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Aggregation States and Bistable Light Switching of (Liquid Crystalline Polymer)/(Low Molecular Weight Liquid Crystal) Mixture Systems

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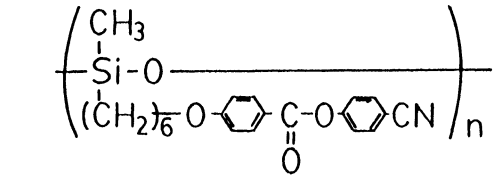
Binary mixtures composed of side chain type-liquid crystalline polymer (LCP) and low molecular weight liquid crystal (LMWLC) of which chemical structure is similar to the mesogenic side chain of LCP were prepared. Good miscibility between LCP and LMWLC was obtained in a mesophase state over a whole range of concentration. Response time of molecular reorientation by an imposed electric field remarkably decreased with an increase in the fraction of LMWLC. A new type of reversible and bistable electro-optical effect based on light scattering was proposed for the mixture system in a smectic state.

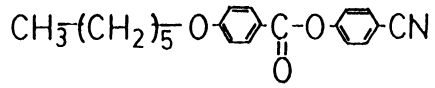
Thermotropic liquid crystalline polymers with mesogenic side chain groups have both characteristics of polymers and liquid crystals. Recently, electro-optical properties of thermotropic liquid crystalline polymers have been studied extensively. However, liquid crystalline polymers (LCP) in a mesomorphic state are more viscous than low molecular weight liquid crystals (LMWLC). Therefore, the magnitude of response time of LCP to an external stimulation such as electric and magnetic fields is much greater than that of LMWLC. We have investigated aggregation state - permeation property relationships of polymer/LMWLC mixture films.[1-5] In this study, we prepared the mixture system[6] composed of side chain type LCP and LMWLC of which chemical structure is similar to the mesogenic side chain of LCP. Aggregation state, phase transition behaviors and two types of electro-optical effect of the mixture system have been

1. polymer liquid crystal



poly(4-cyanophenyl 4'-hexyloxy benzoate methyl siloxane) (PCPHS)

2. liquid crystal



4-cyanophenyl 4'-hexyloxy benzoate (CPHOB)

Fig.1. Chemical structures of samples.

investigated.

The chemical structures of LCP and LMWLC are shown in Fig. 1. PCPHS and CPHOB were used as LCP and LMWLC, respectively. PCPHS/CPHOB mixture films were cast from an acetone solution. The phase transition behaviors and the aggregation state of the PCPHS/CPHOB mixture were investigated on the basis of DSC measurement, polarizing optical microscopic observation and X-ray diffraction study. The electro-optical effect of the mixture films was evaluated under a.c. electric field. The samples for an electro-optical measurement were sandwiched between indium tin oxide (ITO)-coated glass plates which were transparent electrodes. The distance between the two electrodes was maintained at 4 m by a PET spacer. A change of transmission light (He-Ne laser) intensity through the cell was detected by means of a photodiode and was recorded with digital storage oscilloscope.

The phase diagram of PCPHS/CPHOB mixture system is shown in Fig. 2. CPHOB is miscible over a whole range of PCPHS concentration in isotropic and mesophase states. The glass transition temperature, Tg, of PCPHS decreased with an increase in CPHOB ratio due to a plasticizing effect of CPHOB. A smectic phase was observed in a mesophase region above the PCPHS fraction of 40wt%. In the case below the PCPHS fraction of 40wt%, the mesophase of mixture was nematic.[7)]

We investigated the electro-optical effect of PCPHS/CPHOB mixture system based on birefringence. The composite films were sandwiched between two ITO-coated glass plates of which the surfaces had been rubbed in one direction to obtain a homogeneous alignment of molecules. An application of a.c. electric field of 1 kHz to the mixture film with a homogeneous alignment resulted in a decrease of transmission light intensity under the crossed polarizers due to reorientation of liquid crystalline molecules from a homogeneous alignment to a homeotropic one. The response time, $_R$, was defined as the time period for which transmission light intensity dropped to 50% after applying an electric field. Figure 3 shows log $_R$-log V plots for various PCPHS/CPHOB mixture systems with different mixing ratios. The response speed

