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Preparation and structure of polymer networks by polymerization of liquid crystalline monomers in DC electric field

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Mixtures of mono- and diacrylates showing liquid crystalline (LC) phases were polymerized in a DC electric field. The orientation of chromophores in polymer networks depended on the direction of dipole moment as well as the polymerization conversion of the LC monomers. The polymer networks with selective molecular orientation parallel or perpendicular to the network substrate were obtained by polymerization of LC monomers with or without the DC electric field. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: liquid crystalline monomers; anistropic polymer network; DC electric field)

INTRODUCTION

Several studies have recently been reported on polymer films with anisotrople molecular alignment in relation to the bulk polymerization of liquid crystalline (LC) monomers such as acrylate, methacrylate, vinyl ether, and epoxide derivatives[1–14]. Anisotropically oriented films could be obtained by polymerization of LC monomers on the substrate with rubbing treatment to obtain a unidirectional orientation or a low-strength magnetic field. We have also reported the preparation of polymer films with anisotropic molecular alignment by polymerization of LC monomers having diene moieties on the substrate with rubbing treatment[15,16].

On the other hand, it is well known that the orientation of low molecular weight LC molecules corresponds not only to the magnetic field, but also to an electric field. Ober *et al.* have reported the preparation of the polymer networks in an AC electric field[17]. However, we reported that the anisotropically oriented films could be prepared easily by polymerization of LC monomers in DC electric field[18]. The ability of the director to align along the DC electric field is due to the electric nature of the LC molecules. Permanent electric dipoles result when one end of a molecule has a net positive charge while the other end has a net negative charge. When the DC electric field is applied to the liquid crystal, the dipole molecules tend to orient themselves along the direction of the field. Therefore, the polymerization in the DC electric field is considered a useful method to control the molecular orientation in the polymer networks. Thus, the polymerization provides the polymer networks with selective molecular orientation, parallel or perpendicular to the network substrates, by switching the DC electric field. Polymer networks with spatially selective molecular orientations are expected to be a suitable, e.g. optical materials such as optical waveguide microdevices and optical compensators. We report here the bulk-polymerization of azobenzene derivative LC monomers in a DC electric field, and investigate the molecular orientation in the polymer networks.

EXPERIMENT

Materials

Figure 1 shows the acrylate compounds and radical initiator used in this study. To a solution of 10.6 g (90 mmol) of 4-cyanoaniline in 250 mL of 50 vol% sulfuric acid was added dropwise a solution of 6.2 g (90 mmol) of sodium nitrite in 60 mL of water at such a rate that the temperature did not exceed 5°C. At the same temperature, a solution of 9.4 g (100 mmol) of phenol in 150 mL of 2 N sodium hydroxide was added slowly to the resulting diazonium salt solution. After stirring for 2 h at room temperature, a precipitate was filtered and washed with water until the wash water became neutral. The precipitate was suspended in a 50 vol% ethanol, and was acidified with concentrated hydrochloric acid to afford 12 g (60%) of 4-cyano4′-hydroxyazobenzene. To a mixture of 9.1 g (41 mmol) of 4-cyano-4′-hydroxyazobenzene and 4.3 g (43 mmol) of triethylamine in 100 mL of tetrahydrofuran, 3.9 g (43 mmol) of acryloylchloride was added at 60°C. The mixture was brought to ambient temperature, and after stirring for 72 h, 300 mL of chloroform was added. Subsequently, the organic layer was washed with water, and dried over magnesium sulfate. Purification was carried out by column chromatography on silica gel using chloroform as an eluent, followed by recrystallization from a mixture of ethanol/acetone (6/1) to give 4.6 g (41%) of 4-acryloyloxy-4′-cyanoazobenzene (abbreviated as CA). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 6.2–6.8 (3H, vinyl), 7.4–8.2 (8H, aromatic). IR (KBr, cm^{-1}): 1740 ($\upsilon_{C=O}$), 2320 (υ_{CN}). Elemental analysis: calculated for $C_{16}H_{11}N_3O_2$, C 69.3, H 3.99, N 15.2; found, C 69.1, H 3.99, N 15.4. Other azobenzene acrylates with methoxy (MA) and nitro (NA) groups at the 4′ position were prepared in the same manner as CA.

