Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Imprinting In Polymer Stabilized Liquid Crystals

Mary Claire A. Micaller [a], Zenaida B. Domingo [a] & Leonorina G. Cada [b]

[a] National Institute of Physics, University of the Philippines, Diliman, Quezon City

[b] Institute of Chemistry, University of the Philippines, Diliman, Quezon City

Version of record first published: 24 Sep 2006

To cite this article: Mary Claire A. Micaller, Zenaida B. Domingo & Leonorina G. Cada (2001): Molecular Imprinting In Polymer Stabilized Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 245-254

To link to this article: http://dx.doi.org/10.1080/10587250108029953

Mol. Cryst. and Liq. Cryst., 2001. Vol. 368, pp. 245-254
Reprints available directly from the publisher
Photocopying permitted by license only

Molecular Imprinting In Polymer Stabilized Liquid Crystals

MARY CLAIRE A. MICALLER[a], ZENAIDA B. DOMINGO[a] and LEONORINA G. CADA[b]

[a]*National Institute of Physics, University of the Philippines, Diliman, Quezon City and* [b]*Institute of Chemistry, University of the Philippines, Diliman, Quezon City*

An initial investigation on the probability of molecular imprinting on polymer stabilized liquid crystal systems is presented. In this study, no alignment layer was used and traditional molecular imprinting monomers- vinyl pyrridine and methyl methacrylic acid – were mixed with nematic and chiral-nematic LCs. Initial electro-optic measurement show that the transmittance behavior of the films is dependent on the interaction between the LC and the polymer. For the nematic set, the scattering and transparent state is due to the orientation of the LC molecules anchored at the LC-polymer interface. For the chiral set, the stabilization of the textures leading to a scattering or transparent state is again due to the anchoring of the polymer on the LC molecules around it.

Keywords: PSLC; chiral-nematic; molecular imprinting

INTRODUCTION

As an initial investigation of the capability of traditional molecularly imprinted polymers to imprint liquid crystals, polymer stabilized liquid crystal systems were prepared without any alignment layer. After initial characterization, the original LC was washed out from the substrate and fresh LC was then injected. Details of the sample preparation will be discussed in the next chapter while the results of the electro-optics tests and SEM of the network morphology will be presented in the Results and Discussion.

EXPERIMENT

Sample Preparation

Polymer stabilized liquid crystal samples were prepared using nematic (SET A) and cholesteric (SET B) liquid crystals. For SET A, nematic E7 was used while for SET B, nematic E48 was doped with 5% TM74A, a cholesteric LC. For both sets, the liquid crystals were mixed with monomers vinyl pyridine and methacrylic acid in ~97:3 (LC:monomer) ratio by weight. The 3wt% for the monomer is actually composed of 85%monomer, 13.5% crosslinker (ethylene glocol dimethacrylate, EDMA) and 1.5% photoinitiator (azobisisobutyronitrile, AIBN). The photoinitiator and crosslinker enhances the polymerization of the monomers.

Using capillary method, the mixtures were sandwiched between clean ITO-coated glass plates. The thickness of the film was controlled using 23.8 μm mylar spacers. After sealing the substrates with epoxy, the samples were polymerized using a UV source with wavelength 365 nm for three hours. From each mixture, a reference and field cured sample was made. The field-cured film was polymerized with 8V AC applied across the substrate.

Sample Characterization

Textures of the samples after polymerization were observed through a polarizing microscope. The transmittance behavior of the samples with increasing voltage was then measured using a He-Ne laser probe. After this testing, the original LC was washed out using dichloromethane and fresh LC was then injected using capillary method. However, for the second injection it was observed that capillary through the substrate is only possible if excess LC is present on top of the substrate. Thus, the sample produced is thicker compared to the initial preparation. Once the second injection is complete, the samples' transmittance with increasing voltage was then measured. Finally, the LC from the sample was extracted through injection of dichloromethane for SEM observation. Prior to solvent injection, the sealant material on the top and bottom part of the substrate was removed. Once the film appears non-birefringent under OPM, the rest of the sealant material is removed and the substrates are carefully pulled apart. Each plate was then metallized for three minutes using Ag-Pt.

RESULTS AND DISCUSSION

Nematic Set

The nematic set was in the isotropic phase prior to polymerization as manifested by the clearing of the liquid crystal upon addition of monomer. That is, the nematic E7 is soluble in the monomers vinyl pyridine and methacrylic acid. Since the liquid crystal is in the isotropic phase, any external field applied will have no aligning effect on it. But as polymerization progress, the polymer forms and the LC reverts to its mesogenic state. At this point the liquid crystal can be affected by any aligning factors such as an external field. This isotropic to LC transition during the polymerization process could result to localized domains occupied by liquid crystal enclosed in a highly randomized polymer network. This morphology is supported by the SEM photomicrographs of the samples.

