

# Anisotropic networks with stable dipole orientation obtained by photopolymerization in the ferroelectric state

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## Anisotropic networks with stable dipole orientation obtained by photopolymerization in the ferroelectric state

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SPECIAL TOPICS



# Anisotropic networks with stable dipole orientation obtained by photopolymerization in the ferroelectric state

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In this study a ferroelectric liquid crystal (FLC) monoacrylate (*S*)-4-(1-ethoxycarbonyl-1-ethoxy)phenyl 4'-(11-acryloyloxyundecyloxy)biphenyl-4-carboxylate was used. Room-temperature spontaneous polarization of the monoacrylate was measured to be 190 nC/cm<sup>2</sup>. The monoacrylate was provided with 10% LC diacrylate. After inducing macroscopic molecular and dipolar orientation in the ferroelectric phase, polymerization within the reactive system was induced photochemically. In this way an anisotropic polymer network with a spontaneous polarization was produced. Within this network the crosslinks were formed by the diacrylate molecules. The anisotropic network was transparent and highly birefringent. The system showed high thermal stability and remained anisotropic even after being heated to elevated temperatures. The presence of dipolar orientation within the anisotropic networks was characterized by piezoelectric measurements. The piezoelectric coefficient within these networks was found to be highly dependent on the direction of the applied strain. The highest value was measured in the direction perpendicular to the molecular orientation and was 29 pC/N. © 1995 American Institute of Physics.

## I. INTRODUCTION

Polymeric systems with a stable dipole orientation are of great interest as they show piezo and pyroelectricity<sup>1</sup> and can also be used in the production of various nonlinear optical effects.<sup>2,3</sup> Polymeric systems with a macroscopic dipole orientation can be divided into two classes:<sup>1</sup> Electrets and Ferroelectric polymers. Polymer electrets are obtained by poling amorphous polymers under high electric fields around their glass transition temperatures ( $T_g$ ). Upon cooling the system below the  $T_g$  of the polymer the dipole orientation becomes frozen in. However, the dipole orientation in such systems is not stable and the orientation tends to decay even at temperatures below the  $T_g$  of the polymer. Ferroelectric polymers, on the other hand, have spontaneous polarization up to their Curie points. Spontaneous polarization within these systems can be aligned macroscopically and remains stable. Ferroelectric polymers can be semicrystalline<sup>4,5</sup> or liquid crystalline.<sup>6-8</sup> Semicrystalline polymers such as poly(vinylidene fluoride) PVDF show ferroelectricity only in one particular crystal form. Therefore they need to be subjected to various heat and mechanical treatments in order to increase the crystallinity and to promote the desired crystal form within them. Copolymerization is also used in order to promote the desired crystal form within ferroelectric polymers.<sup>9</sup> LC polymers and elastomers,<sup>6</sup> on the other hand, can have a ferroelectric phase above their  $T_g$  or their melting temperatures. In such a low viscous LC phase, polarization within the system can be macroscopically aligned with ease under an electric field. In the case of glass forming LC systems, the dipole orientation is frozen by quenching the systems below their  $T_g$ .<sup>10</sup> However, here it is important to point out that in such systems various other LC phases which

might appear between the  $T_g$  and the ferroelectric phase can disturb the order during the glass formation process, and the dipole orientation might be lost.

The Langmuir-Blodgett (LB) monolayer transfer method is also used in the architecture of multilayer films.<sup>11</sup> In a controlled way monolayers of molecules are stacked on top of each other, producing layers with a macroscopic polarization perpendicular to the surface of the substrate.

Here we would like to describe anisotropic networks with a dipole orientation by polymerization of low mass LC molecules in the oriented state. Photopolymerization of low mass liquid crystal (LC) molecules with reactive end groups in a mesophase leads to the formation of anisotropic networks, plasticized networks, and anisotropic gels.<sup>12-18</sup> Thermotropic LC molecules showing various phases are brought into the desired phase by controlling the temperature. Macroscopic orientation of the molecules is induced with ease at specially treated surfaces. Uniaxially buffed polymer surfaces are often used in inducing uniaxial planar orientation whereas surfaces treated with surfactant molecules are used in order to induce homeotropic orientation. Polymerization of such systems can be photochemically induced when provided with a suitable initiator. The polymerization process proceeds isothermally, leading to the formation of a three-dimensionally cross-linked anisotropic network. In our earlier publications it has been shown that nematic<sup>13,14</sup> and cholesteric<sup>15</sup> structures can be frozen in by the photopolymerization process. In the case of plasticized networks (anisotropic networks containing free molecules) polymerization in the ferroelectric phase<sup>16</sup> has also been demonstrated. Here we would like to describe photoinduced polymerization of a low-mass ferroelectric LC system where in addition to the molecular orientation, dipole orientation of the molecules also becomes fixed in the form of a three-dimensional network. Dipolar orientation within the network is characterized by piezoelectric measurements.

