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Observation of transient phase separation process of liquid crystal/ polymer composites obtained by photo-polymerization induced-phase separation and their electro-optical properties

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A transient phase separated structure during the photo-polymerization induced-phase separation process of liquid crystal/polymer composites consisting of a continuous phase of nematic liquid crystal and a three-dimensional polymer network was successfully observed by interrupting UV light irradiation for photo-polymerization. Those transient composites were characterized by a difference in temperature for nematic-isotropic transition point (Tn-i) of the liquid crystal phase, a comparison of morphology for polymer phase between an initial stage and the last stage of phase separation, and an electro-optical performance at each period of phase separation process. It was found that the composite even at an initial stage of phase separation showed a transparent-turbid (light scattering) operation with an electric field and the UV irradiation period required to attain the final voltage-transmittance curve accorded well with that to give a saturation of Tn-i of the liquid crystal phase. A schematic diagram for photo-polymerization induced-phase separation process was proposed according to investigation into characteristics of the liquid crystal/polymer composites having a transient phase separated structure.

Key words: *Liquid crystal/polymer composite, Photo-polymerization induced-phase separation, Transient phase structure, Electro-optical property*

1. Introduction

An electro-optical effect showing transparent-scattering of liquid crystal/ polymer composites consisting of nematic liquid crystal and polymer has been widely used for smart windows for architecture application and optical devices by the advantage of high transparency without polarizing plate in transparent state. Kajiyama et al. have first proposed such a composite, which was obtained by phase separation from homogeneous solution comprising liquid crystal and dissolved polymer in common solvent.[1] Craighead et al has reported an electro-optical effect of device using the composite obtained by impregnating liquid crystal into porous polymer film.[2]

The emulsion method, in which multiple micro-droplets comprising nematic liquid crystal were dispersed into polymer matrix, and the polymerization induced-phase separation method, in which liquid crystal is phase-separated during polymerization of low molecular weight curable compound from an isotropic homogeneous solution dissolving liquid crystal into the compound, were proposed to improve the contrast ratio in transparent-scattering characteristics of liquid crystal/polymer composites by Fergason and Doane et al.[3),4)]

Gunjima et al. and Hirai et al. have reported that polymer phase showing a three-dimensional network having a correlation length of several microns was formed in a continuous liquid crystal phase in the

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composite via spinodal decomposition by high speed photo-polymerization induced-phase separation in radical chain photo-polymerization system using acrylic prepolymer.5),6) The bicontinuous phase type composite showed a higher efficiency of light scattering because not only index-mismatching between a liquid crystal droplet and a polymer matrix but also that among adjacent liquid crystal domains were available.7) Besides, it operated with a driving voltage of 10 Vrms(Volt root mean square) or less because smaller area of interface between liquid crystal domain and polymer network led to smaller fraction of liquid crystal molecules of which alignments were fixed at the interface with polymer phase. Kunigita et al. have proposed a projection display which combined projection optics with dot-matrix display panels using the composite driven by TFT and Niiyama et al. have reported hysteresis on electro-optical characteristics and response time in gray scale of device using the composite displaying a moving image.8)-10)

As to the phase-separated structure for a bicontinuous phase type composite, the formation process in theoretical aspect has been precisely investigated by Kyu et al and Nakazawa et al. after the early study by Hirai et al.11)-13) The effects of the polymerization condition such as temperature, intensity of light irradiation and so on in photo-polymerization induced-phase separation process on the phase structure have been studied by Li et al. and the author et al.14) On the other hand, study in real space by an experimental method on the formation process of the phase structure for practical liquid crystal /polymer composites showing a low driving voltage has been limited though several studies through analysis in Fourier space such as diffraction and scattering properties have been reported.15),16) Phase separation process was closely examined in this study through direct observation of the phase structure and electro-optical characteristics for the composites with a transient phase-separated structure obtained by interrupting of UV light irradiation for photo-polymerization after a predetermined period regarding bicontinuous phase type liquid crystal/polymer composite obtained by photo-polymerization induced-phase separation method showing a driving voltage of 10 Vrms or less. This is the first study on direct observation in real space for a phase structure change of the liquid crystal/polymer composite during polymerization process by a non-destructive method.