Figures 1- 3 show that the polymer strands have grown in random directions around voids that could have been occupied by the liquid crystals.

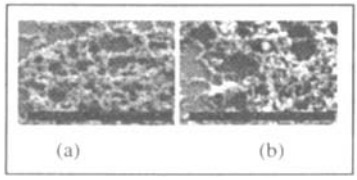


FIGURE .1 Network morphology of E7: n-VP viewed under SEM (a) reference (b) field-cured

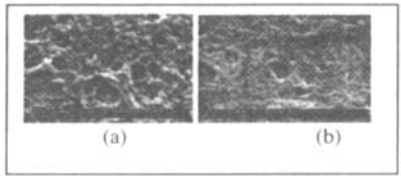


FIGURE. 2 Network morphology of E7:PMMA viewed under SEM (a) reference (b) field-cured

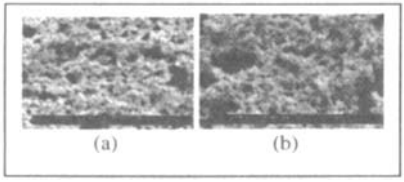


FIGURE. 3 Network morphology of E7:n-VP:PMMA viewed under SEM (a) reference (b) field-cured

OPM photomicrographs right after polymerization show that indeed, once polymerization is complete, the nematic E7 reverts to its liquid crystalline state as evinced by the marbled texture observed for all samples.

For all mixtures, the reference films appear more homogeneous relative to the field-cured samples. In the field-cured samples, areas of disclinations, which appear as patches of black in the photos can be observed. This means that for the field-cured samples, there are more discontinuities from the average direction of **n**. These discontinuities result to more scattering in the off state of the field-cured samples as seen from their low initial transmittance relative to their reference counter parts.

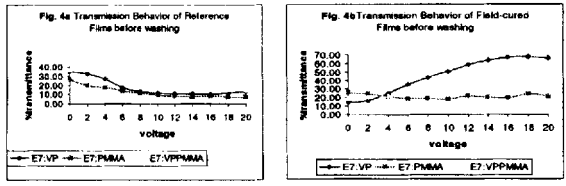
These disclinations could be explained by examining in detail what happens at the LC-polymer interface and within the LC sites during polymerization. On the onset of polymerization, both reference and field cured samples are in the isotropic phase, that is the molecules are in random order. Once the polymer starts to form, the LC phase separates from the polymer and resides within the voids of the polymer network. The direction of **n** within the voids will be determined by alignment conditions. Deviation from this direction could come from the anchored molecules at the LC-polymer interface, which has a preferred orientation arising from the interaction that can occur between the polymer and the LC. Such orientation can be frozen as the polymer hardens similar to what was observed by K. Amundosn in his 1998 article. [1]

For the reference sample, molecules oriented randomly will be anchored at the LC-polymer interface. This is because while the polymer forms, these molecules were still in the isotropic phase. Since the anchored molecules are random, it cannot impose a general direction on the bulk LC within the voids because each anchored molecule may impose its direction but then another can simply cancel its effect. In the absence of an alignment layer or by an external field, only the intermolecular forces would then determine the direction of **n**. This direction is simply the average direction of each molecule within the voids. Statistically, each molecule deviates in almost the same amount from this average direction, thus lesser disclinations. This general direction is maintained after polymerization.

But for the field-cured sample, as the LC phase separates from the polymer, it will align along the direction of the electric field. This external field would largely determine the direction of **n**. The

molecules that are anchored over the LC-polymer interface and the bulk LC both align along the field. Note that at this point in the polymerization process, the polymer is just starting to form and its interaction with the LC is not yet that strong compared to the aligning effect of the field. But once polymerization is complete, the field is removed and the polymer again freezes the orientation of the anchored molecules. Which in this case has a preferred orientation along the previous direction of the field. Such preferred orientation competes with intermolecular forces in determining the relaxation of the bulk LC within each void. Such competition yields domains with different preferred direction, i.e. each void has a different **n**. These preferred direction of each domain give rise to the disclinations observed in field-cured sample.

This model could also explain the transmittance behavior of the samples with increasing voltage. Figure 4a shows that all reference samples exhibit a general behavior of decreasing transmittance as voltage is increased. As the voltage is raised the bulk LC aligns along the field while the anchored molecules remain at random directions thus, resulting to the scattering of light.