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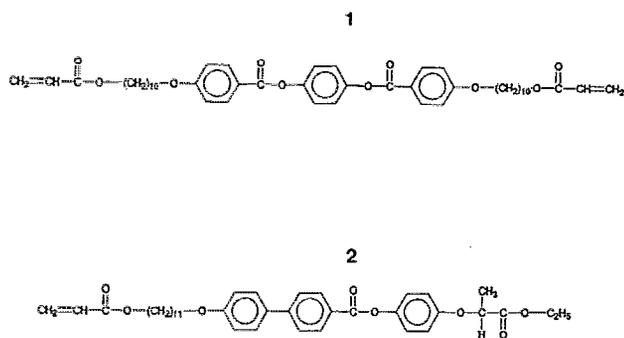


FIG. 1. Structure of the LC acrylates 1 and 2.

## II. EXPERIMENT

The synthesis of the chiral monoacrylate will be published in a separate article. The photoinitiator was Irgacure 651 (Ciba Geigy). The uniaxial orientation of the molecules was induced in cells provided with uniaxially rubbed nylon layers. The cell gap could be chosen to be 2 or 60  $\mu\text{m}$ . The refractive index measurements were carried out using an Abbe refractometer which could be thermostated up to 140  $^{\circ}\text{C}$ . Dielectric measurements were performed using a Hewlett-Packard 4194A Impedance/Gain-Phase analyzer. For spontaneous polarization and the piezoelectric measurements a Kiethly 617 electrometer was used. Dynamic mechanical thermo analysis (DMTA) was performed using a Polymer Laboratories DMTA equipment.

## III. RESULTS AND DISCUSSION

### A. Monomers

Structures of the reactive molecules used are shown in Fig. 1. The transition temperatures of the monomers used in the study are shown below:

1	K	82 $^{\circ}\text{C}$	$S_c$	108 $^{\circ}\text{C}$	N	149 $^{\circ}\text{C}$	I
2	K	62 $^{\circ}\text{C}$	$S_c^*$	78 $^{\circ}\text{C}$	$S_a$	106 $^{\circ}\text{C}$	I
10% 1 in 2	K	65 $^{\circ}\text{C}$	$S_c^*$	70 $^{\circ}\text{C}$	$S_a$	102 $^{\circ}\text{C}$	I

It can be seen that the monomeric chiral monoacrylate 2 is crystalline at room temperature and it shows chiral smectic- $C(S_c^*)$  (ferroelectric) and smectic- $A(S_a)$  phases. In the supercooled state the monoacrylate also shows another tilted smectic phase transition at around 35  $^{\circ}\text{C}$ . The crosslinker diacrylate 1 is also crystalline at room temperature and it shows smectic  $C$  and nematic phases. The transition temperatures of the mixture containing 10% w/w monomer 1 which was used in the polymerization experiments are also shown in the above table. It can be seen that the mixture shows the same phases as the chiral monoacrylate 2. However, due to the presence of the diacrylate 1 all the liquid crystal transition temperatures are depressed slightly. This decrease is probably due to the absence of the smectic  $A$  phase in 1 which shows the nematic phase instead.

