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Photo-polymerization of liquid crystalline monomer in oriented liquid crystal phase

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Abstract

A new approach to synthesize liquid crystalline polymer with narrow polydispersity index (PDI) was developed. Photo-polymerization of 4-cyanophenyl-4′-(6-acryloyloxyhexyloxy)benzoate (RM23) in nematic liquid crystals with macroscopic orientation was studied. The effects of the monomer concentration on the molecular weight and PDI of the resulting polymers were studied through gel permeation chromatography (GPC) and polarized optical microscopy. The low PDI of 1.19 and 1.22 was obtained in the reverse and normal modes, respectively. The PDI and molecular weight increased with monomer concentration.

Keywords: Photo-polymerization; 4-Cyanophenyl-4′-(6-acryloyloxyhexyloxy)benzoate; Liquid crystal; Macroscopic orientation; Synthesis

Polymer stabilized cholesteric texture (PSCT) light shutter can be used to make smart windows and electronic papers [1–4]. In PSCT, the monomer is mixed with cholesteric liquid crystal and photo-initiator. The mixture is then UV-irradiated for photo-polymerization. After UV curing, the polymer network is formed to stabilize the alignment of the liquid crystals. It has been confirmed that the resulting polymer network formed in nematic liquid crystal is aligned along the orient direction of the liquid crystal. The anisotropy of the network is believed to be created by the aligning effect and anisotropic diffusion properties of the liquid crystal during the polymerization [5]. In other words, the macroscopic orientation of the liquid crystals in liquid crystal cells could affect the formation and the orientation of the cross-linked polymer bundles.

RM23 is a typical acrylate monomer which has been used to prepare side-chain liquid crystalline polymers (SCLCPs) [6]. Because the homopolymer of RM23 shows a low glass transition temperature (T_g) and broad mesophase, RM23 has also been copolymerized with various liquid crystalline monomers bearing different photosensitive groups to synthesize liquid crystalline copolymers [6–8]. To date, both the homopolymer and copolymer of RM23 are usually prepared via radical polymerization in solvent. In that case, the polymerizable RM23 molecules are separated from each other by the solvent molecules and the RM23 molecules orient randomly in solvent. On the contrary, the molecules of nematic liquid crystals orient parallel to each other within a size of about the wavelength of light and this size could be further enlarged by some alignment approaches such as polyimide (PI) film and electric-field [5]. If the liquid crystal has a homogeneous or homeotropic macroscopic orientation over the whole

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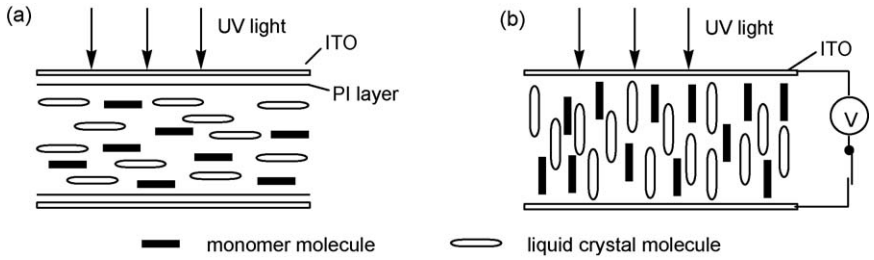

Fig. 1. Models of the alignment of molecules in the reverse mode cell (a) and the normal mode cell (b).

reaction system provided by the alignment approaches, from the point of view of polymerization, the polymerization happened in such an environment will be much different from that happened in common solvent. In this paper, a special environment is developed for the polymerization of liquid crystalline monomer RM23 by choosing nematic liquid crystal phase with certain macroscopic orientation as the reaction medium.

The mixture of monomer (RM23 from Merck), photo-initiator (IRGACURE 651 from Ciba Chemicals) and liquid crystal (E31LV from Merck) was filled into cells consisting of two parallel ITO glass substrates at above 80 °C. The cell thickness was 11 μm controlled by glass fiber. The initiator/monomer (w/w) ratio of 1/10 was used except otherwise specified. Fig. 1 illustrates the models of the alignments of both the liquid crystal and the monomer in the reverse and normal mode cells. In the reverse mode cell, both the liquid crystal and the monomer are aligned along the glass substrates because of the effect of the PI alignment layers. In the normal mode cell, both the liquid crystal and the monomer are aligned perpendicularly to the glass substrates because of the response of liquid crystal to electric-field. After UV curing, the cells were extracted with tetrahydrofuran (THF) for the GPC measurements. As shown in Fig. 2a, the PDIs of the formed linear polymers were increased with increasing monomer concentrations both in the reverse and normal modes. Comparing to the PDI (2.31) of the homopolymer of RM23 synthesized in benzene with 2,2′-azobisisobutyronitrile (AIBN) as the initiator [6], almost all the polymers synthesized in liquid crystals showed relatively smaller PDIs. As the monomer concentration was 3%, narrow PDIs of 1.19 and 1.22 were obtained in the reverse and normal modes, respectively. The number average molecular weight (M_n) and weight average molecular weight (M_w) of the resulting polymers are shown in Fig. 2b. The results showed that the M_n and M_w increased linearly as the monomer concentration was increased. The relationship between the monomer concentration and the molecular weight was in good agreement with the first-order kinetics of the radical polymerization.

In the reverse mode cell, the texture of the mixture with 3% monomer before UV curing was black under crossed polarizer and analyzer as shown in Fig. 3a. Similarly, all other mixtures with different monomer concentrations showed the same black textures before UV curing, which was good evidence to prove the well alignment function of PI alignment film. The textures of the mixtures after UV curing were very similar to each other. For the mixtures with initial monomer concentrations of 3%, 10% and 25% after UV curing, a uniform dark red texture was observed as shown in Fig. 3b. The uniform textures indicated that the linear polymer had been uniformly formed and dispersed in

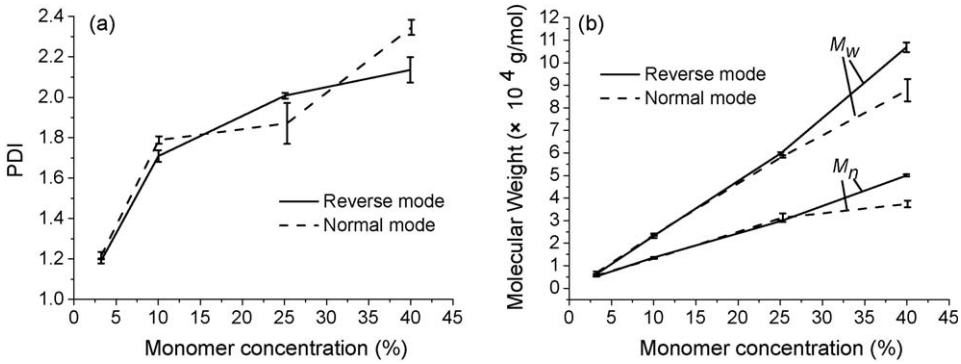

Fig. 2. PDI (a) and molecular weight (b) as a function of the monomer concentration in the reverse mode and normal mode cells, error bars represent means ± S.D. for $n = 3$.