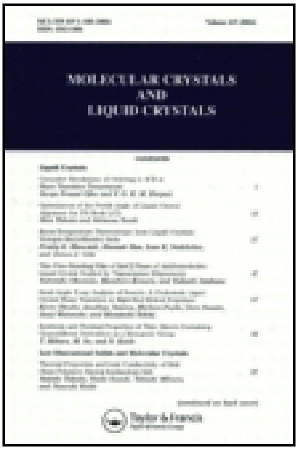

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Free-Standing Polymer-Stabilized Ferroelectric Liquid Crystal Film: Chemical Study of Phase Separation

Hideo Fujikake [a], Jun Yonai [a], Hiroto Sato [a], Yuzuru Tsuchiya [a], Hiroshi Kikuchi [a], Yoshiki Iino [a], Masahiro Kawakita [a] & Kuniharu Takizawa [a]

[a] NHK Science & Technical Research Laboratories, 1-10-11 Kinuta, Setagaya-Ku, Tokyo, 157-8510, Japan

To cite this article: Hideo Fujikake, Jun Yonai, Hiroto Sato, Yuzuru Tsuchiya, Hiroshi Kikuchi, Yoshiki Iino, Masahiro Kawakita & Kuniharu Takizawa (2001): Free-Standing Polymer-Stabilized Ferroelectric Liquid Crystal Film: Chemical Study of Phase Separation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 397-404

To link to this article: http://dx.doi.org/10.1080/10587250108025319

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 397-404
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Free-Standing Polymer-Stabilized Ferroelectric Liquid Crystal Film: Chemical Study of Phase Separation

HIDEO FUJIKAKE*, JUN YONAI, HIROTO SATO,
YUZURU TSUCHIYA, HIROSHI KIKUCHI, YOSHIKI IINO,
MASAHIRO KAWAKITA and KUNIHARU TAKIZAWA

*NHK Science & Technical Research Laboratories, 1–10–11 Kinuta,
Setagaya-Ku, Tokyo 157–8510 Japan*

This paper describes a chemical study of a new free-standing ferroelectric liquid crystal film containing a rigid fiber network polymer formed by photopolymerization-induced phase separation. The liquid crystal and acrylate polymer separated from a homogeneous solution were individually dissolved by different solvents, and examined by high-performance liquid chromatography and gel permeation chromatography, respectively. The liquid crystal component segregated from the solution including 20wt% monomer had a purity of more than 96%, and contained less than 3% of decomposition products and a little remaining monomer, less than 0.3%. The measured molecular weight of the segregated polymer exhibited a broad distribution from 10^3 to $10^6$with a mean polymerization degree of about 100, which increased with monomer concentration. Such a free-standing composite film containing a rigid polymer network is applicable to a shock-resistant ferroelectric liquid crystal display panel because the transparent substrates are supported by the composite film.

INTRODUCTION

A fine polymer structure [1] dispersed in ferroelectric liquid crystal [2] (FLC) is useful for protecting the fragile smectic layer structure of FLC from mechanical shock and force. The mechanical stability of free-standing films containing the polymer and FLC can overcome the problem of the fragile FLC alignment structure of a conventional surface-stabilized FLC device [3] with high-speed electrooptic response, which is desired to realize a video image display. The FLC/polymer composite film is also applicable to a future flexible-sheet display, which has the advantage of large-size and light-weight panel structures, because the dispersed polymer firmly supports the flexible plastic substrates.

---

* Corresponding author: fujikake@strl.nhk.or.jp

We have already proposed a new free-standing FLC film containing an aligned fiber network polymer,[4] which stabilizes and protects smectic layers of FLC. The FLC/polymer composite film features mechanical stability, a high-speed response, and grayscale capability based on spatially-distributed FLC domain switching.[5] Although thorough separation of the FLC and polymer is needed to enhance the mechanical stability and improve the FLC switching behavior, no analysis method of the phase separation has been established so far, and few reports on quantitative analysis of the photopolymerization-induced phase separation[6] have been made.

In this paper, the chemical constituents of our polymer-stabilized FLC (PSFLC) film are clarified using several liquid chromatography methods. The purity of separated FLC material and the molecular weight of the segregated polymer were evaluated. From these experimental results, the polymerizing conditions needed to control the phase separation are discussed to design a free-standing PSFLC film.

PHASE SEPARATION

The composite film of FLC and polymer materials was formed by photopolymerization-induced phase separation with molecular alignment.[7] The monofunctional liquid crystalline acrylate monomer[8] (UCL-001, Dainippon Ink & Chem.) was homogeneously mixed with an FLC material (CS-1030, Chisso). As the nematic-phase solution sandwiched between rubbed polyimide alignment layers (AL-1254, JSR) was irradiated with ultraviolet (UV) light with a wavelength of 365 nm, the monomer aligned with FLC molecules was polymerized. As a result, aligned acrylate polymer shown in Fig.1 was synthesized. The copolymer of the figure was made from the two kinds of acrylate monomer materials with rigid liquid crystalline molecular structures X, and the materials were in advance mixed in a concentration ratio of 1:1. The thickness of the composite film was less than 2 μm.