The refractive indices of the monoacrylate 2 are shown in Fig. 2. It can be seen that they remain almost constant as a function of temperature in the  $S_c^*$  phase. In the  $S_a$  phase

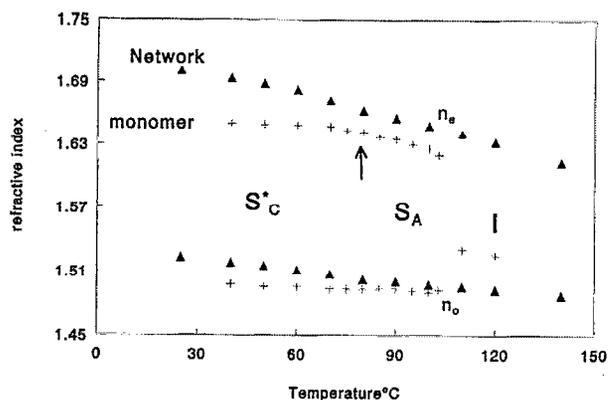


FIG. 2. Refractive indices as a function of temperature. + = monoacrylate 2,  $\blacktriangle$  = anisotropic network containing 10% 1.

the extraordinary refractive index decreases slightly with increasing temperature before the system becomes isotropic at 106  $^{\circ}\text{C}$  above which a single refractive index is measured. Here it is important to note that in the  $S_c^*$  phase, due to the tilted orientation of the molecules, the measured values for the refractive indices shown in Fig. 2 are expected to be slightly different than the true values.

The spontaneous polarization measurements were carried out by applying a triangular voltage across a cell containing electrodes and simultaneously measuring the current through the cell. In Fig. 3 the change in the current is plotted as a function of voltage. The peaks in the curves are associated with the spontaneous polarization ( $P_s$ ) reversal. In order to make sure that the peaks are not caused by the ionic impurities, the movement of the molecules which cause the polarization reversal was optically followed. This was done by placing the cell between crossed polarizers and measuring the intensity of the transmitted light. In Fig. 3 the intensity of the transmitted light is also plotted as a function of voltage. It is clear that the current peaks and the change in the intensity appear simultaneously, showing that the peaks are due to the  $P_s$  reversal. The sign of the spontaneous polarization was determined to be positive [ $P_s(+)$ ] and its magnitude was

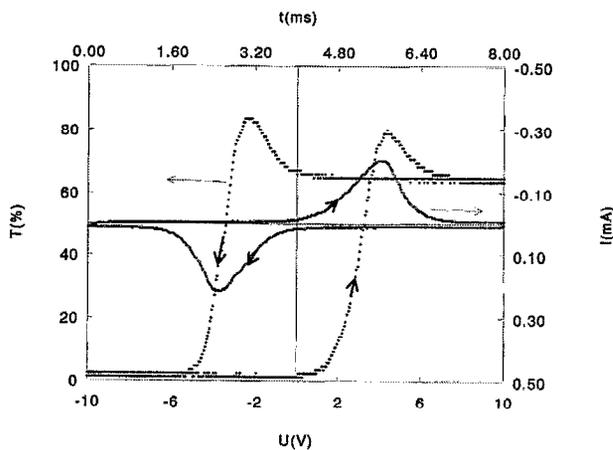


FIG. 3. Light intensity and the current through the cell as functions of cyclic voltage/time for the monomeric mixture.

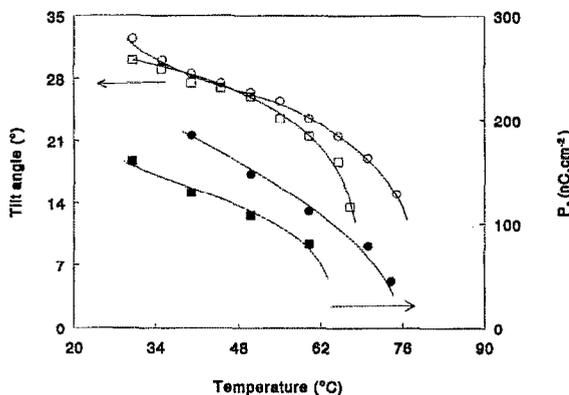


FIG. 4. Spontaneous polarization (solid symbols) and the tilt angle (open symbols) as functions of temperature.  $\circ$ =pure 2,  $\square$ =the mixture containing 10% 1.

estimated by integrating the current peak over time and dividing it by twice the active area of the electrodes. In Fig. 4  $P_s$  is plotted as a function of temperature for pure monoacrylate 2 and the mixture containing 10% 1. It can be seen that in both cases the spontaneous polarization decreases with temperature and becomes zero in the smectic-A phase. It is also clear that at a given temperature  $P_s$  is lower for the mixture than for the pure monoacrylate. This is as expected since only the dipoles of the chiral molecules contribute to the  $P_s$  of the system. Another property characterizing the smectic phase is the angle the director makes with respect to the smectic layer normal (tilt angle). The tilt angle was estimated by measuring the extinction angle between the two states as the polarity of the applied field across the cell is reversed. Half of this angle represents the angle molecules make with respect to the smectic layer normal. In Fig. 4 the angle is also plotted as a function of temperature for the monoacrylate 2 and its mixture containing 10% 1. Here again it can be seen that the tilt angle follows the same trend as the spontaneous polarization and decreases with increasing temperature. Furthermore at a given temperature the mixture containing 10% 1 also gives a smaller tilt angle than the pure chiral monoacrylate. In both cases the tilt angle reduces to  $0^\circ$  in the smectic-A phase.

