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Polymer network as a template for control of photoconductivity of a liquid crystal semiconductor

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We report a novel method of confining a photoconducting liquid crystalline material using a polymer templating approach. The attractive feature of this approach is that the magnitude of the photocurrent of the photoconducting material does not diminish, i.e. it is unaltered by the polymer matrix. The results are compared with another method of encapsulation that was recently reported and wherein the photoconductivity decreases upon having the photoconducting material in the polymer matrix. The difference in the behaviour between the two methods is explained using a nanophase segregation model. The method described is particularly suitable for creating patterned photoconductors.

1. Introduction

Because of their low cost and ease of processing, organic photoconductors have been playing an increasing role in xerographic copiers and laser printers, and as the carrier transport layer in electroluminescent displays [1]. But the photoelectric properties of organic materials, even molecularly doped polymers, are less than ideal, owing to the amorphous nature of the prepared films [2]. In view of the difficulties in realizing 'single crystal' conventional polymer films, liquid crystals are being proposed as promising candidates [3]. Liquid crystals (LCs) have attracted considerable attention due to their distinct electro-optic characteristics that have formed the basis of display devices [4, 5]. In contrast, their electronic transport properties are only beginning to be studied, but promising results have already been obtained [6–11]. For example, they exhibit extremely large ($\sim 10^8$) anisotropy in electronic conductivity, becoming near-one-dimensional conductors [8]. LCs having very fast photoconductivity have also been realized, with the charge carrier mobilities in the order of 10^{-4}–10^{-1} cm^2 V^{-1} s^{-1} [7, 9, 11], the latter approaching the inter-sheet mobility values for graphite [12]. This has been possible because, compared with other organic materials or molecularly doped polymers, self-organizing molecular semiconductor LCs exhibit alignment close to that of molecular crystals, but maintain a liquid-like fluidity. The advantage that both the discotic and smectic types of LCs hold is that this liquid-like structure is responsible for the dynamic nature of the structural defects resulting in a *self-healing* system. This may be contrasted with the presence of static defects in the case of polymers and organic single crystals. Smectic LCs have the further attraction that many materials exhibit several smectic phases with different degrees of ordering of the molecules. A particular calamitic (or rod-like) mesophase, which has shown interesting transport properties, is the crystal B phase [11, 13, 14]. Although this phase possesses three-dimensional positional order, the interlayer ordering is energetically extremely weak [4]; the molecules can still rotate about their long axes, thus perpetuating the *self-healing* mechanism, as in the case of true smectic phases.†

Funahashi and Hanna [11] synthesized and reported the transport properties of the alkylphenylalkyloxynaphthalene materials, which exhibit interesting photoconducting properties with a high mobility. We have shown that a suitable composition of two homologues of this naphthalene series can enhance the photoconductivity anisotropy (the ratio of the photoconducting current along and perpendicular to the layer normal) by nearly an order of magnitude [14]. Recently, Yoshimoto and Hanna have prepared composites of the naphthalene compound by adding

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†Earlier researchers [11, 13] have referred to this phase in 8PNP-O12 as a smectic B phase. But our X-ray studies [14] showed that this phase possesses long range ordering in all three dimensions and therefore should be labelled crystal B phase. It must be pointed out, however, that due to the remaining rotational degree of freedom of the molecules, this phase retains certain smectic-like features.

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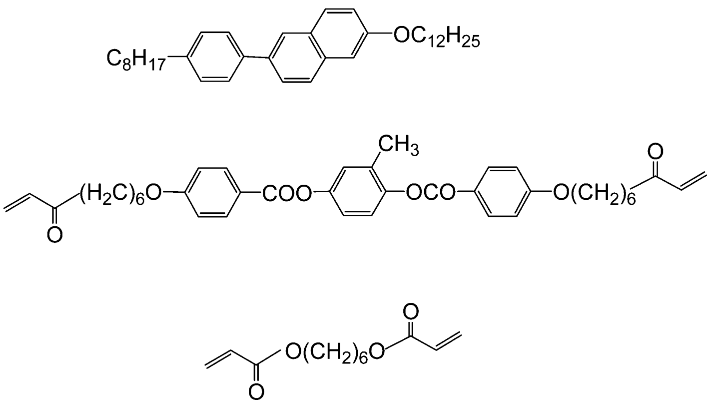