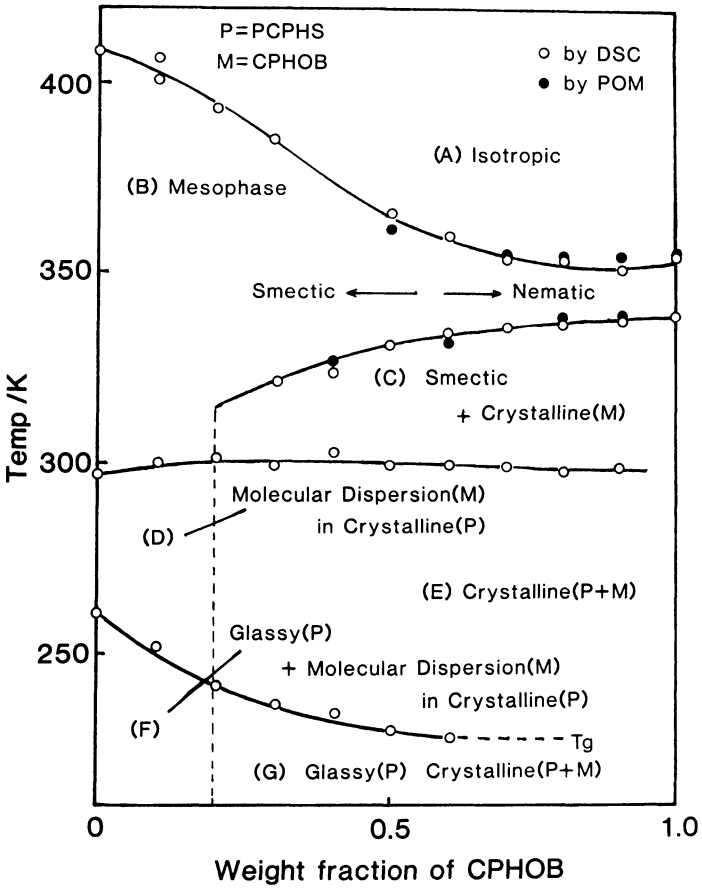


Fig.2. Phase diagram of PCPHS/CPHOB mixture system.

increased remarkably by mixing with CPHOB. The response time was inversely proportional to the 2nd power of the intensity of electric field. This response characteristic indicates that driving force for reorientation of liquid crystalline molecules is attributable to the dielectric anisotropy of LC molecule.

The electro-optical effect based on light scattering was also studied under various conditions of a.c. electric field. The samples were sandwiched between two non-treated ITO-coated glass plates. Transmission intensity of He-Ne laser through the mixture film without any optical polarizers was measured by photodiode. The distance between the mixture film and the photodiode was 305 mm. In this measurement, the response time was conventionally defined as the time period being necessary for a change from 10% to 90% of transmission light intensity. As shown in Fig. 4, the PCPHS/CPHOB (60/40) mixture system in a smectic state transmitted 86% of an incident light of He-Ne laser in the case of the as-cast film of 4 m thick. The transmitted light intensity strikingly decreased to 5% after applying 100 V a.c. electric field of 1 Hz due to a remarkable increase of light scattering. Furthermore, application of 100 V a.c. field of 1 kHz made the transmission light intensity increased to 94% within a few seconds. The degree of light intensity difference (contrast) between light scattering and non-scattering could be changed reversibly by imposing an electric field with different frequencies. Even if an electric field was removed, each turbid and transparent state remained unchanged as it was, indicating bistable light switching. In the case of the PCPHS/CPHOB (40/60) mixture film in a nematic state, the response speed became faster than that for the PCPHS/CPHOB(40/60) mixture film in a smectic state, and also, the transparent state could not be maintained without continuous application of an electric field. That is, there was no memory effect in the case of the PCPHS/CPHOB mixture film in a nematic phase. The proposed

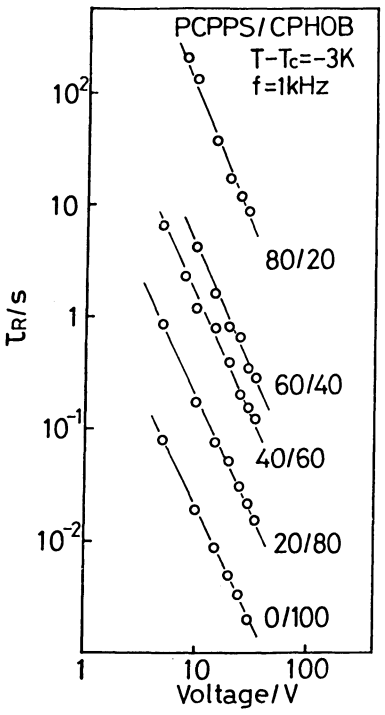


Fig.3. Applied voltage dependence of response time for PCPHS/CPHOB mixture system. T_c;phase transition temperature between mesophase and isotropic states.

