Reverse-mode thermoresponsive light attenuators produced by optical anisotropic composites of nematic liquid crystals and reactive mesogens

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ABSTRACT

Polymer network liquid crystals (PNLCs) whose optical transmittance state switches between transparence at low temperatures and haze at high temperatures were fabricated from mixtures of nematic liquid crystals (LCs) and reactive mesogens (RMs). This PNLC structure is simple but effective, namely, consists of micro-scale domains of orientation-ordered LCs and anisotropically polymerized RMs. The domains form through photopolymerization induced phase separation with inhomogeneous irradiation projected by laser speckling techniques. This irradiation method enables you to control the size and shape of phase-separation domains, and these PNLCs can be applied to novel thermoresponsive optical devices; optical isolators, thermometric sheets, and smart windows.

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1. Introduction

Polymer network liquid crystals (PNLCs) consist of a binary (or more) system of phase separation, that is, liquid crystal (LC) molecules locally aggregated surrounded by a polymer network [1–3]. If these phase-separation domains are distributed to form optical inhomogeneity at a micrometer scale, they can efficiently scatter visible and near-infrared light. LCs, which have birefringence and respond to extrinsic stimuli such as heat, electric fields, and light, are undoubtedly indispensable for the photonics industry. In particular, PNLCs whose advantages include the direct control of the light intensity and propagation direction, have been proposed for applications to flexible displays and spatial light modulators for information processing [4–6]. Furthermore, pioneering research into PNLCs is ongoing, such as switchable mirrors, variable-focusing lenses, chemical and humidity sensors [7–10], and smart windows for buildings and automobiles [11,12].

Our interest in PNLCs lies in the thermotropic behavior arising from phase transitions of LCs, specifically, the thermoresponsive change in optical clarity between transparence and haze. Thermoresponsive PNLCs have the advantage of being simple structures to assemble and utilize, and not requiring power sources or transparent electrodes. In particular, from the viewpoint of controlling solar irradiation, conductive films used as transparent electrodes may lower near-infrared transmittance. Thermoresponsive PNLCs have considerable promise for extending their applications into new industrial, business, healthcare, and domestic fields, such as optical isolators for glare safety, thermometric sheets

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for health checks, and autonomous smart windows for indoor comfort. PNLCs commonly composed of nematic LCs and isotropic polymers display a thermoresponsive optical behavior, that is, thermal switch between a hazy state at low temperatures (T_{low}) and a transparent state at high temperatures (T_{high}) [13,14]. However, the reverse-mode (transparence at T_{low} and haze at T_{high}) is logically difficult using this type of PNLC because the refractive indices of LCs in the nematic state cannot be adjusted to the refractive index of isotropic polymer. Some groups have achieved the reverse-mode thermoresponse by producing elaborate structures such as thermoplastic/thermoset/LC ternary phases, homeotropic-oriented phase separation of polymer with cholesteric LCs, or its-advanced hierarchical structures [15–17].

Our reverse-mode thermoresponsive PNLCs have a simple structure consisting of only nematic LCs and reactive mesogens (RMs). The PNLCs were developed by designing the structures (i) to match the refractive index of the LC phase in the nematic state with that of the polymer phase and (ii) to have a domain size of phase separation suitable for large light scattering at visible and near-infrared wavelengths. The concept is as follows.

LCs in the nematic state below T_{NI} are birefringent, and the refractive indices are divided into the components for two orthogonal polarization azimuths, that is, n_o and n_e, for ordinary and extraordinary rays, respectively, as shown in Fig. 1(a). As the temperature rises above T_{NI}, these two refractive indices converge

to become $n_i = (n_e + 2n_o)/3$ in the isotropic state. If the polymer phase in PNLCs is isotropic and has a refractive index of n_p equal to n_i, the PNLCs thermally switch the clarity between haze below T_{NI} and transparence above T_{NI}, which we call the normal-mode thermoresponsive optical behavior. To produce the reverse-mode thermoresponse with nematic LCs, such as switching between transparence below T_{NI} and haze above T_{NI}, the polymer phase in PNLCs must have birefringence with refractive indices n_{po} and n_{pe} equal to n_o and n_e, respectively. At temperatures below T_{NI}, the PNLC is optically homogeneous because $n_{po} = n_o$ and $n_{pe} = n_e$, and consequently has the transparent state, whereas it becomes inhomogeneous and has the opaque state due to nonzero deviations, $n_{pe} \neq n_i$ and $n_{po} \neq n_i$, when the temperature rises above T_{NI}.

We employed a bifunctional main-chain RM as a raw material for the anisotropic polymer. This type of RM has a molecular structure like LCs, called mesogen, and two functional groups at the ends of the body. This structure has the advantage of polymerization while maintaining uniaxial order in its molecular orientation. The uniaxial orientation ordering of RMs were stabilized during and after polymerization by rubbing treatment on substrate surfaces, and then an anisotropic polymer phase was formed with refractive indices that matched those of the LC phase in the nematic state.