8-PNP-O12

RM82

HDDA

Figure 1. Chemical structures of the materials used in the present study.

a crosslinkable monomer, and photopolymerizing the monomer [15]. They found that the mobility values were not significantly affected by this process of confinement (in two dimensions), but the magnitude of the photocurrent decreases significantly—about one order of magnitude for about 5% of monomer in the liquid crystal host. Furthermore, the photocurrent value was seen to be strongly dependent on the phase in which the polymerization was achieved. Although a new approach, the main drawback of this method is that because the photopolymerizable monomer does not support liquid crystallinity, the stability of the liquid crystalline phase of the mixture (of the naphthalene compound and monomer) is decreased. Here we report a novel method of confining the photoconducting liquid crystalline material by forming a polymer template. The two salient features of this approach are (i) retention of the liquid crystalline properties including the magnitude of the photocurrent, and (ii) built-in ability to pattern the photoconducting and non-conducting regions. We shall also give an explanation based on the nanophase segregation model to interpret our results as well as those of Yoshimoto and Hanna.

2. Experimental

The chemical structures of the materials used are shown in figure 1. The liquid crystalline photoconducting host material is 2-(4-octylphenyl)-6-dodecyloxynapthalene (8-PNP-O12), which exhibits an Isotropic (I) 120.8°C smectic A (Sm A) 100.3°C crystal B (CrB) 64.7°C crystal sequence. Photoconductivity measurements have been carried out using a set-up described in an earlier paper [14] and described briefly here. The cells used were fabricated with ITO-coated glass plates treated either (i) with a polyimide solution and rubbed unidirectionally to obtain planar alignment or (ii) coated with a silane solution to obtain homeotropic alignment of molecules. The light source used was a 365 nm enhanced intensity-stabilized mercury-xenon source (Hamamatsu L7212-01, Japan). An IR-block filter was inserted in the beam path just before the sample to eliminate local heating effects. The actual power of the radiation falling on the sample was measured using a power meter (Hamamatsu C6080-03) held in the sample position. The photocurrent was measured using an electrometer (Keithley 6517A) in the force-voltage-measure-current mode. In this mode the built-in bipolar 1 W voltage source was used to apply a bias voltage to the sample.

3. Results and discussion

First we discuss the results obtained in the CrB phase of pure 8-PNP-O12. Figure 2 shows the photocurrent response to a UV illumination of 3 mW cm^{-2} and a bias voltage of 30 V in the planar ($I_\perp$) and homeotropic ($I_{||}$) geometries. In the planar geometry, turning the UV illumination ON results in an abrupt and substantial increase in the current density. In contrast, with the sample in the homeotropic geometry the current density remains practically the same irrespective of the presence or absence of the radiation. Furthermore, the value of the dark current is also essentially the same ($\sim$a few nA cm^{-2}) in both geometries. The calculated photocurrent anisotropy δI ($=I_\perp/I_{||}$) is 45, which is about a factor of three higher than the value reported in the literature [11] and our own earlier measurement [14] for this material. This is because the electrical purity of the present batch of the compound is much higher than the previous batch, as was confirmed by determining the ionic current in the isotropic phase.

As the purpose of the investigation was to establish the influence of confinement of the photoconducting liquid crystalline material in a polymer environment, we first prepared a mixture of 8-PNP-O12 with 5% by weight of 1,4-di-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82 from E Merck, see structure in