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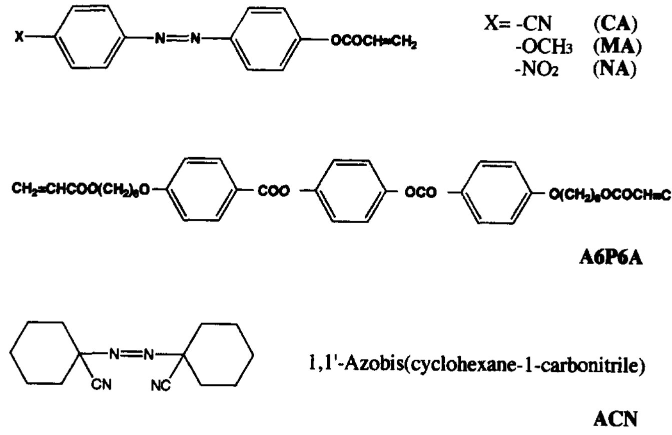


Figure 1 The structure of the liquid crystalline monomers and radical initiator

Data for MA: ^{1}H n.m.r. ($\mathrm{CDCl_3}$,) δ (ppm): 3.8 (3H, methyl), 5.9–6.8 (3H, vinyl), 6.8–7.9 (8H, aromatic). IR (KBr, cm^{-1}): 1730 ($\upsilon_{C=O}$). Elemental analysis: calculated for $C_{16}H_{14}N_2O_3$, C 68.1, H 4.99, N 9.93; found, C 67.6, H 5.11, N 9.76. Data for NA: ^{1}H n.m.r. ($\mathrm{CDCl_3}$,) δ (ppm): 6.0–6.8 (3H, vinyl), 7.3–8.5 (8H, aromatic). IR (KBr, cm^{-1}): 1340, 1540 (υ_{NO}), 1730 ($\upsilon_{C=O}$). Elemental analysis: calculated for $C_{15}H_{11}N_3O_4$, C 60.6, H 3.73, N 14.1; found, C 60.5, H 3.89, N 14.2.

Diacrylate compound, A6P6A, was synthesized according to the method reported previously[10]. ^{1}H n.m.r. ($\mathrm{CDCl_3}$,) δ (ppm): 1.2–2.0 (16H, methylene), 3.8–4.2 (8H, methylene), 5.6–6.6 (6H, vinyl), 6.8–8.2 (12H, aromatic). IR (KBr, cm^{-1}): 1725 ($\upsilon_{C=O}$). Elemental analysis: calculated for $C_{38}H_{42}O_{10}$, C 69.3, H 6.43; found, C 67.6, H 6.47. The thermal radical initiator, 1,1′-azobis(cyclohexane-1-carbonitrile) (ACN) was purchased from Wako Pure Chemical Industries.

Mixtures of azobenzene monomers and A6P6A were prepared as follows. Each azobenzene monomer and A6P6A were dissolved in chloroform. After nitrogen was introduced into the resulting chloroform solutions, chloroform was evaporated under a nitrogen atmosphere. For making the polymerization samples, the thermal radical initiator, ACN, was added to the monomer mixtures at a concentration of 1 mol%.

Thermotropic properties

Thermal phase transition behaviour of three azobenzene monomers, A6P6A and their mixtures was examined by means of differential scanning calorimetry (DSC, Seiko I&G SSC-5020) and polarizing microscopic observation (Olympus BHSP polarizing microscope; Mettler FP80 and FP82 hot stage and controller). The peak temperatures obtained by DSC measurements were taken as the phase transition temperatures.

Bulk thermal polymerization

Into two glass plates, 2 mg of each LC monomer mixture containing 1 mol% of ACN was loaded, and was heated at various temperatures for prescribed time. After polymerization, the sample was removed from the glass plates and was subjected to gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF-80M + KF-SOM; eluent, tetrahydrofuran). The conversion of mixtures was determined by measuring the residual amount of monomers in the samples after polymerization because of insolubility of samples due to cross-linking with the difunctional LC monomer, A6P6A.

Samples for polymerization in DC electric field were prepared by melting the monomer mixtures at around 105°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. The ITO glass cell containing each monomer mixture was connected to a DC power supply, and was heated at various temperatures for 30 min.

Electrooptic measurement

The ITO glass cell containing each LC monomer mixture without ACN was thermostated, placed between two crossed polarizers, and connected to the DC power supply. A laser diode (670 nm, 10 mW) was used as an analysing light source. The polarizing direction was set at an angle of 45° with respect to the rubbing direction of the cell. The change in transmittance of the light of the laser diode was measured with a photodiode.