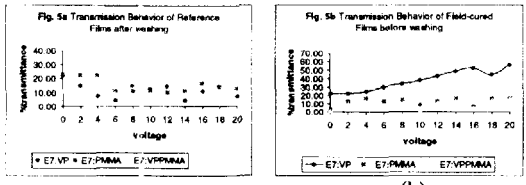
(a) (b)

FIGURE 4: Transmittance behavior of (a)reference (b) field-cured before washing

For the field-cured sample, Figure 4b shows the reverse. At off state, domains of different orientation scatter light. As the field is increased the bulk begins to align along the field, similar to the direction of the anchored molecules, thus resulting to the transmission of light. However for the E7:PMMA mixture, the field-cured film no longer switches, that is, the transmittance is almost independent of voltage. This could be due to a very strong anchoring of the original orientation of the LC by the polymer. Another hypothesis that could be explored in future studies to explain this non-switching is the presence of a very few number of voids in the polymer morphology of this sample.

From the model discussed above, we note that the transmittance at off and on state is dependent on the orientation of anchored molecules (i.e. scattering is a result of the difference between the orientation of anchored molecules and non-anchored molecules). The strength of these anchoring is then determined by the interaction occurring at the LC-polymer interface.

After injection of fresh LC the marbled texture was again observed. However, the transmittance behavior was not replicated. The transmittance values swing from a low to high or high to low value over the voltage range considered as seen in Fig. 5.



(a) (b)

FIGURE 5: Transmittance behavior of (a)reference (b) field-cured after washing

Chiral-Nematic Set

Unlike the nematic systems, the E48:TM74A PSLC remained in the LC phase after addition of monomers. For the reference films of all mixture, the grandjean texture was observed. Meanwhile for the field-cured samples, the finger print texture was stabilized after polymerization.

Of all samples, the E48:TM74A:n-VP reference and field-cured PSLC, closely meets the expected network morphology. Figure 6a shows that for the reference film, the network is composed of thin strands that twist around like a whirlpool along an axis perpendicular to the substrate. This morphology matches the orientation of the helical axis in a grandjean texture. Figure 6b on the other hand shows that for the field-cured sample these strands appear to bunch up to form thicker fibrils whose ends are attached to the substrate indicative of the homeotropic orientation of LC molecules. The finger print texture is a result of the competition between these homeotropically aligned polymer fibrils and intermolecular interaction.

For the reference film of the E48:TM74A:PMMA, individual fiber of the PMMA sample is not so distinguishable even at high magnification (Fig. 7a). On closer inspection though, braided strands radiate from a central looped fiber. The twisting of the strand could be

due to the chirality of the molecules. Unlike the n-VP sample, the loops formed are quite large. Figure 7b shows, that like the nematic PSLC, the chiral sample exhibits a flat morphology with no void. For the n-VP:PMMA sample, a pattern was observed even at low magnification for the field-cured film. Figure 8b show that polymer network formed in a helical fashion. This pattern was not present for the reference sample. At high magnifications, Fig. 9a shows that, the reference film are composed of plate-like structures with bead-like projections over its surface. The plates are interconnected with voids between them. The field-cured film, meanwhile has fibers that are made up of grain-like structures linked in a curved fashion (Fig. 9b).

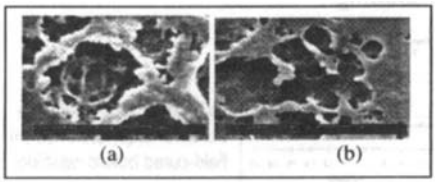


FIG.6 Network morphology of E48:TM74A: n-VP viewed under SEM (a) reference (b) field-cured

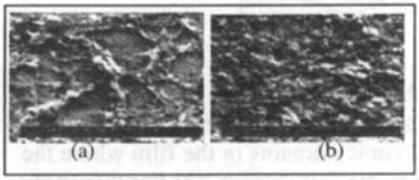


FIG.7 Network morphology of E48:TM74A: PMMA viewed under SEM (a) reference (b) field-cured

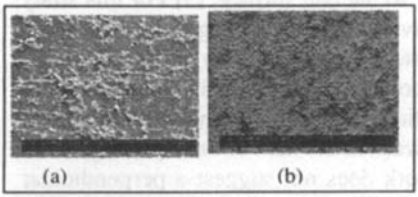


FIG.8 Network morphology of E48:TM74A: n-VP: PMMA at low magnifications (a) reference (b) field-cured

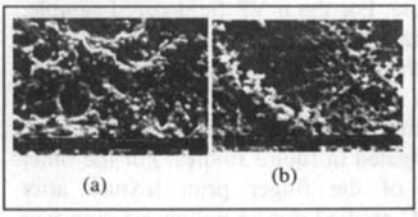
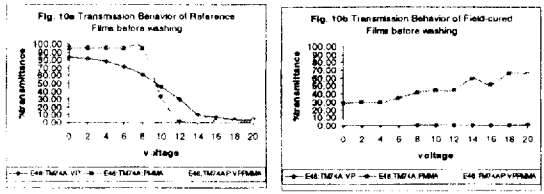