2. Experiment

2.1 Preparation of liquid crystal/polymer composites

Fig.1 shows the liquid crystal material, the prepolymer and the photo-initiator used in this study. The nematic liquid crystal mixture (LC) was used for the liquid crystal material and the prepolymer (P-A) was prepared as a homogeneous mixture in composition fraction shown in Table 1 which comprises one oligomer having two acryloyloxy groups and two monomers having one acryloyloxy group. Urethane acrylate was used as a reactive oligomer, which was synthesized in a presence of a tin catalyst from 2 mol of 2-hydroxyethylacrylate and 1 mol of isocyanate terminated urethane oligomer synthesized in a presence of the same catalyst from 2 mol of isophorone diisocyanate and 1 mol of poly(propylene glycol) having number average molecular weight of about 1000. The monomer A was a dehydrated compound from acrylic acid and mixed branched isomer of monohydroxy alcohol of which the carbon number was 13 (Tridecanol [mixed branched isomer], Tokyo Kasei Co., Ltd.) and 2-hydroxyethylacrylate was used for the monomer B. Uncured pre-mixture (M-A) was prepared as a homogeneous solution in which benzoin isopropyl ether (BIPE) of 3 wt% to P-A mentioned above was added as a photo-initiator into isotropic solution in which P-A was completely dissolved into liquid crystal in a predetermined amount by heating.

nematic liquid crystal material

Tn-i = 84 ℃, Δn = 0.218, Δε = 12.0, η = 25 mPa·s at 25 ℃

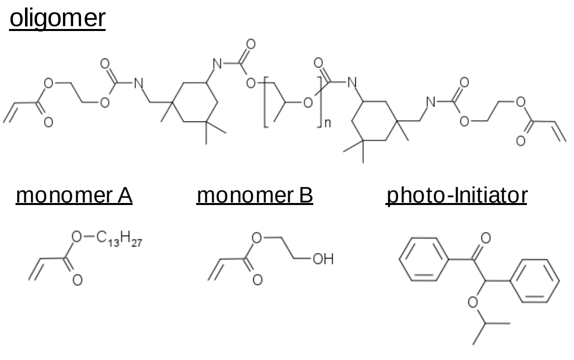

Fig.1 Physical property of liquid crystal material and chemical structures of prepolymer and photo-initiator.

Table 1 Composition of prepolymer mixture (wt%)

Oligomer	Monomer A	Monomer B
51.2	12.2	36.6

Secondly, glass cells used for evaluation of electro-optical characteristics were prepared in such a procedure hereinafter. A pair of glass substrates on which transparent electrodes made of ITO were formed was laminated facing each electrode, having distance between those substrates of 13 μm by resin beads spacers and being sealed by epoxy resin in peripheral portion of the substrate. M-A comprising 65 wt% of nematic liquid crystal was injected into the cell after the M-A was heated to be a homogeneous isotropic solution. P-A in the M-A was polymerized by BIPE during of UV light irradiation for a predetermined period having intensity of 10 mW/cm^2 on both sides of the cell from HgXe lamp having main wavelength of 365 nm after cooling the cell to be at 0.5 °C higher temperature than that at which the liquid crystal segregated from the isotropic solution of the M-A during decreasing temperature in thermostatic chamber, and the liquid crystal/polymer composite was obtained from the M-A by photo-polymerization induced-phase separation.

2.2 Measurement of temperature for nematic-isotropic transition point of liquid crystal phase in transient liquid crystal/polymer composites

The temperature for the nematic–isotropic transition point of the liquid crystal phase in the composite cell was measured by observing the cell sandwiched between a pair of crossed polarizers using bright-field transmission optical microscope (BH-2, Olympus Co., Ltd.) while heating the cell at a heating rate of 1 °C/min by a thermal stage (FP82HT, Mettler-Toledo Inc.).

2.3 Observation for phase structure

The phase structure of the liquid crystal/polymer composite in the cell was observed in a non-destructive method (Observation method A) at 100 °C which was higher temperature than that for the nematic-isotropic transition point of the liquid crystal material used for the composite by transmission bright field optical microscope with a thermal stage.

Secondly, the liquid crystal was extracted from the composite by bicyclohexyl as an extractant via cutting plane of the glass substrate and the composite in the cell during immersion in it at 40 °C for 60 min. The polymer structure was observed (Observation method B) at room temperature by a transmission optical microscope after evaporation of bicyclohexyl in 266 Pa at 80 °C for 60 min.