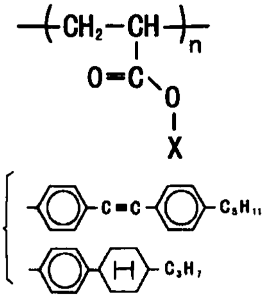

FIGURE 1 Molecular formula of the synthesized polymer.

In the present study, we created an anisotropic network morphology of polymer fiber as a fibril aggregation[9] aligned parallel to the rubbing direction of the alignment layers on the substrates. The polymer morphology formed at a polymer concentration ratio of 20wt% was observed with a polarizing microscope, as shown in Fig.2. The bright parts in the figure showed the formed polymer network. The polymer fiber network spread out three-dimensionally in the PSFLC film between the substrates. A scanning electron microscope (ESEM-2700 supplied by Nikon Instec) captured a more detailed image of polymer formed with a 30wt% concentration, as shown in Fig.3, when the FLC material was removed.

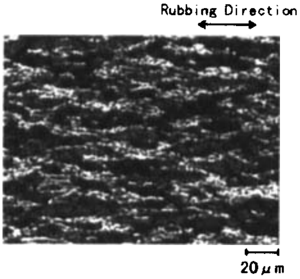

FIGURE 2 Polarizing microscope photograph of the polymer network.

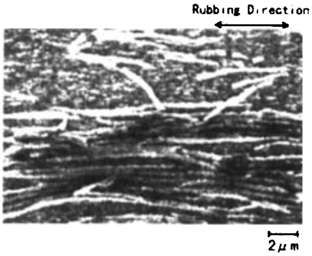

FIGURE 3 Scanning electron microscope photograph of the polymer fibers.

FLC PURITY

The PSFLC film formed by the above method was chemically analyzed in the sequence shown in Fig.4. The composite film on a substrate was separated into the two materials by different solvents. The microscope images of Fig.5 show the change in the substrate with solvent separation.

From the formed composite film shown in Fig.5(a), the FLC material was first dissolved out with ultrasonic vibration cleaning using ethanol. Subsequently, the remaining polymer shown in Fig.5(b) could be dissolved out with tetrahydrofuran (C_4H_8O) solvent, until the polymer morphology disappeared as shown in Fig.5(c).

FIGURE 4 Experimental sequence for the chemical analysis of the PSFLC film.

The chemical constituents of the extracted FLC solution were then


(a) Before Dissolution (b) After Ethanol Dissolution (c) After Tetrahydrofuran Dissolution

FIGURE 5 Optical microscope photographs of the PSFLC film dissolved by solvents.

separated using a high-performance liquid chromatography (HPLC) system (Alliance System 486, Nihon Waters) shown in Fig.6(a). The extracted FLC material was dissolved with a solvent of acetonitrile CH_2CN (95wt%) and water (5wt%), and the solution permeated a column having a diameter of 4.6 mm and length of 150 mm, filled with octadecyl with a non-polarity molecular structure coated on silica gel with a 3-μm diameter (Develosil ODS-HG, Nomura Chem.).

In this case, the FLC molecules with larger electric polarization remained in the column for shorter times. Each concentration of various FLC components separated by retention time was detected by ultraviolet light absorption, because aromatic compounds in the FLC and monomer molecules strongly absorbed UV light with a wavelength of 254 nm. The FLC components extracted from the composite film with an FLC concentration of 20wt% were separated by the above method, as shown in Fig.7. Comparing the absorption intensities of the extracted FLC materials with those of an original pure FLC material, we evaluated the

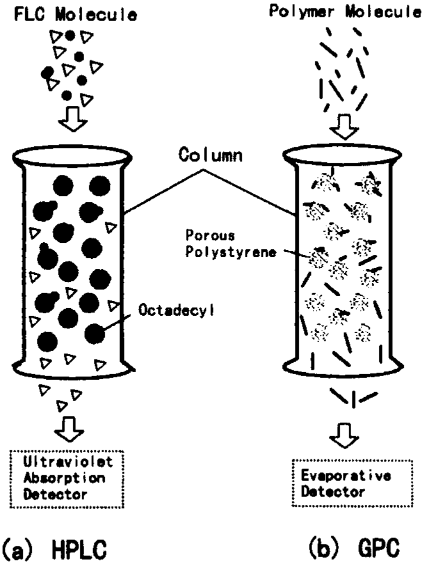

FIGURE 6 Principle of liquid chromatography methods for the chemical analysis of the composite film.

constituents of the FLC and their amount. We found that the segregated FLC had a purity of more than 96%. It also contained an unknown material of less than 3% and a remaining monomer, less than 0.3%.