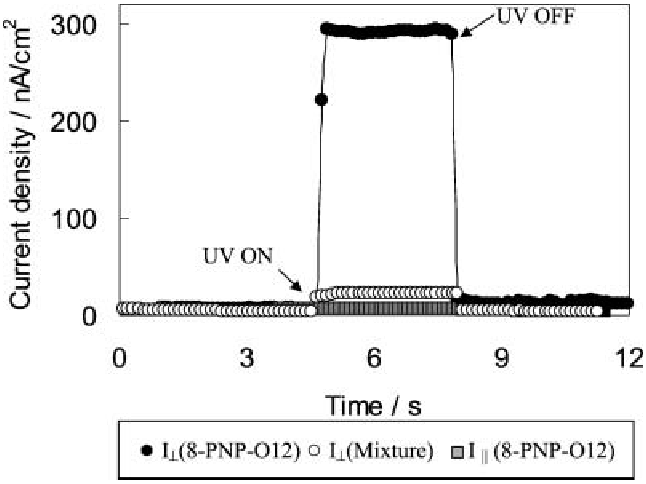

Figure 2. Time-resolved photocurrent response under steady state UV illumination in the crystal B phase of pure 8-PNP-O12, with the molecules aligned in the planar ($I_\perp$, filled circles) and homeotropic ($I_{||}$, filled gray squares) configurations. For the sake of clarity, the current density measured in the dark state, with its value being nearly identical to that for the homeotropic geometry, is not shown. The current density measured in the planar geometry ($I_\perp$) for the mixture of 8-PNP-O12 and 5% RM82 polymerized *in situ* (for details see the text), with its largely diminished value, is shown as open circles; while the data in the homeotropic geometry ($I_{||}$) are indistinguishable from those for the pure compound and therefore not shown here. In all cases, the illuminated electrode was positively biased with 30 V and the light intensity was 3 mW cm^{-2}.

figure 1), a crosslinkable monomer and a small concentration of a photoinitiator, by employing the standard method of obtaining anisotropic gels [16]. However, the difference between the RM82 monomer and 1,6-hexanediol diacrylate (HDDA), the monomer used by Yoshimoto and Hanna, is that RM82 in its monomeric form is liquid crystalline exhibiting a nematic phase. This feature should result in a better mixing of the host 8-PNP-O12 and the monomer before polymerization and thus a uniform dispersion of 8-PNP-O12 molecules.

To make the composites we proceeded conventionally by filling the measuring cell with the mixture and exposing it to actinic light (UV light with a peak wavelength of 365 nm) using a low power UV source (Edmund Scientific) for 10 min. This led to the free radical polymerization of RM82 molecules resulting in a polymer network (PN) configuration. The photocurrent data were obtained with this PN configuration both for planar ($I_\perp$) and homeotropic ($I_{||}$) geometries. While the magnitude of $I_\perp$ decreases by more than an order of magnitude compared to that for the pure compound (see figure 2), the behaviour of $I_{||}$ is quite similar to that for the pure compound. The data for the PN configuration, shown in figure 2, were obtained by polymerizing the sample when the mixture was maintained in the CrB phase. Similar results, although with a further decrease in the value of $I_\perp$ were obtained when the polymerization was performed in the isotropic and SmA phases of the mixture. These results are in qualitative agreement with those of Yoshimoto and Hanna. Thus it appears that the PN configuration results in the lowering of the photocurrent values of the host liquid crystal.

To find out if the presence of the polymer network itself was responsible for the lowering of the photocurrent, we performed experiments before polymerizing the cell. From the transition temperature data we confirmed that a period of 3 s, during which the UV radiation was ON for the photocurrent measurements, was too small for any polymerization to take place. To our surprise we found that even in this case the photoconducting property was almost lost (the photocurrent values are the same as that for the polymerized sample). Later, we shall explain these features using a nanophase segregation model. From these results it is clear that when RM82 is used, the conventional method of confinement leads to a loss in the photoconducting properties of the host material. To overcome this problem we have taken a radically different approach, which we refer to as a template approach, for confining the host material.

To prepare the polymer template we used E7 (a room temperature eutectic mixture from E Merck, showing the nematic phase) as a specimen liquid crystal. As will be seen later this material plays the role of providing the skeleton for the formation of the template. A mixture of E7, 5% by weight RM82 and a small concentration of a photoinitiator were filled in glass cells similar to those described previously (polyimide coated and rubbed) and illuminated with the actinic light. This, as expected, results in a polymer network. The next step involved the removal of E7 and any remaining RM82 monomer by immersing the cells in pure acetone. Complete removal was ensured by taking the cells out after a week and also confirmed by noting that the cells appeared optically nearly isotropic (almost dark under an optical microscope with crossed polarizers), as against the strongly birefringent field of view before polymerization. The polymerization was performed with a photo-mask to create a pattern such that we had two types of regions: those that were exposed to and others that were not exposed to the UV radiation. Subsequent removal of E7 and the remaining RM82 resulted in a polymer template with regions with and without the polymer bundles. The host 8-PNP-O12 material was then filled into the cell. To ensure that the