## B. Polymerized network

The mixture containing 10% of 1 (90% of 2) provided with the initiator was placed in the isotropic state in a cell where it formed a  $60\text{-}\mu\text{m}$ -thick layer. The sample was then cooled into the smectic-A phase where it became uniaxially oriented. Subsequently it was cooled down to  $35^\circ\text{C}$  and an electric field ( $4\text{ V}/\mu\text{m}$ ) was applied across the sample in order to align the ferroelectric polarization. Applying the electric field caused the molecules to become oriented at an angle of about  $30^\circ$  with respect to the rubbing direction. Subsequently the sample was irradiated with UV light in order to initiate the polymerization of the system which led to the formation of a three-dimensional network. After polymerization the network remained highly birefringent, and the tilt angle the molecules made with respect to the rubbing direction, became frozen in. Various properties of the net-

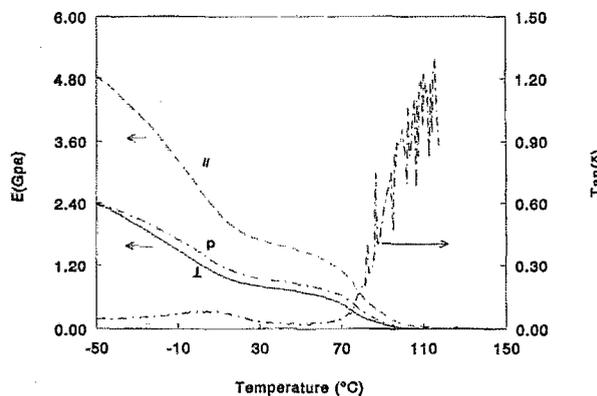


FIG. 5. Loss tangent and the elastic modulus of the anisotropic network as functions of temperature for various directions of applied strain.  $\parallel$ =in the direction parallel,  $\perp$ =perpendicular to the molecular orientation,  $P$ =in the direction of rubbing.

work were subsequently characterized. In Fig. 2 the refractive indices of the network are plotted as a function of temperature. It can be seen that both the extraordinary and the ordinary refractive indices decrease slightly with increasing temperature. This decrease is caused to a large extent by the decrease in the density of the system. The tilt angle which the molecules make with respect to the rubbing direction was also measured as a function of temperature. Up to  $200^\circ\text{C}$  no change in the direction of molecular orientation was observed. The thermo-mechanical properties of the network are shown in Fig. 5 where the dynamic tensile elastic modulus and loss tangent measured at 1 Hz are plotted as functions of temperature. It can be seen that the network has a glass transition temperature of  $80^\circ\text{C}$  above which it becomes rubbery. The sample also shows a strong secondary relaxation peak at around  $10^\circ\text{C}$ . This secondary relaxation has a strong effect on the elastic modulus which shows a rapid increase below this transition. Furthermore, in this figure the large difference in the modulus measured in different directions once again clearly demonstrates the anisotropy of the sample.

The polymer network could not be switched under the influence of the electric field, as opposed to the monomeric samples, showing the effect of the crosslinks. We investigated the dielectric behavior of the network by measuring the dielectric loss and the dielectric constant as functions of frequency at various temperatures. The results are shown in Fig. 6. In this figure no loss peaks can be seen. This indicates that molecular relaxation is absent within this frequency range.