RESULTS AND DISCUSSION

Thermotropic properties

The thermotropic properties are given in *Table 1*. Either a schlieren or marbled texture was observed for the azobenzene monomers. Results based on the DSC measurements and polarizing microscopic observation reveal that three azobenzene monomers show a nematic phase as the LC phase. A6P6A shows only the nematic phase on heating, while smectic C (S_C) phase as well as the nematic phase are observed on cooling. The phase transition temperatures from the nematic phase to the isotropic phase of the azobenzene monomers were much higher than 100°C, at which temperatures the polymerization took place during injecting the molten azobenzene monomers containing ACN into the ITO glass cell. The difunctional LC monomer, A6P6A, was used as a LC cross-linking agent to fix the

Table 1 Thermotropic properties of the LC monomers

Phase transition temperature (°C)								
CA	K	141	N	167	I			
NA	K	133	N	144	I			
MA	K	99	N	117	I			
A6P6A[a]	K	107	N	148	I			
A6P6A[b]	K	75	Sc	80	N	145	I	

[a] On heating
[b] On cooling

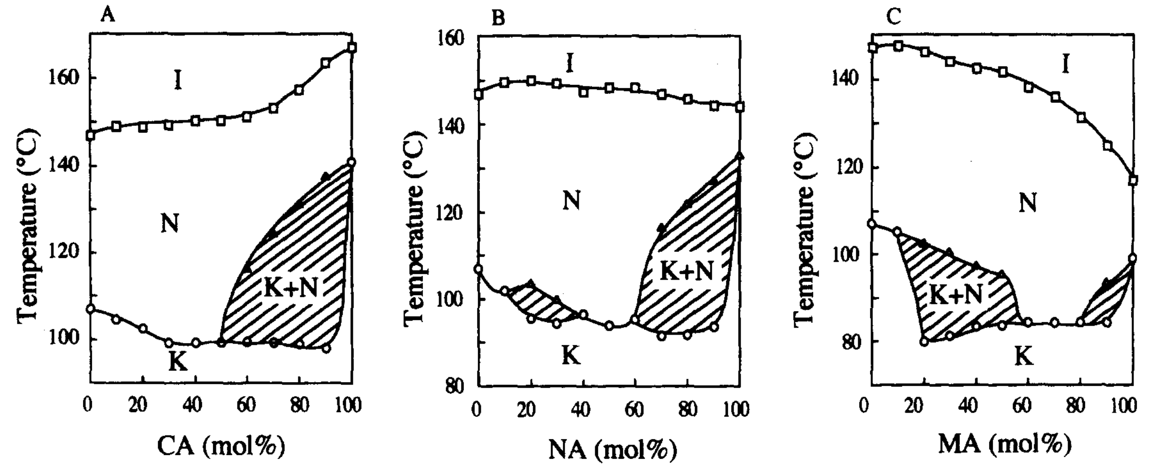


Figure 2 Binary phase diagrams of the monomer mixtures. A, CA/A6P6A; B, NA/A6P6A; C, MA/A6P6A; K, crystalline phase; N, nematic phase; I, isotropic phase

molecular orientation of the LC azobenzene chromophores. In addition, the phase transition temperature of A6P6A was lower than those of the azobenzene monomers, CA and NA. In order to lower the phase transition temperature, therefore, the eutectic mixtures composed of each azobenzene monomer and A6P6A were prepared. *Figure 2* shows the binary phase diagrams for the mixtures of each azobenzene monomer and A6P6A. Although the melting point of the azobenzene monomers from the crystalline phase to the nematic phase was decreased by doping of A6P6A, the phase composed of crystalline phase and nematic phase was observed. Consequently, the mixtures of 50 mol% of each LC azobenzene monomer and 50 mol% of A6P6A were used for polymerization in the DC electric field. The mixtures are abbreviated as X/A6P6A, where X is the LC azobenzene monomers, CA, MA and NA.