It is thought that the unknown material was a decomposition product of the FLC, because the same absorption peak was detected in the FLC material irradiated by UV light without doping monomer. The impurity concentration also increased as the UV irradiation intensity became stronger, as shown in Fig.8. This impurity may induce unstable electrooptic behavior of PSFLC films because it can provide ions and radicals in the dispersed FLC. The optical damage to the FLC material should be reduced by optimizing the UV intensity and spectrum. [10]

Figure 9 shows the total amount of the detected FLC. When the FLC was mixed at a 80wt% concentration, the detected FLC concentration reached more than 77wt% in the composite film. Since no chemical reaction between the

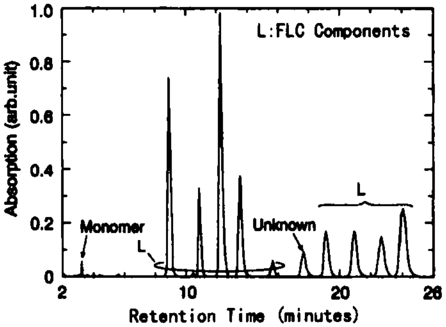

FIGURE 7 Chromatograph of the segregated FLC.

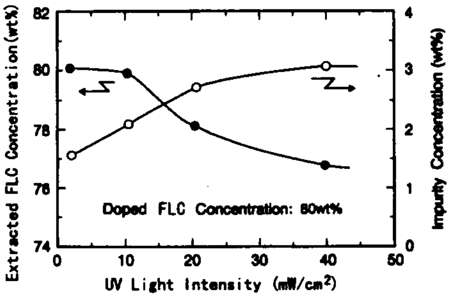

FIGURE 8 Concentration of the extracted FLC for different UV irradiation intensities.

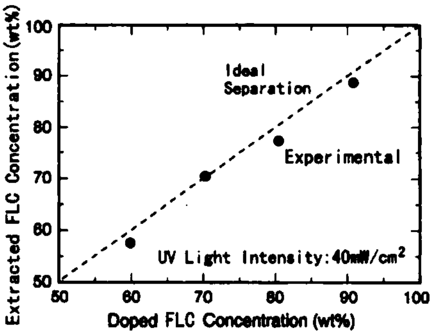

FIGURE 9 Detected FLC concentration ratios of the composite films.

FLC and polymer was recognized in the above analysis, this confirms that the formation method based on photopolymerization-induced phase separation is useful for fabricating PSFLC films.

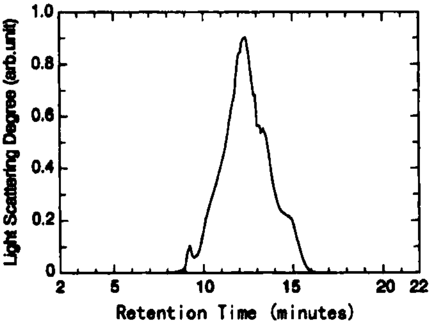

FIGURE 10 Chromatograph of the segregated polymer.

MOLECULAR WEIGHT

From the polymer/ tetrahydrofuran solution of Fig.4, the molecular weights of the polymer were evaluated using a gel permeation chromatography (GPC) system (510GPC, Nihon Waters) shown in Fig.6(b). The polymer with larger molecular weight rapidly passed through a column having a diameter of 7.5 mm and a total length of 600 mm filled with porous polystyrene (PLgel-5μ, Polymer Labs.) with a 5-μm diameter, because the polystyrene gel effectively captures polymer that has a smaller molecular weight. So the retention time increased with decreasing molecular weight of the obtained polymer. The change in amount of polymer passing through the column was measured with an evaporative detector that senses small light scattering from polymer. The components of the polymer obtained from the solution with 20wt% monomer were separated according to retention time, as shown in Fig.10.

The measured retention time for each polymer component was then converted into a molecular weight by using the conventional relationship between retention time and molecular weight of the standard polymer of narrowly distributed polystyrene (EasiCal, Polymer Labs.). The distribution of molecular weight of the polymer formed at various FLC concentrations was shown in Fig.11. The molecular weight curve of the polymer segregated from the solution containing 80wt% FLC had a broad distribution from 10^3 to 10^6. It is found that polymer with various molecular weights was formed in the FLC-rich solution.

By calculating the ratio of the obtained molecular weight of the polymer to the average molecular weight (295) of the monomer, we evaluated the mean degree of polymerization of the polymer as about 100 at 80wt% FLC concentration.

We also recognized that the mean molecular weight drastically increased with decreasing FLC concentration, as shown in Fig.12. When the polymer concentration was more than 20wt%, the mechanical strength for sustaining substrates was achieved. The polymer concentration and degree of polymerization are important indices to heighten the mechanical stability of the PSFLC.

