Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: B. Carbonnier, A. Best, T. Pakula, M. Benmouna & U. Maschke (2004): Light Scattering from Monomeric and Electron Beam Cured Acrylate/E7 Systems, Molecular Crystals and Liquid Crystals, 409:1, 183-189

To link to this article: http://dx.doi.org/10.1080/15421400490431237

Mol. Cryst. Liq. Cryst., Vol. 409, pp. 183–189, 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431237

LIGHT SCATTERING FROM MONOMERIC AND ELECTRON BEAM CURED ACRYLATE/E7 SYSTEMS

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A static light scattering study of monomeric (uncured) and Electron Beam (EB) cured Tripropyleneglycoldiacrylate (TPGDA) and E7 (a nematic Liquid Crystal) systems is reported. This study includes a detailed investigation of the structural properties in terms of temperature, composition and scattering angle. Knowledge of the phase diagrams helps us to achieve a better understanding of the scattering curves and rationalize data in terms of the LC configuration inside droplets. The depolarized component of the scattered intensity measured under cross polarizers exhibits patterns reminiscent of anisotropic objects. The results can be correlated to the electro-optical responses of the investigated systems relevant to applications in display technology and smart windows.

Keywords: electron beam curing; light scattering; liquid crystal; polarized optical microscopy; polymer; polymer dispersed liquid crystal

The first author (B. C.) gratefully acknowledges the support of the Max-Planck-Institut für Polymerforschung and the Centre National de la Recherche Scientifique.

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INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) have been developed within the past two decades and are potentially useful for electro-optical applications. They can be switched electrically from a cloudy, light scattering to transparent states (see references 1, 2 and references cited therein). The process of Polymerization Induced Phase Separation (PIPS) is among the most used methods for PDLC elaboration. It allows to have a wide range of interesting materials by tuning their properties for specific applications [1–3]. Adjusting the electro-optical response for a given application requires to have a good control of various parameters including refractive indices of liquid crystals and polymer matrices, density and size distributions of the liquid crystal droplets within polymer. These characteristics are mainly influenced by the kinetics of polymerization/cross-linking and the concomittant phase separation process. In this paper, we describe the angular dependence of the scattered light intensity of monomer and electron-beam cured blends of tripropyleneglycoldiacrylate (TPGDA) and the liquid crystal E7. To avoid the necessity of making large and uncertain corrections due to multiple scattering effects [4,5], it is desirable to work with samples in the form of thin films on glass plates. In the absence of an applied electrical field, optical axes of individual LC droplets align randomly. Hence, each droplet presents a different refractive index to light impinging perpendicular to the film surface. The resulting spatial variation of the refractive index causes the film to scatter incident light.

The purpose of this paper is to address the problem of light scattering from a suspension of nematic liquid crystal droplets in a solid polymer matrix. We assume that the configuration of droplets is bipolar and limit ourselves to the case of liquid crystals with a positive dielectric anisotropy $\Delta\varepsilon = \varepsilon_\perp - \varepsilon_\parallel > 0$. Hence, the investigated films are quite opaque to incident light in the absence of an external field (off-state). This opacity is due to the strong scattering of light originating from random fluctuations in the orientation of droplet directors.

In this paper we consider a model system of E7/TPGDA cured with EB radiation at a composition 70/30 by weight. This is a model system exhibiting the optimal conditions for high performance electro-optical response functions [6].

EXPERIMENTAL PART

Materials and Sample Preparation

The nematic LC used in this study was the eutectic mixture E7 from Merck Eurolab (Darmstadt, Germany), composed of three cyanobiphenylenes and

one cyanoterphenylene derivatives. Nevertheless, E7 exhibits a single nematic-isotopic transition temperature ($T_{NI} = 61°C$). TPGDA was obtained from Cray Valley, France. A blend composed of 30 weight percent (wt-%) TPGDA and 70 wt-% E7 was mechanically stirred at room temperature until the mixture becomes homogeneous. Cured samples were prepared by submitting the initial reactive mixture uniformly applied on a glass plate to electron beam radiation.

Uncured samples were prepared by sandwiching a drop of the mixture between two round glass slides while cured samples were used without further modification.

Samples were submitted to a heating rate of 5°C/min from room temperature to 80°C and left for 5 min in the isotropic state. Then samples were cooled at a rate of −2°C/min. Thermo-optical and thermo-light scattering behaviour of samples were examined during the cooling ramp.

Electron Beam Curing

The Electron Beam (EB) generator was an Electrocurtain Model CB 150 (Energy Sciences Inc.). The samples were placed in a tray which was passed in an inert atmosphere under the irradiation source on a conveyor belt. The applied dose was 105 kGy.

POM Measurements

A thermo-optical study was performed using a polarized optical microscope from Zeiss (Germany), equipped with a heating-cooling stage (Linkam THMS 600) and a temperature control unit (Linkam 91). Optical micrographs were recorded using a Hitachi KP-D50 color digital camera.