2.4 Electro-optical characteristics

Electro-optical characteristics of the liquid crystal/polymer composite cell were evaluated at 40 °C in a thermostatic chamber by Schlieren optics having collection angle of 5 degrees shown in Fig.2. The intensity of the transmitted light through the cell was measured by a photo-diode with band-pass filter having center wavelength of 540 nm and half-band width of 20 nm using a halogen lamp as an incident light source. The transmittance was measured on applying ac voltage of 30 Hz in rectangular waveform between the transparent electrodes of the cell with a voltage increasing rate of 10 Vrms/min using a functional generator (3114A, Hewlett-Packard Co.) and a high speed amplifier (4010, NF Corp.) as a power supply for driving.

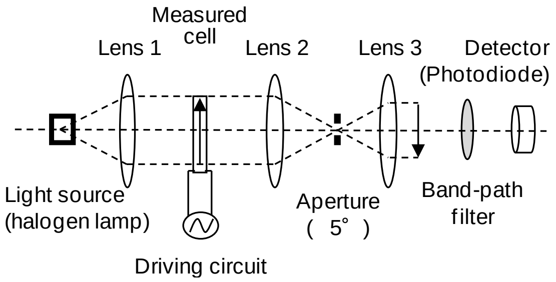

Fig.2 Schematic representation of the measurement system for electro-optical properties of liquid crystal/polymer composite cells using Schlieren optical system.

3. Results and discussion

3.1 Phase diagram of liquid crystal and prepolymer

It is very important to evaluate a phase diagram for a formation of phase-separation structure because the optimum polymerization temperature is determined based on it in polymerization induced-phase separation. Fig.3 shows a phase separation temperature at which M-A becomes turbid by segregation of the liquid crystal from M-A in decreasing temperature and a phase mixing temperature at which the M-A becomes homogeneous state by dissolution of the liquid crystal in M-A in increasing temperature. The intensity of the transmitted light from He-Ne laser as a light source through M-A in clear bottle was measured by a photo-diode for M-A being stirred by magnetic stirrer installed in thermobath, which was controlled in temperature increasing and decreasing rate of 1 °C/min. The segregation temperature (Ts) and the dissolution temperature (Td) correspond to temperatures at which M-A starts to become turbid in decreasing temperature and at which the whole of M-A becomes transparent in increasing temperature, respectively.

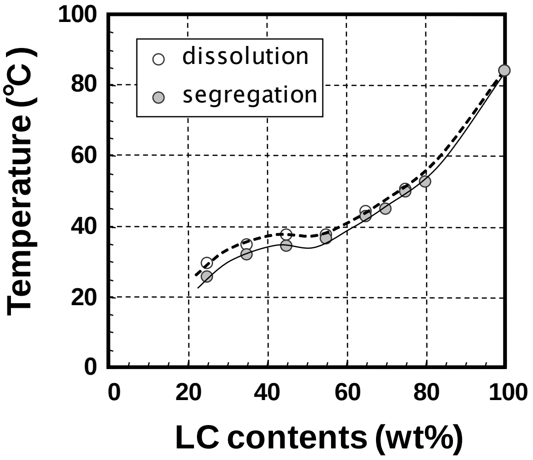

Fig.3 Phase diagram of M-A (LC/P-A/BIPE). Solid line shows segregation temperature on cooling and broken line shows dissolution temperature on heating.

It was found that M-A comprising liquid crystal of 65 wt% was positioned in the phase diagram so as to show a segregation phenomenon of liquid crystal from P-A since the temperature difference between Ts and Td was small. Besides, polymerization induced-phase separation at a temperature higher than Ts and near Ts is required for obtaining the composite with uniform morphology from M-A.

3.2 Temperature for nematic-isotropic transition point of liquid crystal phase in liquid crystal/ polymer composites

The liquid crystal/polymer composite cells were prepared by photo-polymerization induced-phase separation of M-A comprising liquid crystal of 65 wt% with UV light irradiation of 10 mW/cm^2 from each side of the cells at Ts+0.5 °C in decreasing temperature. Fig.4 shows the temperatures for the nematic-isotropic transition point of the liquid crystal phase in the composites obtained by various periods of UV light irradiation. The temperature was measured just after the composite was obtained by photo-polymerization induced-phase separation and after leaving it at room temperature for 12 h.

