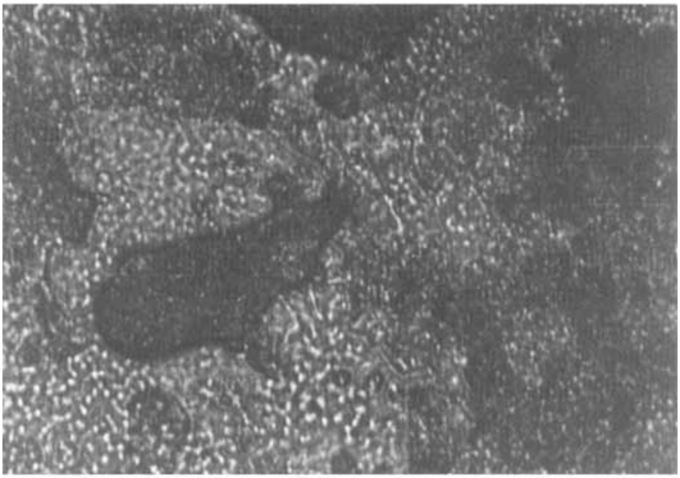


(a)

FIGURE 3 Microphotographs of PET/60 PHBA taken at 250°C for a cell, type A, P II A, magnification 100× (a) an initial texture without applied voltage (b) spherulit domains obtained after 4 hours at a voltage of 100 V, $f = 50$ Hz, middle focusing (c) the same optic texture, down focusing.



(b)



(c)

FIGURE 3 (*continued*)

not change at first. When the temperature increased to 270°C and the electric field was still further applied, the optical picture altered and a large-scale schlieren texture was observed (Figure 4b) similar to the often observed schlieren texture in low-molecular liquid crystals. Approximately after 2 hours the texture became more distinct, better expressed. The increase of the temperature reduces the viscosity of the polymer and the electric field can influence the sample more easily.

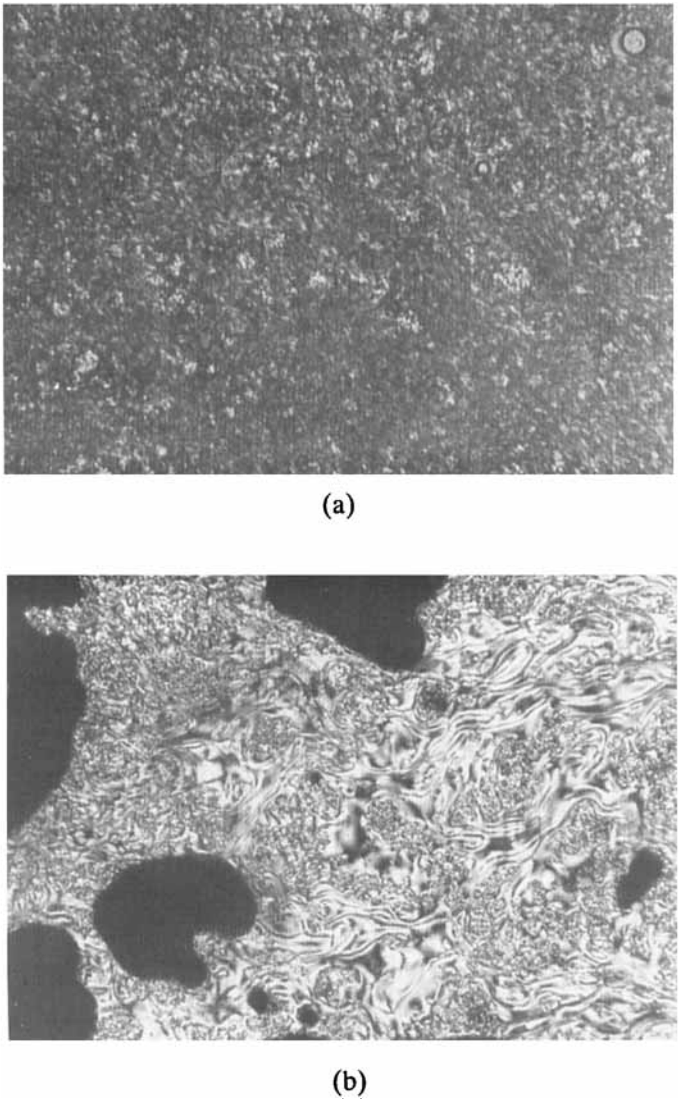


FIGURE 4 Microphotographs of PET/60 PHBA for a cell, type A, P I A, magnification 100× (a) an initial texture at 250°C obtained by pressing of the polymer film, without applied voltage (b) coexistence of small-scale schlieren texture and large-scale schlieren texture at 270°C. The texture is obtained after 3 hours heating to 280°C under a voltage of 100 V, f = 50 Hz.