When the UV irradiation intensity was varied, the molecular weight of the polymer showed a small change, as shown in Fig. 13, although the number of free radicals for polymerizing increased in the FLC/monomer solution with the stronger UV irradiation. The slight decrease in molecular weight at strong UV intensities may be caused by suppression of molecular drafting needed for polymerizing due to aggregation and stabilization of the polymer in the phase separation

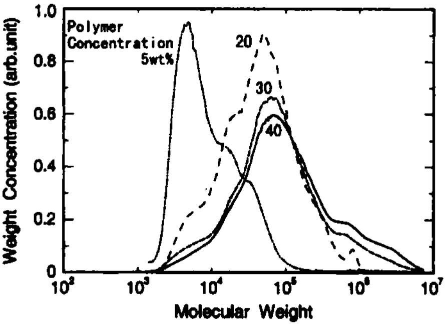

FIGURE 11 Molecular weight of the segregated polymer.

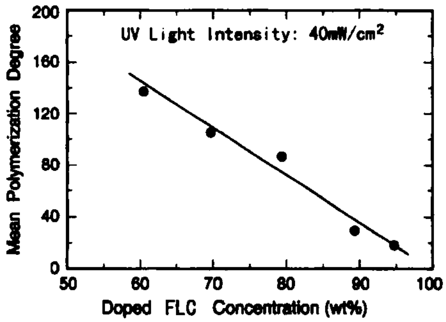

FIGURE 12 Molecular weight dependence of the polymer on FLC concentration.

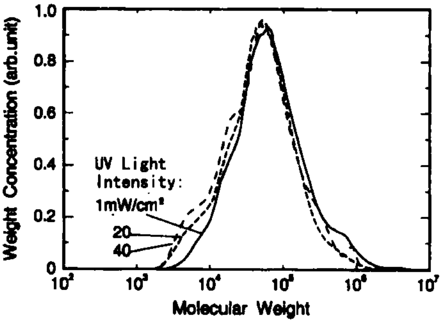

FIGURE 13 Molecular weight of the segregated polymer for various UV light irradiation intensities.

process. We also confirmed that the aggregated polymer contained a small amount of FLC materials (less than 0.01wt%) by HPLC analysis of the polymer solution. The high-purity of the polymer accounted for the mechanical strength of the composite film.

CONCLUSIONS

We clarified the purity of the FLC and the molecular weight of the polymer in a free-standing PSFLC film formed by photopolymerization-induced phase separation. The FLC and polymer materials were almost completely separated in the composite film, but the FLC contained a few wt% of decomposition product. It is necessary to reduce chemical damage to the FLC material caused by ultraviolet irradiation. The molecular weight of the aggregated polymer increased with increasing polymer concentration and had a broad distribution up to 10^6.

The obtained rigid polymer network with higher polymer concentration will allow PSFLC films to use plastic sheet substrates. A detailed study of the smectic layer structure in the polymer network should be performed.

ACKNOWLEDGEMENTS

We thank T. Ando of Nikon Instec Corp. for taking the scanning electron microscope pictures and T. Murashige of the Science University of Tokyo for his experimental cooperation.

References

[1] H. Molsen and H.S. Kitzerow, *J. Appl. Phys.*, *75*, 710 (1994).

[2] R.B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. Phys.*, *36*, L69 (1975).

[3] N.A. Clark and S.T. Lagerwall, *Appl. Phys. Lett.*, *36*, 899 (1980).

[4] H. Fujikake, T. Aida, J. Yonai, H. Kikuchi, M. Kawakita and K. Takizawa, *Jpn. J. Appl. Phys.*, *38*, 5212 (1999).

[5] H. Fujikake, K. Takizawa, H. Kikuchi, T. Fujii, M. Kawakita and T. Aida, *Jpn. J. Appl. Phys.*, *36*, 6449 (1997).

[6] N.A. Vaz, G.W. Smith and G.P. Montgomery, Jr:, *Liq. Cryst.*, *146*, 1 (1987).

[7] E. Shimada and T. Uchida, *Jpn. J. Appl. Phys.*, *31*, L352 (1992).

[8] S. Kataoka, Y. Taguchi, Y. Iimura, S. Kobayashi, H. Hasebe and H. Takatsu, *Mol. Cryst. Liq. Cryst.*, *292*, 333 (1997).

[9] Y.K. Fung, D.K. Yang, S. Ying, L.C. Chien, S. Zumer and J.W. Doane, *Liq. Cryst.*, *19*, 797 (1995).

[10] H. Fujikake, K. Takizawa, H. Kikuchi, T. Fujii, M. Kawakita and T. Aida, *Jpn. J. Appl. Phys.*, *37*, 895 (1998).