Figure 3 shows the changes in transmittance of the three X/A6P6A mixtures as a function of the applied DC voltage at 140°C, at which temperature all mixtures exist in the nematic phase. The transmittance remained nearly constant by application of the DC voltage up to 30 V/5 μm, while it decreased steeply above this voltage. The polarized microscopic observation revealed that the LC monomers were aligned in the plane of the ITO glass plate in a direction parallel to the rubbing in the nematic phase without DC electric field. The CA/A6P6A and NA/A6P6A mixtures, in the region of the ITO electrode between crossed polarizers, became dark by application of the DC electric field higher than 30 V/5 μm to the nematic phase, while the MA/A6P6A mixture did not. Computer simulation based on the PM3 semi-empirical method[19] revealed that the dipole moment of both CA and NA is oriented nearly parallel to the long axis of the molecules. The estimated values of the dipole moment are 6.0 and 8.2 D for CA and NA, respectively. Although Hikmet *et al.* have reported that the dielectric anisotropy of A6P6A is negative[20], the dielectric anisotropy of the C A/A6P6A and NA/A6P6A mixtures might be positive due to the direction and higher

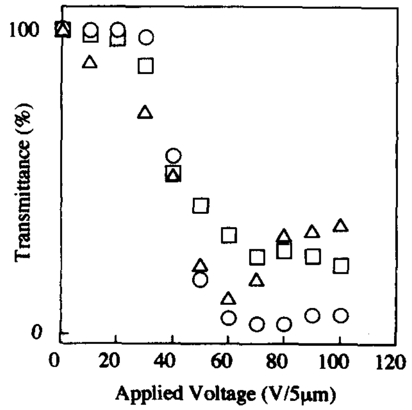


Figure 3 Changes in the transmittance of the monomer mixtures in the ITO glass cell by application of DC electric field. ○ CA/A6P6A; □ NA/A6P6A; △ MA/A6P6A

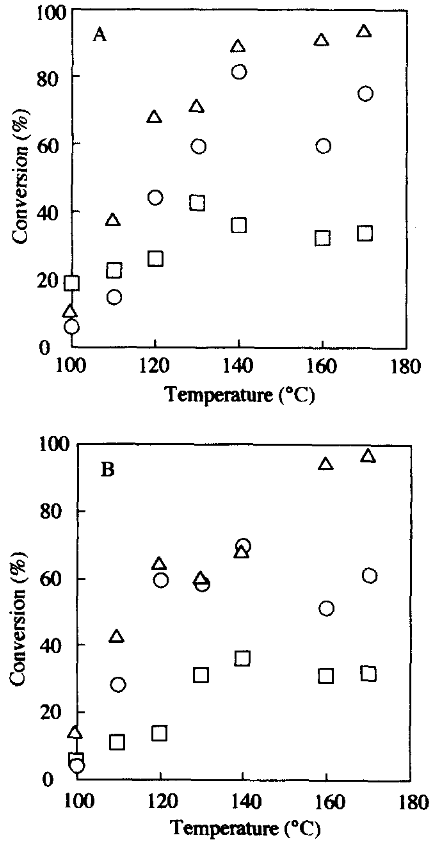


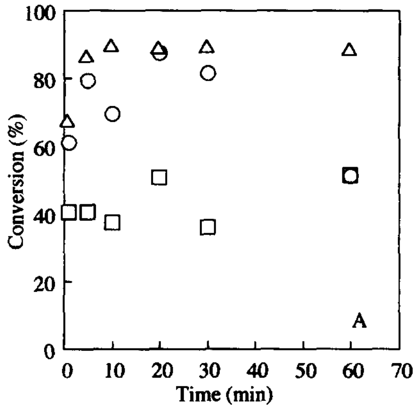
Figure 4 Temperature dependence of the conversions of the azobenzene monomers (A) and A6P6A (B) in the monomer mixtures. The bulk polymerization was carried out for 30 min. ○ CA/A6P6A; □ NA/A6P6A; △ MA/A6P6A

values of dipole moment of CA and NA molecules. Thus, the CA/A6P6A and NA/A6P6A mixtures were aligned out of the plane of the ITO glass plate by application of the DC electric field, that is, they were oriented parallel to the direction of the DC electric field. On the other hand, the dipole moment of MA is oriented approximately perpendicular to the long axis of the MA molecule and the value of the dipole moment was 2.4 D. Thus, the dielectric anisotropy of the MA/A6P6A mixture is expected to be negative. Therefore, the decrease in the transmittance may be interpreted in terms of an electro-hydrodynamic instability (Carr Helfrich effect) due to the negative dielectric anisotropy of the MA/A6P6A mixture[21].