The intensity of the transmitted light through the nematic polymer film in the sandwich cell, type A, increased gradually during the time (Figure 5). The alternating voltage was applied on a cell with texture similar to that shown on Figure 3a.

Further, a transversal electric field was applied on cells of a type B with a width of the polymer layer about 100 microns. The texture scatters light isotropically

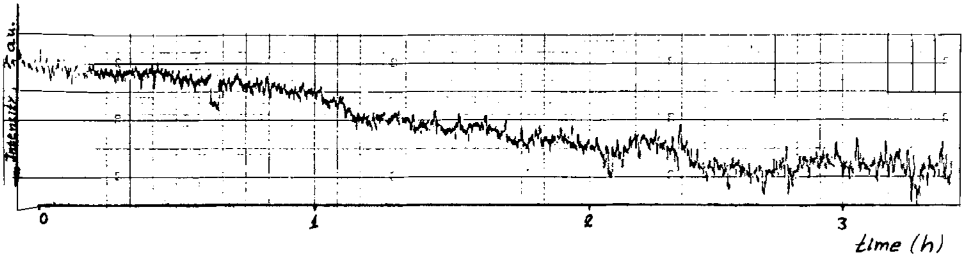
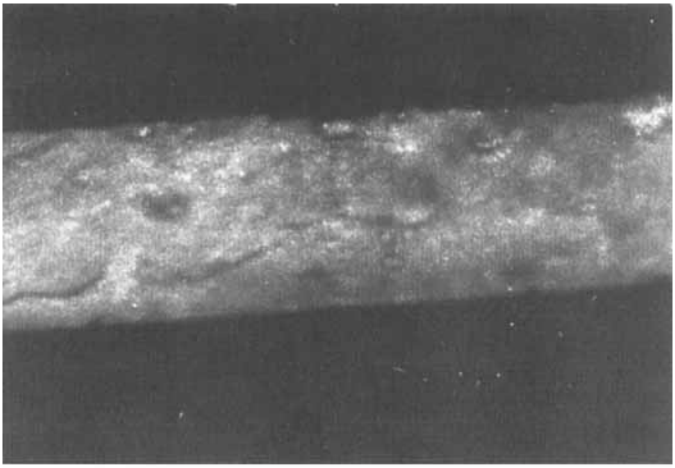


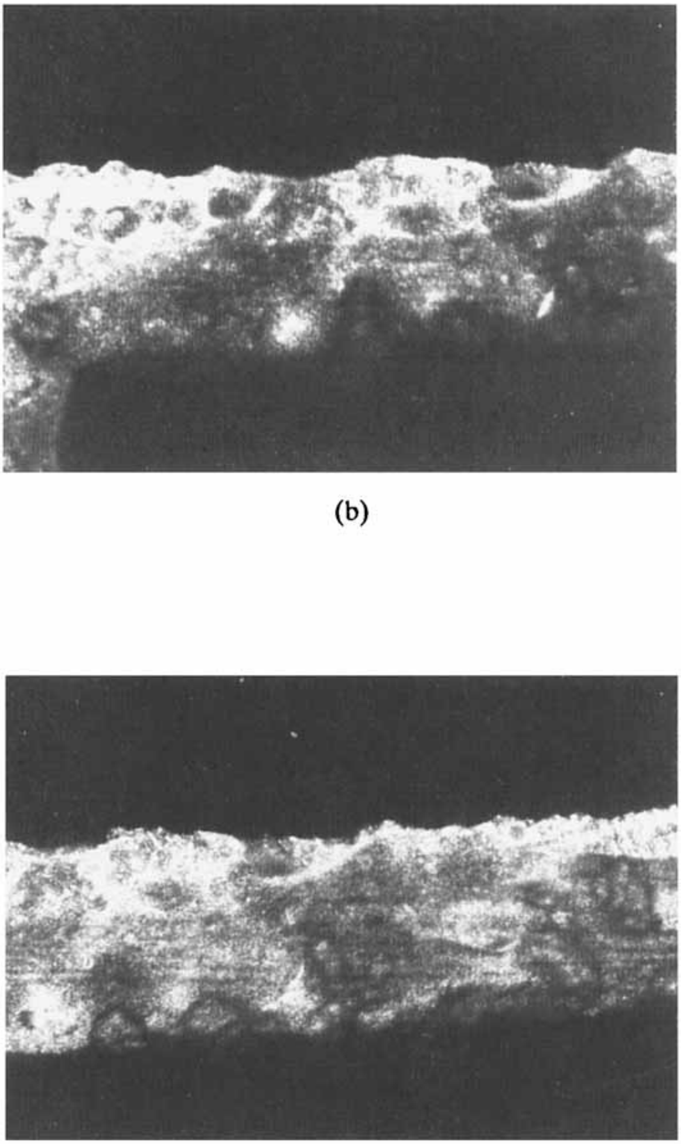
FIGURE 5 The intensity of the transmitted light through the cell, type A, as a function of the time at $U = 220$ V, $f = 50$ Hz, $t = 250$°C.