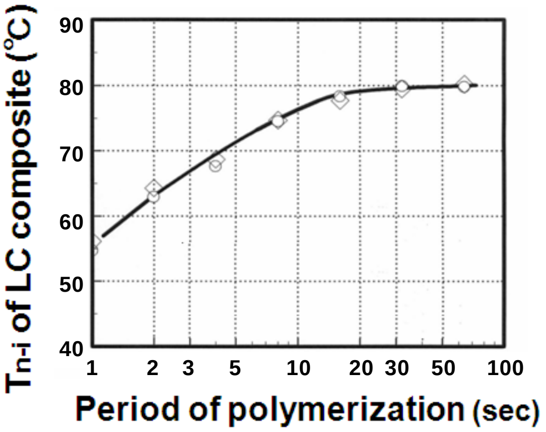

Fig.4 Dependence of UV irradiation period for photo-polymerization on Tn-i of LC in LC/polymer composite. (—○—) shows Tn-i of LC just after polymerization,(—◇—) shows Tn-i of LC after 12h from polymerization.

It was suggested that a phase-separated structure was formed by UV light irradiation of 1s and more since the composite cells were obtained so as to show a turbid appearance by scattering incident light uniformly. As shown in Fig.4, Tn-i of the liquid crystal phase in the composite obtained by short period of UV light irradiation was low and became higher according to increase of the period until irradiation period of around 30s in which Tn-i showed a saturated temperature. It is reasonable to assume that prepolymer of P-A remained in the liquid crystal phase led to the lowering of Tn-i in the early stage of polymerization induced-phase separation and the progress of polymerization by duration of UV light irradiation decreased the residual prepolymer and raised Tn-i. Even saturation temperature for Tn-i of the liquid crystal phase was lower by about 4 °C than that of liquid crystal material used for M-A. It was considered that the lowering was probably caused by residue of a part of P-A or degradation fragments of a part of liquid crystal components deteriorated by UV light in the liquid crystal phase.

Besides, there was no change in Tn-i between just after polymerization induced-phase separation and after leaving at room temperature for 12h. This result clearly shows that a transient structure of the composite under polymerization induced-phase separation process can be evaluated by observation and measurement for the composite cell within 12h from preparation of the cell with various periods of UV light irradiation because the photo-polymerization induced-phase separation can be frozen by interrupting UV light irradiation for photo-polymerization.

3.3 Observation for morphology of liquid crystal/ polymer composites

Figs.5 (a) and (b) show microscope images by "Observation method A" for the liquid crystal/ polymer composites obtained by photo-polymerization induced-phase separation with UV light irradiation period of 2s and 64s, respectively. The author et al. have discovered that the network structure of the polymer phase in the composite can be easily observed by bright-field transmission optical microscopy above a temperature in which liquid crystal phase in the composite shows isotropic phase. The pore sizes of the polymer networks which were shown as bright portions in Fig.5 (a) and (b) were found to be almost the same. Slightly thicker network branches were observed in the composite with irradiation period of 64s. It was confirmed by Fig.5 (a) and (c) that a three-dimensional polymer network was formed with UV light irradiation period of only 2s. Fig.5 (c) shows transmission optical microscope image by "Observation method B" for the composite after the liquid crystal was extracted. The images in round shape shown in nearly center of Fig.5 (a) and (b) were resin spacers which were used for adjusting the distance between a pair of electrodes in the cells.

3.4 Electro-optical characteristics for liquid crystal/polymer composites

Fig.6 shows optical transmittance on increasing applied voltage for the liquid crystal/polymer composite cells obtained by various UV light irradiation periods. The composite showing transparent-turbid (light scattering) switching by an applying and removing voltage was obtained by UV light irradiation period of only 1s. The threshold voltage at which the scattering state changed into transparent state increased rapidly between irradiation period of 1s and that of 4s. The change of electro-optical characteristics which converged after irradiation period of 30s accorded well with the change of Tn-i shown in Fig.4.