Polymerization of LC monomer mixtures

Figure 4 shows the temperature dependence of the conversions of the azobenzene monomers (A) and A6P6A (B), respectively. The polymerization was performed for 30 min at various temperatures without the DC electric field. No significant polymerization occurred in the crystalline phase, while the conversion increased with increasing temperature in both the nematic and isotropic phases. However, the conversion of the NA/A6P6A mixture was much lower than others over the temperature range studied. It is known that the nitro group retards the radical polymerization. The retardation effect of the nitro group resulted in the depression of the conversion of the NA/A6P6A mixture.

Time courses of the conversions of the LC monomers are shown in *Figure 5*. The polymerization was preformed at 140°C without the DC electric field. The initial polymerization rates of both the CA/A6P6A and MA/A6P6A mixtures were much higher than that of the NA/A6P6A mixture. The result is also related to the retardation effect of the nitro group. In addition, the conversion became almost constant after a few tens of minutes. The decomposition rate (k_d) of ACN is approximately one-tenth of 2,2'-azo-bis-isobutyronitrile (AIBN)[22]. Based on the k_d of AIBN at 140°C, the k_d of ACN may be expected to be of the order of 10^{-2} [s^{-1}] at 140°C in the polymerization conditions, although the k_d of ACN was not be determined. Therefore, the decomposition of ACN was almost completed after 10 min. The time dependence of the conversion can be explained as a result of the decomposition rate of ACN at 140°C.



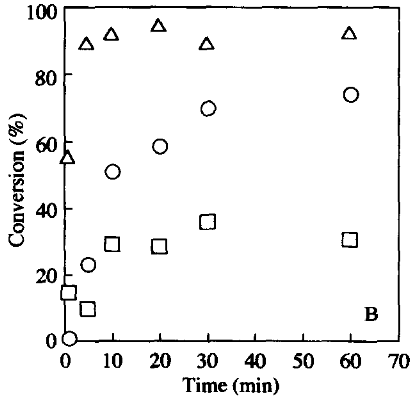


Figure 5 Time courses of the conversions of the azobenzene monomers (A) and A6P6A (B) in the monomer mixtures. The bulk polymerization was carried out at 140°C. ○ CA/A6P6A; □ NA/A6P6A; △ MA/A6P6A

Figure 6 shows the polarized optical micrographs of the polymer networks obtained by polymerization of the three LC monomer mixtures in the ITO glass cell at 140°C for 30 min. The upper half of each figure was obtained by polymerization in the DC electric field of 50 V/μm, and the lower half was obtained without the DC electric field. Although a partial dark region was observed in the polymer network for the NA/A6P6A mixture in the DC electric field, the most part was the crystalline domain both with and without the DC electric field. This is attributed to the retardation effect of the nitro group, resulting in lower polymerization conversion. Uniaxially molecular orientation in the polymer networks was observed for both the CA/A6P6A and MA/A6P6A mixtures by polymerization without the DC electric field. However, the polymerization of the MA/A6P6A mixture in the DC electric field gave the polymer network having multi-domain structure. The hydrodynamic instability of the MA/A6P6A mixture in the DC electric field caused the formation of multi-domain structure. However, the polymer network obtained for the CA/A6P6A mixture in the DC electric field was found to be dark between the crossed polarizers.

To clarify the orientation of the mesogenic chromophores in the networks in detail, the polarized absorption spectra were measured. *Figure 7* shows the polarized absorption spectra of the polymer networks for the three LC monomer mixtures. The polymer networks obtained without the DC electric field for all samples showed a larger absorbance parallel (curve 1) to the direction of the rubbing compared to those in the perpendicular direction (curve 2). This is due to the formation of anisotropic polymer networks along the direction of the rubbing without the DC electric field. In particular, the network for the MA/A6P6A mixture exhibited a larger difference in absorbance parallel and perpendicular compared to those for others. The polymerization conversion of the MA/A6P6A mixture was highest among the three samples. The polymerization conversion is

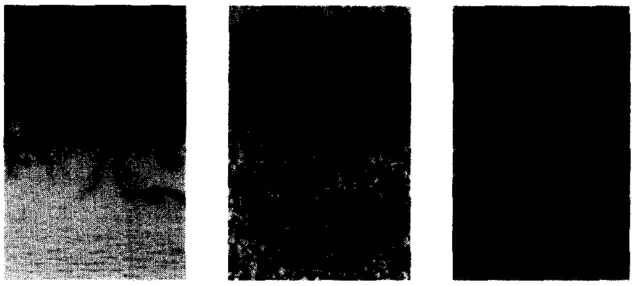


Figure 6 Polarized optical micrographs of the polymer networks obtained by polymerization of the monomer mixtures in the ITO glass cell. The upper half of each figure was obtained by polymerization in the DC electric field of 50 V/μm, and the bottom half was obtained without an electric field