Having shown that the molecular orientation can be frozen in by photopolymerization, we also tried to characterize the dipole orientation within the networks. For this purpose piezoelectricity of the samples was examined. Samples which were 7 mm long and 4.5 mm wide were provided with gold electrodes and subjected to sinusoidally varying strain at 10 Hz and the open field voltage across the samples was measured. In Fig. 7 the peak-to-peak voltage ( $V_p$ ) measured across various samples is plotted as a function of strain in various directions. In this figure it is clear that the samples show piezoelectricity and the potential across the sample increases linearly with applied strain. At a given strain the

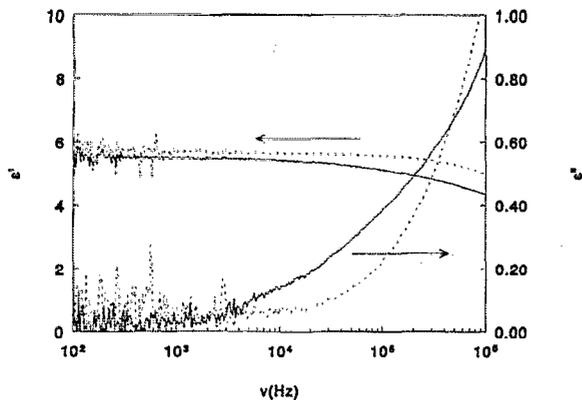


FIG. 6. Dielectric loss and dielectric constant of the anisotropic network as function of frequency measured at various temperatures — =23 °C, ---- =100 °C.

magnitude and the sign of  $V_p$  is highly dependent on the direction of the applied strain. We associate the observed piezoelectricity with the presence of dipole orientation within the system. The fact that at a given strain the sign and the magnitude of the open field voltage depend on the direction of the applied strain indicates that the stress is transferred to the spontaneous polarization in different ways. From the slopes of the curves in Fig. 7 we tried to estimate the piezoelectric coefficient  $d$  in the direction parallel ( $d_y$ ), perpendicular ( $d_z$ ), and in the rubbing direction ( $d_r$ ) using the equation below<sup>1</sup>

$$d = V \epsilon_0 \epsilon A_e / t E \gamma A_c \quad (1)$$

where  $V$  is the open circuit voltage,  $\epsilon_0$  the permittivity of free space,  $\epsilon$  is the dielectric constant,  $A_e$  the active area of the electrode,  $t$  the sample thickness,  $E$  is the tensile modulus in the direction of applied strain  $\gamma$ , and  $A_c$  is the cross sectional area of the sample. The piezoelectric coefficients in various directions were calculated to be  $d_y = 29$  pC/N,  $d_z = 8$  pC/N, and  $d_r = -2$  pC/N. The behavior observed here is different than the behavior observed for the plasticized anisotropic network we studied before.<sup>16</sup> In the previous study the magnitude of the piezoelectric coefficient and the open field volt-

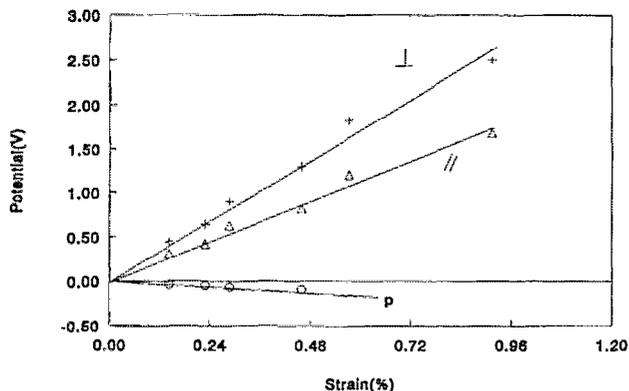


FIG. 7. Open field voltage measured across the anisotropic network as a function of strain applied in various directions. // = in the direction parallel,  $\perp$  = perpendicular to the molecular orientation,  $P$  = in the direction of rubbing.

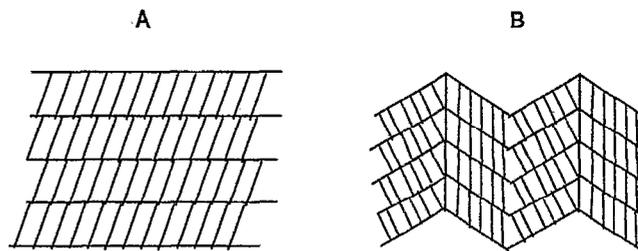


FIG. 8. Various geometries of smectic layer orientation with spontaneous polarization.

age were found to be higher when the strain was applied in the direction of the molecular orientation than in the direction perpendicular to the molecular orientation, showing the opposite behavior to what is observed here.

