

Preparation of Thin Films with Well-defined Molecular Orientation of Chromophores by Polymerization of Liquid Crystalline Monomers in an Electric Field

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Mixtures of mono- and di-acrylates showing a nematic phase are polymerized in an electric field to make thin films with homotropic molecular orientation; the orientation of chromophores in the thin films depends on the direction of the dipole moment of the liquid crystalline monoacrylates.

Several studies have recently been reported on polymer films with anisotropic molecular alignment in relation to the bulk polymerization of liquid crystalline (LC) monomers such as acrylate, methacrylate, vinyl ether and epoxide derivatives.¹⁻¹⁴ Broer and coworkers,⁵⁻¹⁰ Hikmet *et al.*,^{11,12} and Braun *et al.*¹³ have reported that highly cross-linked, anisotropically oriented films could be obtained by photopolymerization of difunctional LC monomers on a substrate with a rubbing treatment to obtain a unidirectional orientation. Hoyle and co-workers described anisotropic network formation by photopolymerization of LC monomers in a low-strength magnetic field, and studied the effect of the magnetic field on the order parameter of polymer thin films with anisotropic networks.¹⁴ However, polymerization on rubbed substrates as well as in a magnetic field gives only polymer thin films with a centrosymmetric orientation of the mesogenic molecules. The orientation of LC molecules can be influenced not only by a magnetic field, but also by an electric field. We report here the effect of an electric field on the molecular orientation of polymer thin films obtained by polymerization of LC monomers.

4-Acryloyloxy-4'-X azobenzenes, where X = cyano (CAzAc), nitro (NAzAc) and methoxy (MAzAc) groups, were synthesized by a conventional azo coupling reaction. In addition, a difunctional LC monomer, A6P6A, was synthesized according to a method reported previously.⁷ All mono- and difunctional LC monomers showed a nematic phase as the liquid crystalline phase. Samples for polymerization were composed of 50 mol% azobenzene LC monomer and 50 mol% A6P6A. A thermal radical initiator, 1,1'-azobis(cyclohexane-1-carbonitrile) was added to the LC monomer mixtures at a concentration of 1 mol%. The phase transition temperatures of the LC monomer mixtures are given in Table 1. Samples for polymerization in the electric field were prepared by melting the LC monomer mixtures at around 110 °C and injecting them into a cell consisting of two parallel indium-tin oxide (ITO) glass plates coated with polyimide, and rubbed together to obtain homogeneous parallel alignment. The cell gap was 5 µm and the area of the ITO electrode was 10 × 10 mm. No significant polymerization occurred during injection of the LC monomer mixtures into the ITO glass cell, maintained at *ca.* 110 °C. Polarized optical microscope observations with crossed polarizers revealed that the LC monomers were aligned in the plane of the ITO glass plate in a direction parallel to the rubbing treatment in the nematic phase. In addition, the CAzAc-A6P6A and NAzAc-A6P6A mixtures, in the region of the ITO electrode between crossed polarizers, became dark after application of a constant electric field to the nematic phase,

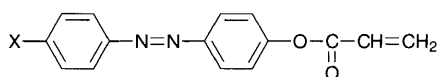
while the MAzAc-A6P6A mixture did not. This implies that the CAzAc-A6P6A and NAzAc-A6P6A mixtures were aligned out of the plane of the ITO glass plate. That is, they were oriented parallel to the direction of the electric field. After polymerization at 140 °C (nematic phase) for 30 min in a constant electric field of 10 V µm⁻¹, the sample was allowed to cool to room temperature while still in the electric field.

Fig. 1 shows the polarized optical micrographs of the thin films obtained by polymerization of the LC monomer mixtures in the ITO glass cell. The upper half of each figure was obtained by polymerization in the electric field, and the lower half was obtained without the electric field. Although a partial dark region was observed in the thin film obtained for the NAzAc-A6P6A mixture in the electric field, both the NAzAc-A6P6A and MAzAc-A6P6A mixtures showed a birefringent texture which was related to the molecular alignment in the plane of the ITO glass plate. Consequently, the thin films obtained for the NAzAc-A6P6A and MAzAc-A6P6A mixtures in the electric field were bright between the crossed polarizers. On the other hand, the thin film obtained for the CAzAc-A6P6A mixture in the electric field was found to be dark between the crossed polarizers. To reveal the orientation of the mesogenic chromophores in the thin films, the polarized absorption spectra were measured. Fig. 2 shows the polarized absorption spectra of the thin film obtained for the CAzAc-A6P6A mixture, both with and without the electric field. The thin film obtained without the electric field showed a larger absorbance parallel to the direction of the rubbing than in the perpendicular direction. This is due to formation of an anisotropic gel network along the direction of the rubbing.⁵ On the other hand, no difference in the absorbance parallel and perpendicular to the direction of the rubbing was observed for the thin film obtained in the constant electric field. These results demonstrate the formation of a polymer thin film with homeotropic orientation. That is, a uniform molecular orientation perpendicular to the surface of

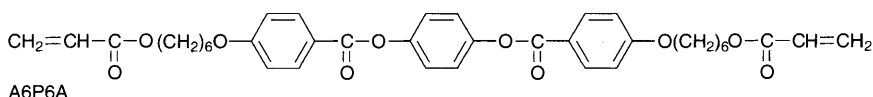
Table 1 Phase transition temperature of XAzAc-A6P6A (50:50 mol%) with a radical initiator [X = CN (CAzAc), NO₂ (NAzAc) or MeO (MAzAc)]

XAzAc	Phase transition temperatures					
	K	99 °C	N	150 °C	I	
CAzAc	K	99 °C	N	150 °C	I	
NAzAc	K	94 °C	N	148 °C	I	
MAzAc	K	84 °C	X ^a	95 °C	N	142 °C I

^a The phase was composed of crystalline and liquid crystalline phases.