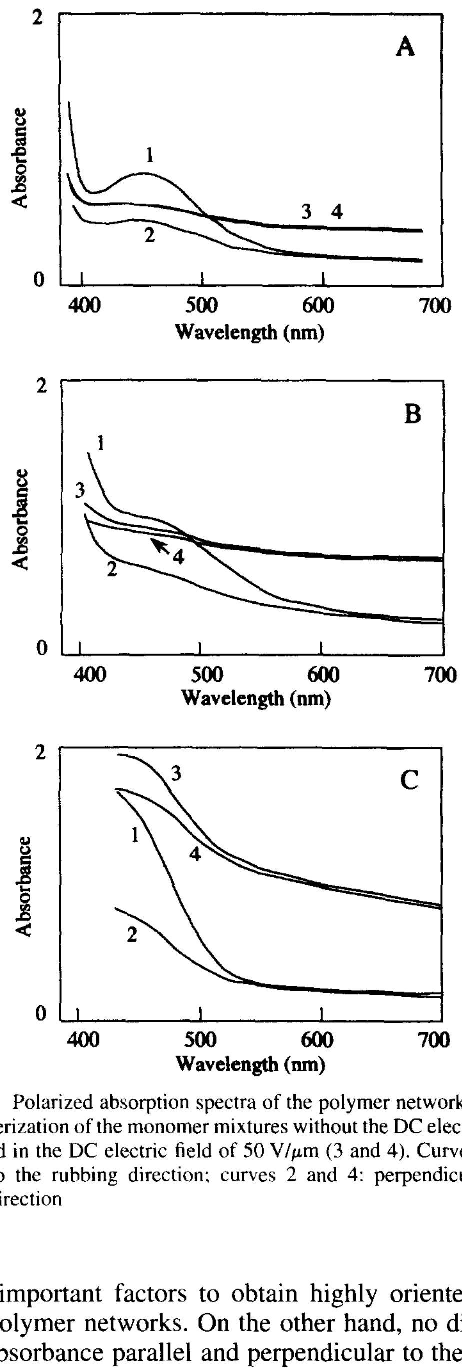


Figure 7 Polarized absorption spectra of the polymer networks prepared by polymerization of the monomer mixtures without the DC electric field (1 and 2) and in the DC electric field of 50 V/μm (3 and 4). Curves 1 and 3: parallel to the rubbing direction; curves 2 and 4: perpendicular to the rubbing direction

one of important factors to obtain highly oriented anisotropic polymer networks. On the other hand, no difference in the absorbance parallel and perpendicular to the rubbing direction was observed for the polymer network obtained by polymerization of the CA/A6P6A mixture in the DC electric field of 50 V/μm. This result demonstrates the formation of a polymer network with homeotropic orientation, namely, a uniform molecular orientation perpendicular to the surface of the polymer substrate was achieved by polymerization of the CA/A6P6A mixture in the DC electric field. Thus, the selective molecular orientation in the polymer networks can be realized by control of the DC electric field. However, the network for the MA/A6P6A showed a significant difference in absorbance. Even in the hydrodynamic instability state, some LC molecules align parallel to the rubbing direction in the vicinity of the glass substrate, because of an anchoring force of the polyimide coat on the glass substrates. In addition, a larger increase in the base line of the network for the MA/A6P6A mixture in the DC electric field was observed with respect to the formation of a multi-domain structure. The polymer network for the NA/A6P6A mixture in the DC electric field shows little difference in the absorbance parallel and perpendicular in a similar way to the CA/A6P6A. The polymer network with selective molecular orientation was obtained for the NA/A6P6A mixture, although the most part was the crystalline domain owing to the lower polymerization conversion.

CONCLUSIONS

Polymerization of the LC monomers in DC electric field was investigated. Preparation of the polymer networks with spatial selective molecular orientation of the LC azo chromophores could be achieved by polymerization of the CA/A6P6A mixture with or without the DC electric field. However, the polymer network with multi-domain structure was obtained for the MA/A6P6A in the DC electric field. The morphology and orientation of the LC chromophores in the polymer networks depended on the direction of the dipole moment as well as the conversion of the LC monomers.

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