FIG.9 Network morphology of E48:TM74A: n-VP: PMMA at high magnifications (a) reference (b) field-cured

In Fig. 10a the transmittance of the chiral-nematic reference samples decreased with increasing voltage. Since a high transmittance value was observed at the off state, this means that the pitch is in the IR region. As the voltage is increased, the material is switched into the focal conic texture and become scattering. This result is similar to the observations of Yang et.al. [2] However, the focal conic texture is a result of the competition between the field and the polymer network. Since there is no alignment layer, the only source of competition for the field is the anchoring effect of the polymer network on the LC molecules. If there was no interaction at all over at the polymer-LC intrerface, then the helical axis should have untwisted and the film should have remained highly transmitting.



(a) (b)

FIGURE 9: Transmittance behavior of (a)reference (b) field-cured before washing

Figure 10b show that for the field-cured film, the transmittance increase with voltage. In Yang's work, the scattering state for the field-cured film is due to the focal conic domains in the film where the polymer network is perpendicular to the cell surface. [3] For this study, the opaque condition was observed to have a finger print texture, which is actually a metastable stage experienced by cholesteric LCs having a homeotropic to focal-conic transition. It is maintained by supplying a field less than the critical field needed to unwind the helix. Another difference from Yang's work is the network morphology. For all field-cured samples, the network does not suggest a perpendicular growth except for the n-VP sample. For the n-VP field-cured sample, the film does not switch and remained opaque over the voltage range considered. This despite of the homeotropic orientation of the polymer network. This means that somehow, a homeotropically oriented polymer network stabilizes the finger print texture Such phenomenon has yet to be investigated in future studies. For the other two samples, the stabilization of the finger print texture after polymerization means that 8V AC applied during polymerization was not enough to fully untwist the helical axis. It only switched the

sample into the finger print state. Upon removal of the field such orientation was maintained and this could only be due to anchoring imposed by the polymer network. During electro-optic measurement, the finger print state then switched to the homeotropic orientation with an increased in voltage as seen in Fig. 10b.

Just like in the nematic case, thick films were obtained after injection of fresh LC. The same textures as in the original preparation were observed. Again, the transmittance behavior was not replicated after the second injection as seen in Fig. 11.

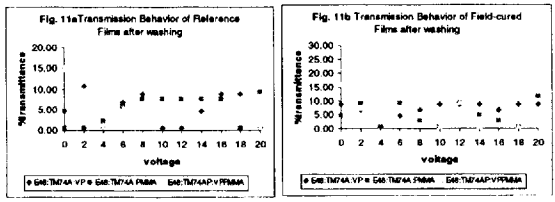


FIGURE 11: Transmittance behavior of (a)reference (b) field-cured after washing

SUMMARY AND RECOMMENDATIONS

For both sets of samples, it was observed that standard textures were observed right after polymerization.. A very important result is the observation of the finger print texture from the field-cured samples of chiral-nematic mixtures. This is important because, usually, this texture is only a metastable stage and is not stabilized at all.

From the discussion above, it is noted that the electro-optic behavior for both the nematic and chiral-nematic set is dependent on the interaction between the LC and the polymer. For the nematic set, the scattering and transparent state is due to the orientation of the LC molecules anchored at the LC-polymer interface. For the chiral set, the stabilization of the textures leading to a scattering or transparent state is again due to the anchoring of the polymer on the LC molecules around it.

The observation of similar textures after injection of fresh LC points to the ability of the polymer to reorient the molecules to their original orientation. This ability and the interaction between the LC and polymer at the interface is a manifestation of the capability of the polymer to imprint LC molecules.

However, the transmittance behavior was not replicated. The cyclic behavior observed for both sets of samples is something novel

and should be a focus of another study. One hypothesis for this cyclic behavior is that, due to the excess amount of LC used at the second injection, optimum ratio between the imprinting specie (LC) and the template (LC sites within the polymer) is not achieved.

Molecular imprinting could be quantified by doing high performance liquid chromatography on the systems. This method will allow quantitative discussion of the molecular imprinting process in PSLCs.

References

[1] K. Amundoson, 1998, Physics Review Letters E, 3.
[2] Liquic Crystal in Complex Geometries–Formed by polymer and porous networks, ed. G. Crawford and S. Zumer, Taylor and Francis, Great Britain, 1996.
[3] Ibid.