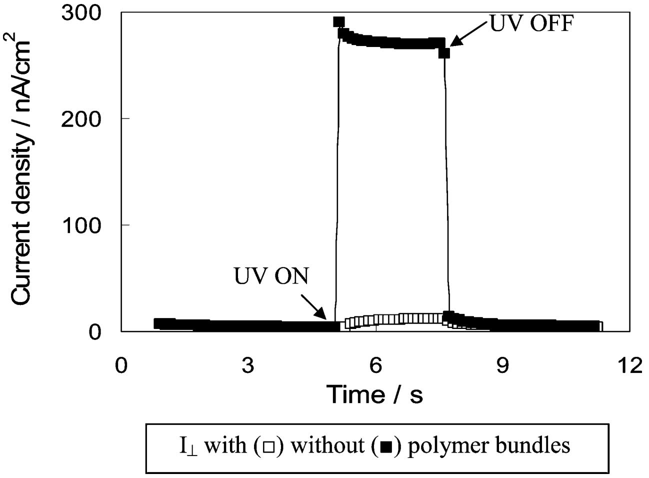

Figure 3. Current density measurements for the polymer-templated cell in the planar configuration ($I_\perp$), with the sample in the crystal B phase, for the region without (filled squares) and with (open squares) polymer bundles.

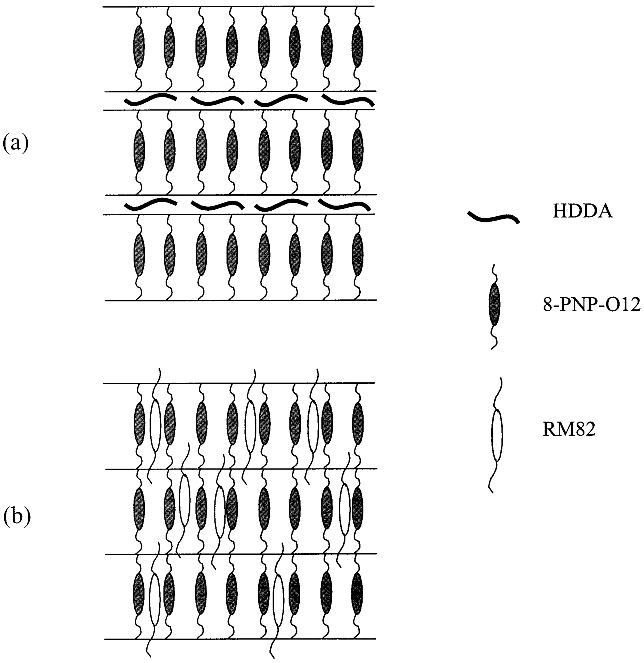

Figure 4. Schematic representation of the molecular arrangement of the mixture of 8-PNP-O12 with two different types of crosslinkable monomers: (*a*) HDDA, a highly flexible molecule and (*b*) RM82, a molecule which shows a liquid crystalline phase in its monomeric form. The HDDA molecules are 'nanophase segregated' and occupy the regions between two layers, whereas the RM82 molecules are incorporated into the layers.

template remained intact during these processes, optical observations were performed on heating the sample to the isotropic phase. Wherever the polymer bundles were present, weakly birefringent but dense strips could be seen, very similar to those seen before filling with the 8-PNP-O12 compound.

Figure 3 shows the photocurrent measurements carried out using this templated cell. A striking difference in the values is observed for the regions containing polymer bundles and without. The region that was not exposed to UV radiation during the preparation of the template, and therefore which does not have the polymer bundles, exhibits the same values of photocurrent as the bulk 8-PNP-O12 sample. In contrast, the region with the polymer bundles has values comparable to that obtained when the entire cell was exposed to the UV radiation.

We now explore the possible cause for the observed behaviour in our experiments and in those of Yoshimoto and Hanna. Our argument is based on the phenomenon of nanophase segregation [17] when layered systems are mixed with photopolymerizable monomers. Based on IR and X-ray studies, Guymon *et al.* [18] demonstrated that the structure of the diacrylate monomer has a dramatic effect on the spatial organization of the monomer–LC (in the smectic C and smectic A phases) mixtures and thus on the polymerized structure (see figure 4). In the case of HDDA, a highly flexible molecule exhibiting only the isotropic phase, it was found that the HDDA molecules phase segregate on a microscopic level and occupy regions between two smectic layers. Thus, when polymerized there will be a complete phase separation between the HDDA polymeric chain and the liquid crystalline molecules. What has not been reported, but should be obvious, is that if the polymerization is performed in the isotropic phase of the LC material then such phase segregation may not take place. In the case of RM82, the monomers themselves exhibit a liquid crystalline phase and therefore have a strong tendency to stay within the smectic layers. Thus they exhibit no nanophase segregation. Even when polymerized the polymer chains remain within the smectic layers but may run through the layers.