prior to applying the voltage (Figure 6a). The applied alternating field ($U = 180$ V) caused brightening of the texture (Figure 6b), which clearly indicates the orientation of the director under the influence of the electric field. Under the action of the electric field for 2 hours band domains appeared. They lie parallel to the electrodes and perpendicular to the electric field direction. The longer the electric field is applied the clearer the band domains become (Figure 6c). By switching off the electric field and increasing of the temperature to 280°C, the band domains disappear, the nematic director disorientates. The gradual increase of the transmitted light intensity through a cell of type B as a function of the time is shown on Figure 7. The process begins after about 40 minutes and completes 3 hours later.



(a)

FIGURE 6 Microphotographs of PET/60 PHBA taken at 240°C for a cell, type B, P II A, magnification 100x (a) an initial texture (b) appearance of band domains after 2 hours at a voltage of 180 V, $f = 50$ Hz (c) clear band domains perpendicular to the electric field after 4 hours at a voltage of 180 V, $f = 50$ Hz.



(b)

(c)

FIGURE 6 (*continued*)

The change of the transmitted light intensity through a cell of type B as a function of the angular position of polarizer and analyzer after 4 hours at $U = 220$ V, $f = 50$ Hz and temperature of 260°C is given on Figure 8. This change is more significant than for a cell without applied voltage at the same conditions.

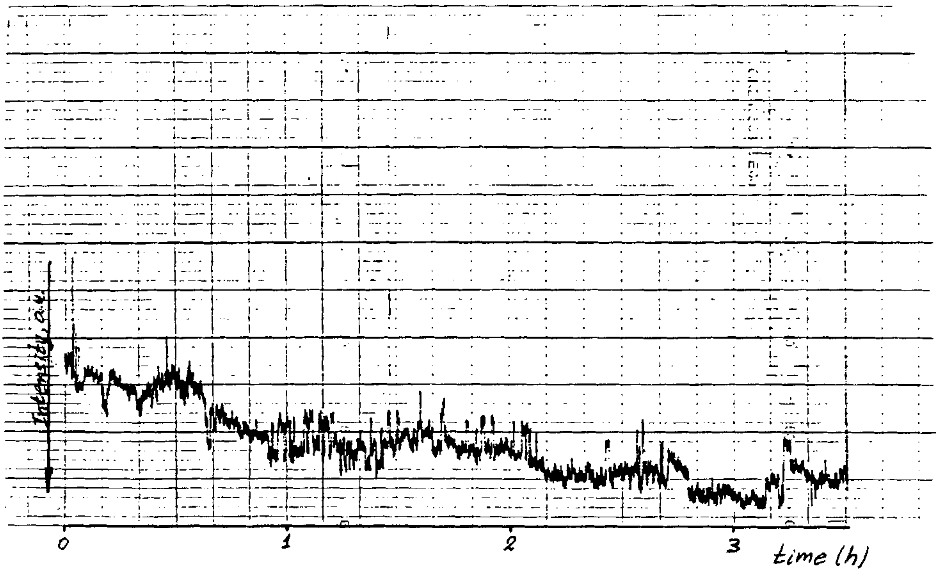


FIGURE 7 The intensity of the transmitted light through the cell, type B, as a function of the time at U = 220 V, f = 50 Hz, t = 250°C.