A change in transmittance of the composite is caused by a change in the alignment of liquid crystal molecules in the liquid crystal domain held in the three-dimensional network of polymer phase. A larger size of liquid crystal domain is believed to lead to a lower threshold voltage because a larger domain has relatively small interface between liquid crystal and polymer. It is suggested that liquid crystal phase comprised a part of prepolymer of P-A in the early stage of phase separation in the aspect of Tn-i profile. It might result in the lower threshold voltage that a substantial size of the liquid crystal domain in the early stage was larger than that in the final stage of phase separation by prepolymer in liquid crystal

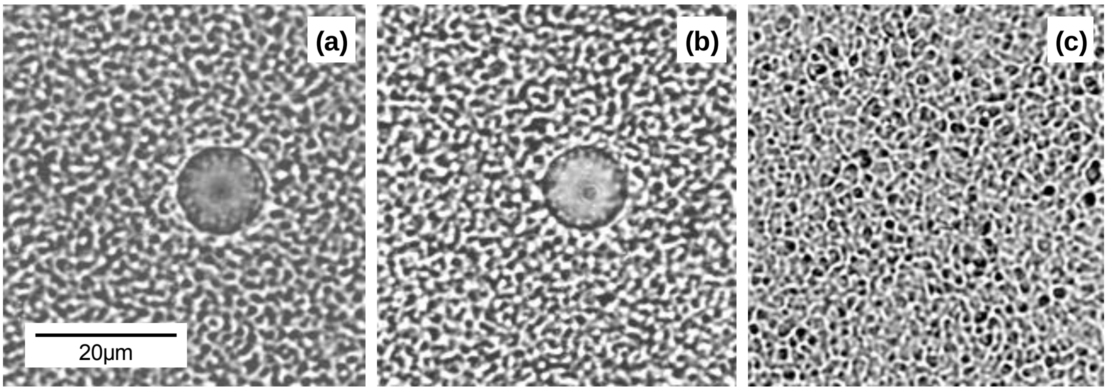

Fig.5 Optical microscope images of LC/polymer composite photo-polymerized with UV irradiation of 2s: (a) / (c), 64s: (b). Images (a) and (b) were observed at 100 ℃ (> Tn-i of LC). Image (c) was observed after extraction of LC by bicyclohexyl.

phase. It was also indicated it that thinner network branches of polymer phase were observed in the composite by UV light irradiation period of 2s in comparison with irradiation period of 64s as shown in Fig.5.

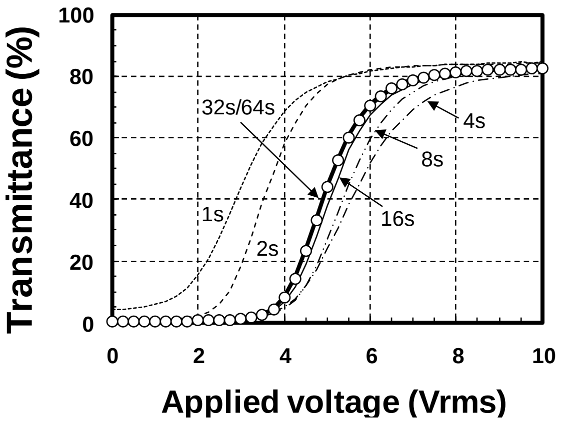

Fig.6 Electro-optical properties of LC/polymer composites obtained by photo-polymerization induced-phase separation with various periods of UV irradiation (2s/4s/8s/16s/32s/64s), which are indicated by arrows in the figure.

On the other hand, the slope of the V-T curve, that is, the change in the transmittance versus applied voltage (ΔT/ΔVrms) became larger between UV light irradiation periods of 4s and that of 30s with almost no change of the threshold voltage. It might lead to an increase of ΔT/ΔVrms that dielectric anisotropy of the liquid crystal domain was restored to the original value of the liquid crystal material by purification of liquid crystal phase with progress of polymerization induced-phase separation.

3.5 Schematic diagram for phase separation of liquid crystal/polymer composites

Fig.7 shows a schematic diagram of estimated composite structure in the early stage of photo-polymerization induced-phase separation. This model is based on the experimental examinations of the change for Tn-i of liquid crystal phase in the composite during phase separation process, the observation of the polymer phase and the change for the electro-optical characteristics. Basic structure of a three-dimensional network and its correlation length in the polymer phase is assumed to be determined by a freezing of concentration fluctuation between the liquid crystal rich phase comprising prepolymer and the polymer rich phase comprising liquid crystal just after phase separation. It is considered that the composite just after phase separation has a phase structure in which a continuous liquid crystal phase comprising prepolymer, which shows a low Tn-i, is held in a continuous polymer network having slightly thin polymer branches, and the liquid crystal phase is divided into multiple liquid crystal domains having a rather large diameter in comparison with that in the final stage of phase separation.