Our PNLCs were fabricated using a method based on photopolymerization-induced phase separation (PPIPS). In PPIPS, an inhomogeneous distribution was formed consisting of LC and polymer domains. As the photoexposure proceeds, the monomers in the mixture polymerize and extrude LCs from the polymerized domains and the LCs become locally aggregated. The monomer functionality affects the domain size of the LC phase, that is, monomers with low functional numbers decrease the domain size [18–23]. According to the previous reports, LC molecules are thought to be either squeezed out from or entrapped in a polymer network, depending on the polymerization rate or hoop stress of the polymer. Thus, the monomer functionality that controls the polymer network density is an essential factor in forming LC domains separately from the polymer. RMs possessing two functional groups at the ends of the body, as used in this study, can undergo stable polymerization with uniaxial orientation ordering. However, PPIPS with this small functionality monomer is known to produce LC domains with a ten-nanometer scale or smaller [21,23], which is not large enough to scatter visible and near-infrared light.

In this study, we propose an inhomogeneous irradiation technique using a laser speckling method. Speckle patterns, which are meso-scale inhomogeneous distributions of light intensity, result from optical interference of coherent or laser light randomly scattered from the coarse surface of a light diffuser. Under irradiation with these speckle patterns, we demonstrate that RMs polymerize selectively faster in the lighter spots of the speckle patterns and then LC molecules aggregate richly in the darker spots. Since the speckle size depends on the distance between the projected position and the light diffuser, the domain size of PPIPS is expected to be artificially controlled in meso-scale, although RMs have low functionality. In this study, we seek speckle patterns appropriate for producing strong light scattering and then fabricate the reverse-mode thermoresponsive PNLCs that possess appropriately large domains of phase separation consisting of orientation-ordered LCs and anisotropically polymerized RMs.
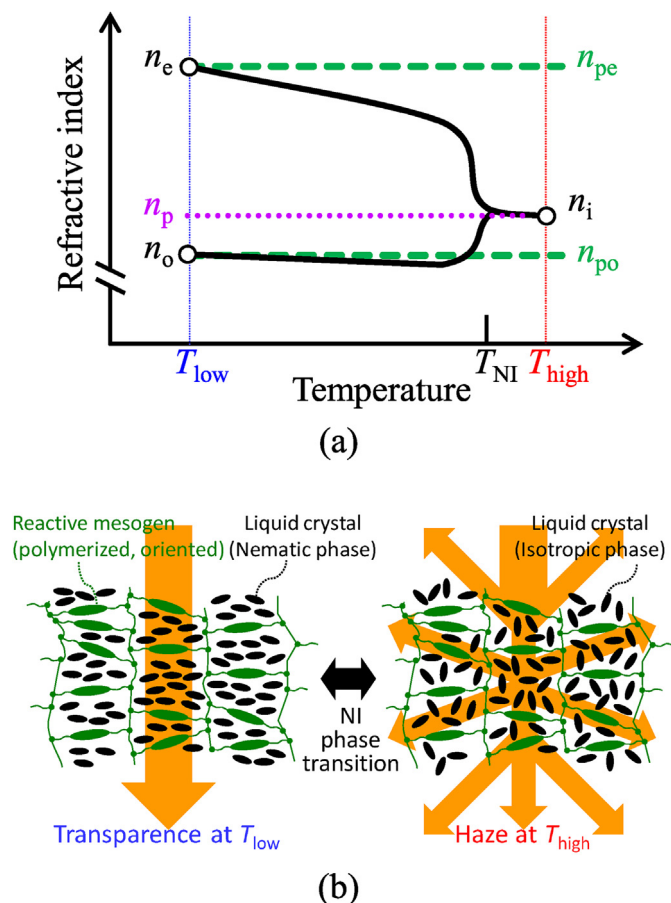

Fig. 1. Reverse-mode thermotropic behavior explained by (a) temperature dependence of refractive index and (b) schematic structures. Solid curves show refractive indices of LC phase in nematic state for (n_o) ordinary and (n_e) extraordinary rays at a temperature below NI transition point, T_{NI}, and in (n_i) isotropic state at a temperature above T_{NI}. Broken and dotted curves show the refractive indices (n_{po}, n_{pe}, and n_p) of the anisotropic and isotropic polymer phases, respectively.

2. Experiments

The PNLCs were fabricated from raw mixtures of LC, RM, and a trace amount of photoinitiators, as listed in Table 1. Three typical cyanobiphenyl LCs were prepared:4-cyano-4'-(pentyl-, hexyl-, and heptyl-)biphenyl, called 5CB, 6CB, and 7CB, respectively (Tokyo