DISCUSSION

The relatively high molecular weight of the examined copolymer presupposes also high melt viscosity. The necessity of applying a relatively high electric field (above 80 V) in comparison with the field applied to the low-molecular liquid crystals has a significant effect on the polymer. Apart from the high voltage, in order to influence the sample the measurements were also carried out at a relatively high temperature in the nematic interval being above 240°C since at such temperature the viscosity of the polymer melt was relatively lower. Within some dozens of minutes

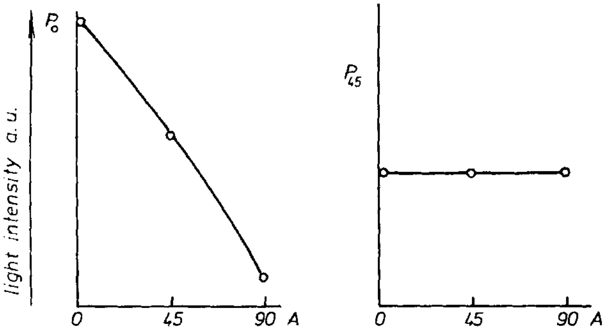
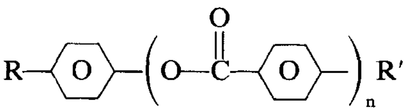


FIGURE 8 The intensity of the transmitted light through a cell, type B, as a function of the angular position of polarizer P and analyzer A after 4 hours at a voltage of 220 V, f = 50 Hz, t = 260°C.

the electric field causes texture changes in the investigated sample (Figures 5 and 7).

In the case of planar sandwich cells with a small-scale schlieren texture (Figure 4a) the polymer chains were orientated mainly planar. At temperatures between 180°C and 220°C the electric field failed to change the orientation of the director, on the account of the high viscosity of the polymer melt and the negative dielectric anisotropy of the liquid crystal which is confirmed by the following considerations. A positive value of the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ is reported[18] by studies of the dielectric permittivity of some nematic phenyl benzoates having the structure



$$R-\langle O\rangle-\left(O-\overset{O}{\overset{\|}{C}}-\langle O\rangle-\right)_n R'$$

where $n = 1, 2.$

When the alkyl groups R and R′ are replaced by alkoxy groups, the dielectric anisotropy became negative. Therefore by the increase of the polarity of the electron—withdrawing groups R and R′—for example a carboxy group—the dielectric anisotropy accepts negative value. These conclusions can be considered valid for the polymer chains built up from the similar phenylbenzoate groups connected with alyphate groups. In the presence of ester bond in the polymer chain, some decrease of the dielectric anisotropy was expected. These assumptions were confirmed by the experiment of Tsvetkov and Kolomiets.[19] They measured the Frederiks threshold on homeotropic copolymer poly(ethylene terephthalate) and its low molecular weight analogue under the influence of magnetic or electric field. The dielectric anisotropy $\Delta\epsilon$ was found to be negative with a value between 1 and 0,2.

At temperature above 240°C the electric field orients the planar arranged molecules, which is expressed optically in a large-scale schlieren texture and separate area of small-scale schlieren textures (Figure 4b).

When the initial orientation of the nematic director was not strictly planar (see Figure 3a) the application of the alternating electric field caused the formation of spherulite domains in the sample. Their formation began after about 30–40 minutes and finished 2–3 hours later. The appearance and development of the domains in dynamic is shown by the intensity transmitted light curve on Figure 5. The spherulite domains can be treated as a kind of a three-dimensional Frederiks threshold which appears at about 80 V. The diameter of the spherulites is in the order of $d = 20$ microns. Tsvetkov and Kolomiets[19] investigated a liquid crystal polymer similar to that studied in the present paper but with lower molecular weight $M = 4000$ and they observed Frederiks threshold at a lower voltage of 40 V and the rise time has been several tens of minutes. Spherulites arranged in bands and similar to those obtained in Figures 3b and 3c but in a magnetic field were obtained by Sun Zheng-Min and Kleman.[8]

In the case of the cell (type B) with transversally applied alternating voltage the polymer molecules are normally expected to be oriented perpendicular to the direction of the electric field. The observed textures in Figures 6b and 6c undoubtedly show, that the nematic director is oriented in the plane determined by the electrodes. The brightening of the initially scattering small-scale schlieren texture of the nematic polymer under the applied voltage with the time (Figure 2) unambiguously showed the arrangement of the nematic polymer director in the plane of the electrodes and perpendicular to the direction of the electric field. The process began at about the 50th minute and finished approximately 3 hours later. It is seen on Figure 8 that the sample is brightest at parallel position of the two nicols which coincides with the orientation of the nematic director. Inversely at crossed position of the nicols, the transmitted light is smallest. When the polarizer was turned on 45°, the rotation of the analyzer did not change significantly the intensity of the transmitted light. An additional evidence of the orientation of the nematic polymer is also the formation of band domains in some of the patterns under an applied voltage (Figures 6b and 6c). The increase of the temperature up to 280°C and the switch off of the voltage causes the disappearance of the band domains. This suggests, that the domains are probably formed during the reorientation of the nematic polymer director.