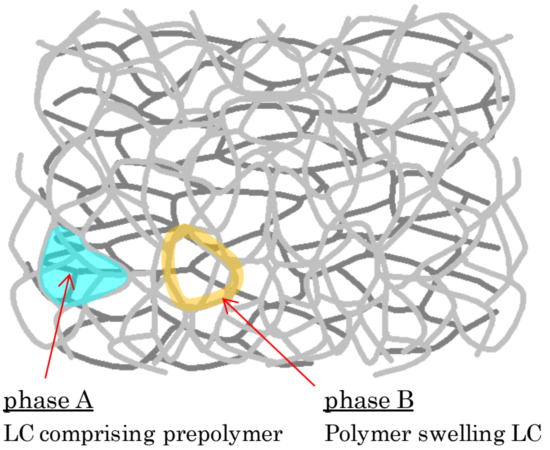

Fig.7 Schematic diagram of proposed model for structure of LC/polymer composite obtained by photo-polymerization induced-phase separation in the early stage of phase separation.

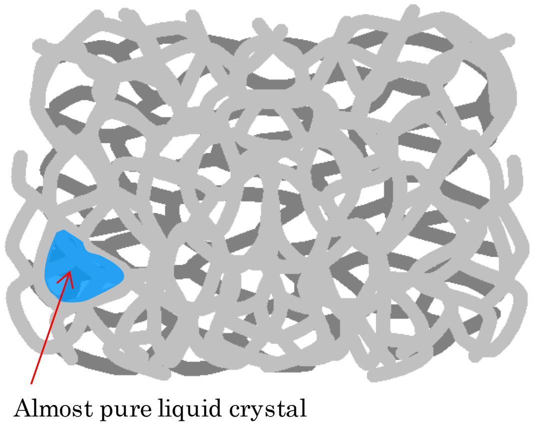

Fig.8 Schematic diagram of proposed model for structure of LC/polymer composite obtained by photo-polymerization induced-phase separation in the last stage of phase separation.

With the progress of polymerization induced-phase separation, the liquid crystal phase is purified by decrease of prepolymer remained in the liquid crystal phase according to the progress of polymerization reaction. The purification of liquid crystal phase leads to an increase in Tn-i and thicker branches in the polymer phase. Fig.8 shows a schematic diagram of estimated composite structure in the last stage of photo-polymerization induced-phase separation. The liquid crystal phase becomes almost pure liquid crystal and polymer network with thick branches is formed as shown in this model.

The change of electro-optical characteristics during phase separation process is well understood by this proposed model regarding formation process of the phase structure. It is considered that change of those electro-optical characteristics is comparatively small because the pore sizes of polymer network have been already determined just after phase separation.

4. Summary and Conclusion

The liquid crystal/polymer composites with a transient phase-separated structure were obtained by interrupting UV light irradiation for photo-polymerization after a predetermined period during the photo-polymerization induced-phase separation process in this study for formation by photo-polymerization induced-phase separation regarding the composites consisting of a bicontinuous phase of nematic liquid crystal and a three-dimensional polymer network.

The phase-separated structure showing transparent and scattering by an applied voltage was obtained by UV light irradiation period of only 1s. Tn-i of liquid crystal phase of the composite became higher with the progress of polymerization induced-phase separation and reached into a steady temperature after UV light irradiation period of around 30s. Low threshold voltage was observed in the early stage of phase separation and the threshold voltage also became higher according to polymerization. UV light irradiation period in which the change of electro-optical characteristics converged almost accorded with the change of Tn-i. Almost the same basic structure of polymer network in the polymer phase was observed both in the early stage and the final stage of polymerization induced-phase separation by a transmission optical microscopy with non-destructive method at a temperature in which the liquid crystal phase showed isotropic phase.

The transient structure and its characteristics in the liquid crystal/polymer composite are well understood by the proposed model regarding formation of phase structure, in which basic structure of polymer network in the polymer phase is determined by a freezing of concentration fluctuation between the liquid crystal phase comprising prepolymer and the polymer phase comprising liquid crystal just after phase separation, and the liquid crystal phase is purified with the progress of polymerization induced-phase separation.

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