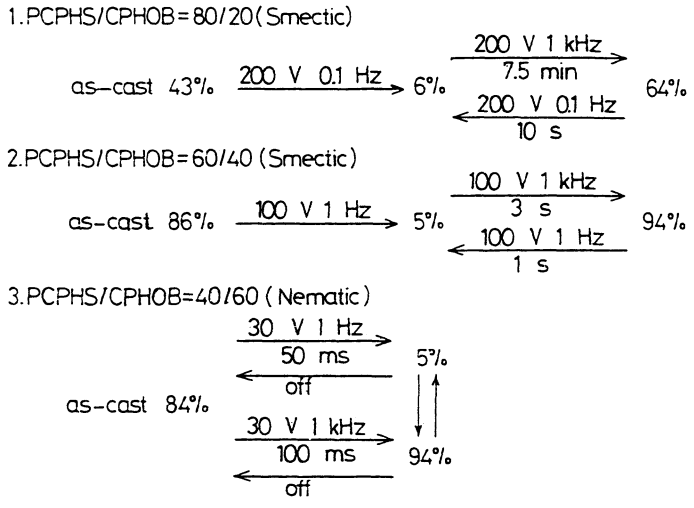


Fig.4. Transmittance change and response time for PCPHS/CPHOB mixture system under various conditions of a.c. electric field.

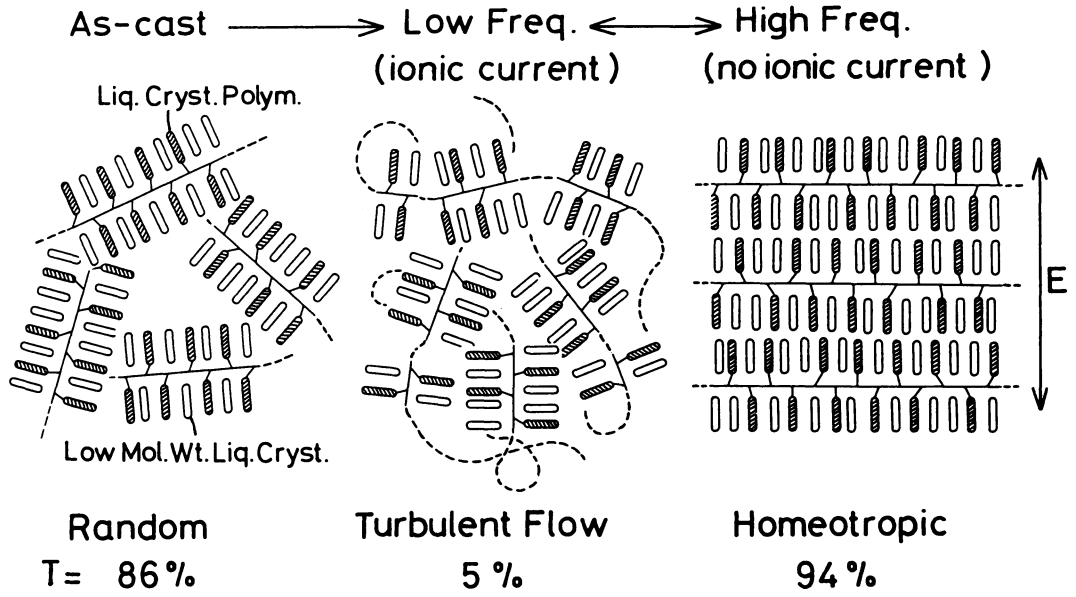


Fig.5. Schematic illustration of the turbid and transparent cases for the PCPHS/CPHOB mixture system under the conditions of different frequencies.

molecular aggregation states are schematically illustrated in Fig. 5 for the turbid and transparent cases. Since application of low frequency electric field induces an ionic current throughout the mixture film, it is reasonable to consider that an induced turbulent flow by an ionic current collapsed a fairly well organized large smectic layer into many small fragments, resulting in an increase in the light scattering and also, a decrease of transmittance up to 5% (from (1) to (2) in Fig. 5) . Since a high frequency field does not induce an ionic current, a large scale homeotropic alignment of smectic layers is easily formed by dielectric characteristics, increasing the transmittance up to 94% owing to remarkable reduction of director fluctuations and/or optical boundaries (from (2) to (3)). Such a bistable and reversible light switching driven by two different frequencies could be newly realized by both characteristics of turbulent effect of LCP main chain and rapid responsibility of LMWLC. We believe that the LCP/LMWLC mixture system is useful value as a novel type of "light valve" exhibiting memory effect (bistable light switching).

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