X = CN (CAzAc), NO₂ (NAzAc), CH₃O (MAzAc)



A6P6A

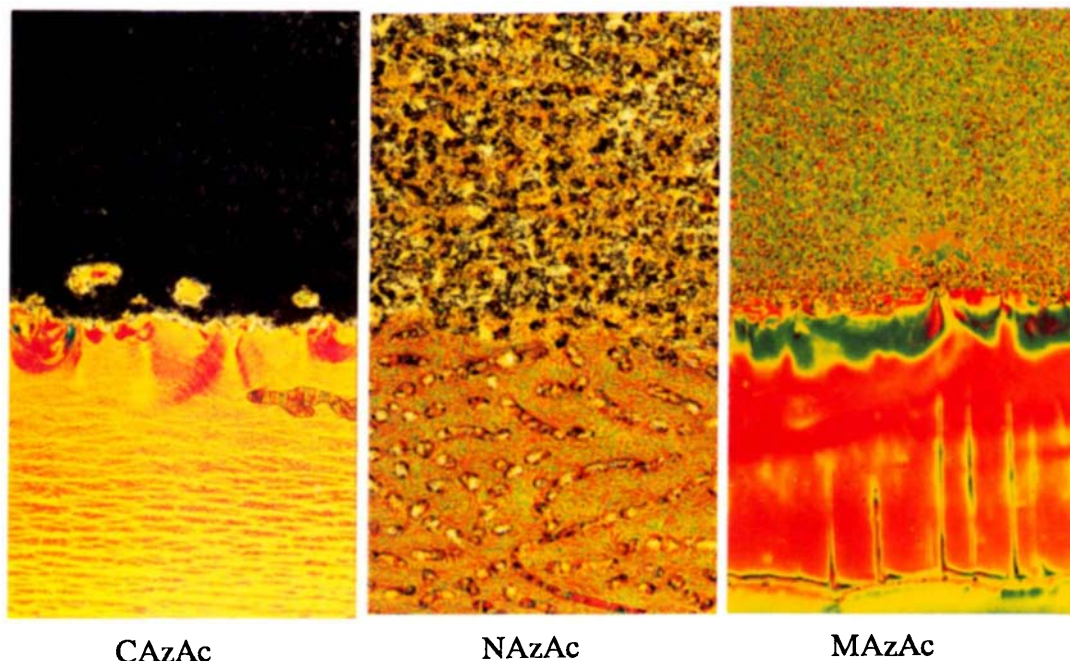


Fig. 1 Polarized optical micrographs of the thin films obtained by polymerization of the CAzAc–A6P6A, NAzAc–A6P6A and MAzAc–A6P6A mixtures in the ITO glass cell. The upper half of the figures was obtained by polymerization in the constant electric field of $10 \text{ V } \mu\text{m}^{-1}$, and the bottom half was obtained without the electric field.

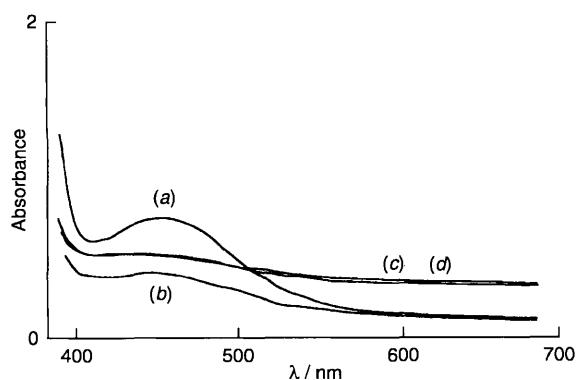
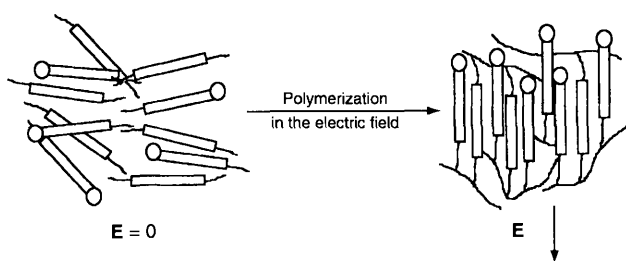


Fig. 2 Polarized absorption spectra of the thin films obtained by polymerization of the CAzAc–A6P6A mixture without the electric field [curves (a) and (b)] and in a constant electric field of $10 \text{ V } \mu\text{m}^{-1}$ [curves (c) and (d)]. [(a) and (c), polarized parallel to the rubbing direction, (b) and (d), polarized perpendicular to the rubbing direction].

the thin film was achieved by polymerization of the CAzAc–A6P6A mixture in a constant electric field as depicted in Fig. 2.

Computer simulation based on the PM3 semi-empirical method¹⁵ reveals that the dipole moment of both CAzAc and

NAzAc is oriented parallel to the long axis of the molecules, while that of MAzAc is oriented approximately perpendicular to the long axis. In addition, the conversion of the CAzAc–A6P6A and MAzAc–A6P6A mixtures to polymer was greater than 80%, while that of the NAzAc–A6P6A mixture was less than 50%. The direction of the dipole moment, as well as the higher conversion of CAzAc, resulted in the formation of the thin film with homeotropic orientation of the mesogenic chromophores.

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