Let us apply these ideas to the photoconductivity measurements of Yoshimoto and Hanna and our own. Yoshimoto and Hanna observed that the value of the photocurrent is dependent on the phase in which the polymerization has been performed, with a maximum value obtained for polymerization in the CrB phase and least in the isotropic phase. This is understandable since polymerization in the CrB would ensure nanophase segregation between the HDDA molecules and the LC molecules, with the HDDA molecules taken out of the layers. Therefore interference of the HDDA molecules with the transport properties of the LC in the plane of the layer (i.e. $I_\perp$) would be minimized, but not

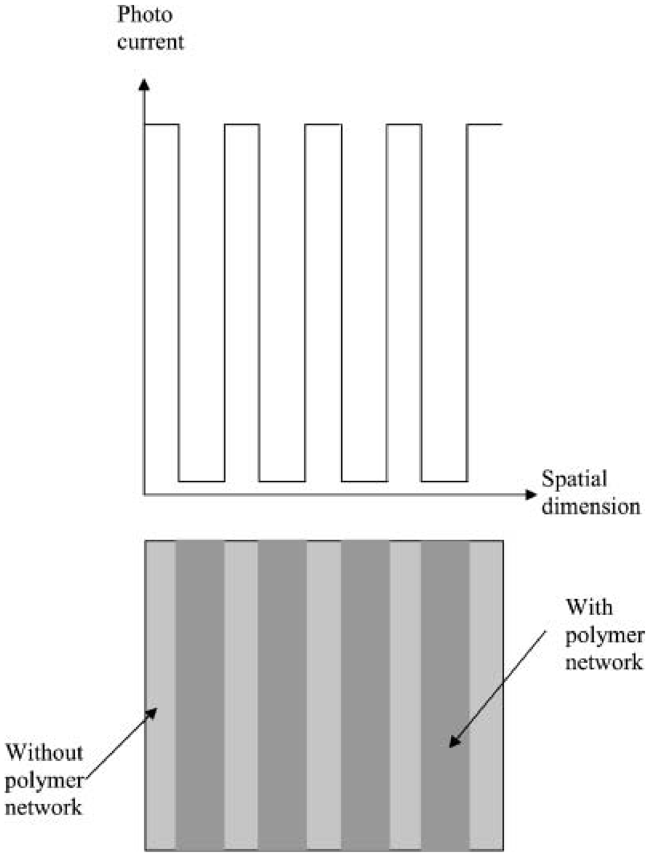

Figure 5. Diagram showing a simple pattern that can be achieved with the polymer template approach presented here.

completely eliminated. By contrast, the polymerization performed in the isotropic phase makes the HDDA molecules intersperse with the LC molecules and therefore impedes the charge transport. In our case, the RM82 molecules will be present within the smectic layers, and when polymerized the polymer chains run through the layers. This is true irrespective of which phase the polymerization was performed. Since they are present within the layer, the RM82 molecules both in their monomeric and polymeric forms, act as charge traps and prevent long range transport. In the template form the polymer bundles are already formed before the inclusion of the host LC molecules and this creates the necessary phase separation, with the LC molecules sitting in channels between sets of polymer bundles. In such a situation the RM82 molecules do not interfere with charge transport and the original photocurrent values are recovered. The recovery of the photocurrent values of the host molecules in a polymer template has important implications. For example, it can be employed to realize photoconducting devices with custom-made (figure 5) patterns achieved using a suitable photo-mask.

4. Summary

We have described a novel method of confining a photoconducting liquid crystalline material using a polymer templating approach. The attractive feature of this approach is that the magnitude of the photocurrent of the photoconducting material does not diminish, i.e. it is unaltered by the polymer matrix. The method described is particularly suitable for creating patterned photoconductors.

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