Furthermore, if the values observed here can be compared with the frequently quoted value of  $d = 29$  pC/N<sup>-1</sup> for the  $\beta$  phase of PVDF with a  $P_s = 13$   $\mu\text{C}/\text{cm}^2$ , assuming that the spontaneous polarization of 130 nC/cm<sup>2</sup> observed in the monomeric state is frozen in during the photopolymerization process, it can be deduced that in the present system the transfer of the force to the dipole orientation within the system is more effective than in that of PVDF with a much higher  $P_s$  as the piezoelectric constants observed for both systems are very similar. These effects are probably the direct result of the presence of the crosslinks within the system which effectively transfer the applied stress to the molecular orientation as well as the layered structure which is present in the chiral smectic  $C$  phase. In Fig. 8 various orientations satisfying the  $S_c$  conditions and having the dipole orientation in the same direction are shown. In this figure two extreme cases satisfying the chiral smectic- $C$  conditions where the molecules are confined in planes parallel to the substrates are shown. In the bookshelf geometry the smectic layers are oriented perpendicular with respect to the rubbing direction whereas the molecules are oriented at an angle. In the second case, the smectic layers are oriented at an angle with respect to the rubbing direction, whereas the molecules are oriented in two different directions [Fig. 8(b)]. We used x-ray diffraction in order to characterize the microscopic structure within the networks. The diffraction pattern obtained for a sample placed flat on to a horizontal x-ray beam is shown in Fig. 9. In this figure several orders of a small angle peak and two wide angle peaks are present. This indicates the presence of the bookshelf structure within the sample [Fig. 8(a)]. This microstructure is different than the microstructure of the anisotropic plasticized network we described in our previous study<sup>16</sup> where the chevron structure (and a different piezoelectric behavior) was observed. This again indicates the importance of the microstructure within the networks with dipolar orientation for their piezoelectricity. Using this diffraction pattern we also estimated the tilt angle that the molecules make with respect to the layer normal to be 22°. This is smaller than the value of 29° measured using optical means in a thin cell. The difference observed here can be associated with the nonplanar but slightly tilted orientation of the molecules with respect to the surfaces.

Finally we would like to show that the ferroelectric sys-

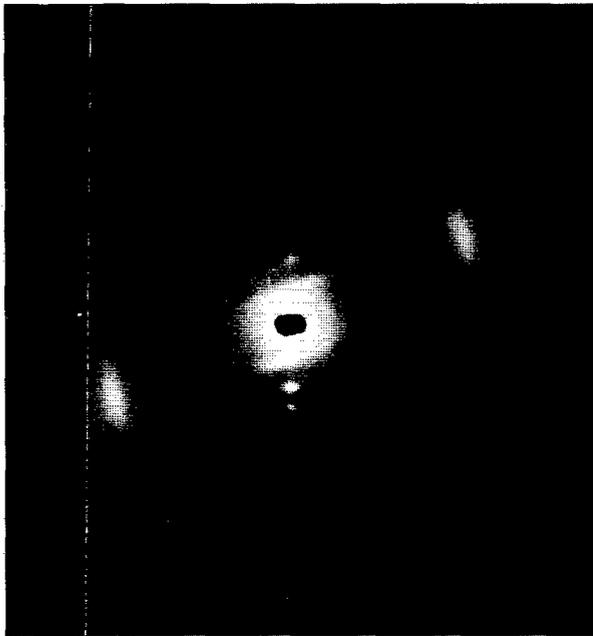


FIG. 9. X-ray diffraction photo of the anisotropic network.

tem can easily be polymerized in a patternwise way. Such a patternwise oriented network can have optical as well as electrical applications such as pyro and piezo detectors. Such a network with a patternwise orientation was obtained by locally applying electric fields in opposite directions. The photo of the network placed between crossed polarizers is shown in Fig. 10. The areas where spontaneous polarization

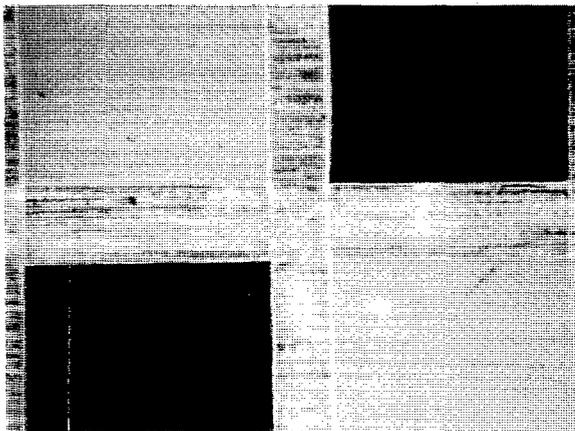


FIG. 10. Photo of a patterned anisotropic network obtained between crossed polarizers.