CONCLUSIONS

The influence of an electric field—direct or alternating—was investigated on a copolymer PET/PHBA in the nematic phase. The dynamic scattering of the light was observed when direct voltage of 50 V was applied. Two kinds of cells were used, planar when the electric field was applied perpendicular to the polymer layer, in direction of the optic axis and transversally when the electric field was applied between two metallic foils in the plane of the polymer. The alternating electric field causing the electrooptical effects was relatively high (140 V–220 V) in comparison with the relevant applied voltage necessary for the reorientation of the low-molecular liquid crystals. This is due to the relatively high molecular weight of the investigated polymer ($M = 15000$) and the consequent high melt viscosity.

Depending on the initial state of the nematic polymer, spherulite domains or pleasing the eye large-scale schlieren textures at temperature of 280°C were observed. In addition, in the transversal geometry new band domains were observed. The negative dielectric anisotropy confirmed by our experiment leads to orientation of the nematic polymer director perpendicularly to the field in both cases under investigation. This process is illustrated with microscopic pictures and optical transmission curves.

The dependence of the intensity of the transmitted light as a function of the voltage time and molecular weight will be considered in a later article.

References

1. G. W. Gray, "The Clifford Paterson Lecture: Liquid Crystals, an area for research and industrial collaboration among chemists, physicists and engineers," *Proc. R. Soc. London A(GB)*, **402**, 1822 (1985).
2. B. Bahadur, "Liquid Crystal Displays," *Mol. Cryst. Liq. Cryst.*, **109**, 3 (1984).
3. V. P. Shibaev, S. G. Kostromin and A. N. Plate, *Polymer Commun.*, **24**, 364 (1983).
4. J. Economy, "Contemporary topics in polymer science," vol. 5, Ed. E. J. Vandeaberg, Plenum Publishing Corp. (New York), 351 (1984).

5. V. P. Shibaev and N. A. Plate, *Adv. in Polymer Sci.*, **60/61**, Liquid Cryst. Polymers II/III, Eds. M. Gordon and N. A. Plate, Springer Verlag (Berlin), 173 (1984).
6. H. Finkelmann and G. Rehage, *Adv. in Polymer Sci.*, **60/61**, Eds. M. Gordon and N. A. Plate, Springer Verlag (Berlin), 99 (1984).
7. H. Ringsdorf and R. Zentel, *Makromol. Chem.*, **183**, 1245 (1982).
8. Zheng-Min Sun and M. Kléman, *Mol. Cryst. Liq. Cryst.*, **111**, 3–4, 321 (1984).
9. A. Blumstein, H. W. Schmidt, O. Thomas, G. B. Kharas, R. B. Blumstein and H. Ringsdorf, *Mol. Cryst. Liq. Cryst.*, **92**, 271 (1984).
10. P. G. Martin and S. I. Stupp, *Polymer*, **28**, 897 (1987).
11. W. R. Krigbaum, H. J. Lader and A. Ciferri, *Macromolecules*, **13**, 3, 554 (1980).
12. W. R. Krigbaum, C. E. Grantham and H. Toriumi, *Macromolecules*, **15**, 592 (1982).
13. J. M. Gilli, H. W. Schmidt, J. F. Pinton, P. Sixou, O. Thomas, G. Kharas and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **102**, 2, 49 (1984).
14. J. M. Gilli, A. Ten Bosch, J. F. Pinton, P. Sixou, A. Blumstein and R. B. Blumstein, *Mol. Cryst. Liq. Cryst.*, **105**, 375 (1984).
15. J. M. Gilli and P. Sixou, *Mol. Cryst. Liq. Cryst.*, **119**, 179 (1984).
16. K. Goranov and S. Fakirov, *Annual Review of Sofia Uni.*, **82** (1988), in press.
17. K. Goranov, S. Fakirov, H. Hinov and A. Zheliaskova, *Mol. Cryst. Liq. Cryst.*, in press.
18. W. H. de Jeu and Th. W. Lathouwers, *Mol. Cryst. Liq. Cryst.*, **26**, 225 (1973).
19. V. N. Tsvetkov and I. P. Kolomiets, *Mol. Cryst. Liq. Cryst.*, **157**, 467 (1988).