is present appear either dark or bright. In the dark areas the molecules are oriented parallel to one of crossed polars whereas in the bright areas the molecules are oriented at an angle of  $30^\circ$  with respect to one of the polars. In the grey areas no electric field was present during polymerization and they have no macroscopic dipole orientation. In these areas the molecules are oriented in the rubbing direction.

#### IV. CONCLUSIONS

Low-mass reactive ferroelectric acrylate mixtures containing reactive diacrylate and monoacrylate moieties can be produced. Macroscopic molecular orientation in the monomeric mixture was induced with ease using a simple surface treatment. Applying an electric field across the sample leads to the alignment of ferroelectric polarization. In this state, polymerization of the system could be initiated, freezing in the macroscopic order. The networks showed high optical and mechanical anisotropy in a very wide temperature range. Dipolar orientation within the system was characterized by measuring the piezoelectricity of the samples. The open field voltage measured across the samples showed a linear dependence on the applied strain. The slope depended on the direction of the applied strain. This behavior is associated with the microstructure within the system which determines the effectiveness of transferring the applied strain to dipole orientation. It was also demonstrated that the orientation in such films can be made to be patternwise and thus suitable in sensor applications where patterning is required.

- <sup>1</sup>R. Hayakawa and Y. Wada, *Advances in Polymer Science* (Springer, Berlin, 1973), Vol. 11, see also the references therein.
- <sup>2</sup>K. D. Singer, M. G. Kuzyk, and J. E. Sohn, *J. Opt. Soc. Am. B* **4**, 968 (1987).
- <sup>3</sup>D. J. Williams, *Nonlinear Optical Properties of Organic and Polymeric Materials*, Washington, 1983, ACS Symp. Ser. No. 233.
- <sup>4</sup>K. Kimura and H. Ohigashi, *Appl. Phys. Lett.* **43**, 834 (1983).
- <sup>5</sup>E. Fukada, M. Date, and N. Hirai, *Nature* **211**, 1079 (1966).
- <sup>6</sup>R. Zentel and B. Martin, *Advanced Materials* **6**, 598 (1994).
- <sup>7</sup>G. Scherowsky, U. Muller, J. Springer, W. Trapp, A. M. Levelut, and P. Davidson, *Liquid Cryst.* **5**, 1297 (1989).
- <sup>8</sup>T. Sekiya, K. Yuasa, S. Uchida, S. Hachiya, K. Hashimoto, and K. Kawasaki, *Liquid Cryst.* **14**, 1255 (1993), see also the references therein.
- <sup>9</sup>K. J. Humphery, G. M. Garner, and R. W. Whatmore, *Ferroelectrics* **76**, 383 (1987).
- <sup>10</sup>D. M. Walba, M. D. Wand, W. N. Thurmes, K. M. Moray, and K. E. Arnett, *Polymer Preprints* **34**, 697 (1993).
- <sup>11</sup>T. Richardson, *Chem. Br.*, p. 1218 (1989), and the references therein.
- <sup>12</sup>D. J. Broer, R. A. M. Hikmet, and G. Challa, *Makromol. Chem.* **190**, 3202 (1989).
- <sup>13</sup>D. J. Broer, G. N. Mol, and G. Challa, *Makromol. Chem.* **190**, 59 (1991).
- <sup>14</sup>R. A. M. Hikmet and J. Lub, *Maassen van den Brink, Macromolecules* **25**, 4194 (1992).
- <sup>15</sup>R. A. M. Hikmet and B. H. Zwerver, *Mol. Cryst. Liq. Cryst.* **200**, 197 (1991).
- <sup>16</sup>R. A. M. Hikmet, *Macromolecules* **25**, 5759 (1992).
- <sup>17</sup>R. A. M. Hikmet, *Adv. Mater* **4**, 679 (1992), and the references therein.
- <sup>18</sup>R. A. M. Hikmet and R. Howard, *Phys. Rev. E* **48**, 2752 (1993).