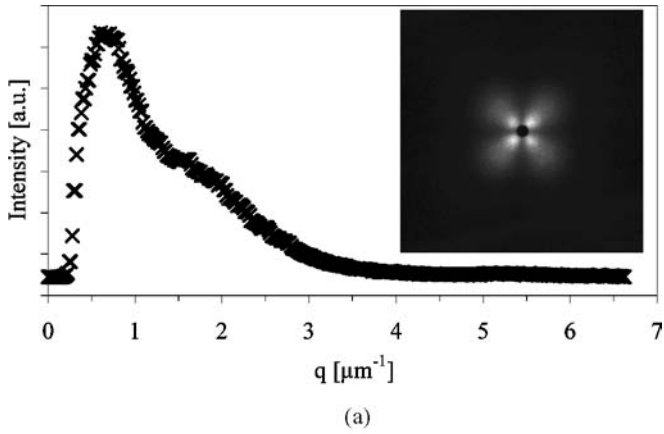
Light Scattering

Light scattering experiments were conducted by using a He-Ne laser ($\lambda = 0{,}6328\,\mu m$, power 10 mW), a set of polarizers, and a Hamamatsu C3077 CDD video camera. The scattered intensities were investigated as a function of temperature using a heating-cooling stage (Linkam THMS 600) and a temperature control unit (Linkam 90). The laser was polarized perpendicular to the scattering plane. In this study, we considered the HV mode which means that the analyzer axis is perpendicular to the polarization direction of the incident beam. The signal was digitized and analyzed with the help of a Small Angle X-Ray Scattering software commercialized by Bruker Analytical X-Ray System (Wisconsin, USA).

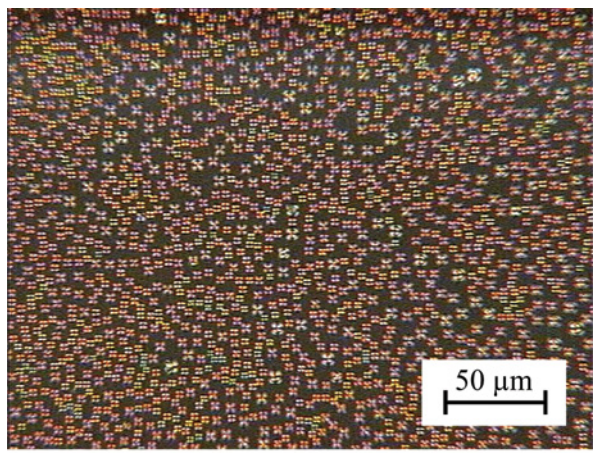
RESULTS AND DISCUSSION

Precursor Mixture

Figure 1a represents the small angle HV light-scattering pattern of the 30 wt-% TPGDA/70 wt-% E7 precursor mixture at -10°C. It shows a



(a)



(b)

FIGURE 1 (a) HV light-scattering intensity versus $q = 4\pi\langle n\rangle\sin(\theta/2)/\lambda$, where θ, λ and $\langle n\rangle$ represent the scattering angle, the incident wavelength, and the mean index of refraction, respectively (precursor mixture made of 30 wt-% TPGDA and 70 wt-% E7 at -10°C). (b) Typical POM micrograph showing a dense regular distribution of spherical droplets (30 wt-% TPGDA/70 wt-% E7, $T = -10^{\circ}$C). (See COLOR PLATE VIII)

non-normalized intensity profile determined by image analysis of HV scattering along an azimuth angle of 45° as a function of the amplitude of the wave vector $q = 4\pi\langle n\rangle \sin(\theta/2)/\lambda$, where θ, λ and $\langle n\rangle$ represent the scattering angle, the incident wavelength, and the mean index of refraction, respectively. Interestingly, the scattering envelop exhibits a maximum near $0.5\,\mu m^{-1}$ followed by a shoulder near $1.5\,\mu m^{-1}$.

The insert of Figure 1a shows a four-lobe pattern typical of anisotropic scattering objects. The central part is symmetrical indicating a nematic order of the liquid crystal molecules in the droplets. This is a characteristic pattern for a radial configuration of nematic droplets. It has been also observed on poly(dimethylsiloxane)/E7 systems [2]. According to this reference, the HV component admits maxima at odd multiples of $\pi/4$ and vanishes at multiples of $\pi/2$. This behavior yields the characteristic four-leaf clover pattern. These considerations can be rationalized with the standard models of scattering from anisotropic objects such as the Raleigh-Gans (RGA) and Anomalous Diffraction Approximation (ADA). However, a detailed account of the present experimental findings including the shoulder of Figure 1a is still lacking and will be the subject of future investigations.

The phase diagram established by Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC) confirms those findings. In particular, it shows that under the conditions of the light scattering experiments the system exhibits two coexisting phases, one of them is a pure nematic liquid crystal phase. Figure 1b gives a typical POM micrograph showing a dense regular distribution of spherical droplets. The four-lobe texture revealed by the light scattering pattern is corroborated by this picture.

EB-cured System

A typical curve showing the small angle HV light-scattering pattern of the corresponding EB-cured system is represented in Figure 2a. In this case, a ϕ-independent circular intensity pattern was recorded where ϕ refers to the azimuth angle measured from the polarization of the incident beam. This pattern is somewhat simpler compared to the case of uncured samples. The scattering envelop reveals a single maximum at nearly the same position (i.e., $q_m = 0.5\,\mu m^{-1}$) followed by a slow decrease of the intensity as q increases. While the precursor mixture gives a pronounced drop of the intensity with q, the drop in the case of the corresponding polymerized sample is slower. The figure insert shows a bright spherical spot in contrast to the four-lobe pattern of the precursor system. Several parameters have to be taken into account to explain the observed behavior and differences between uncured and cured samples. Comparison should be made on

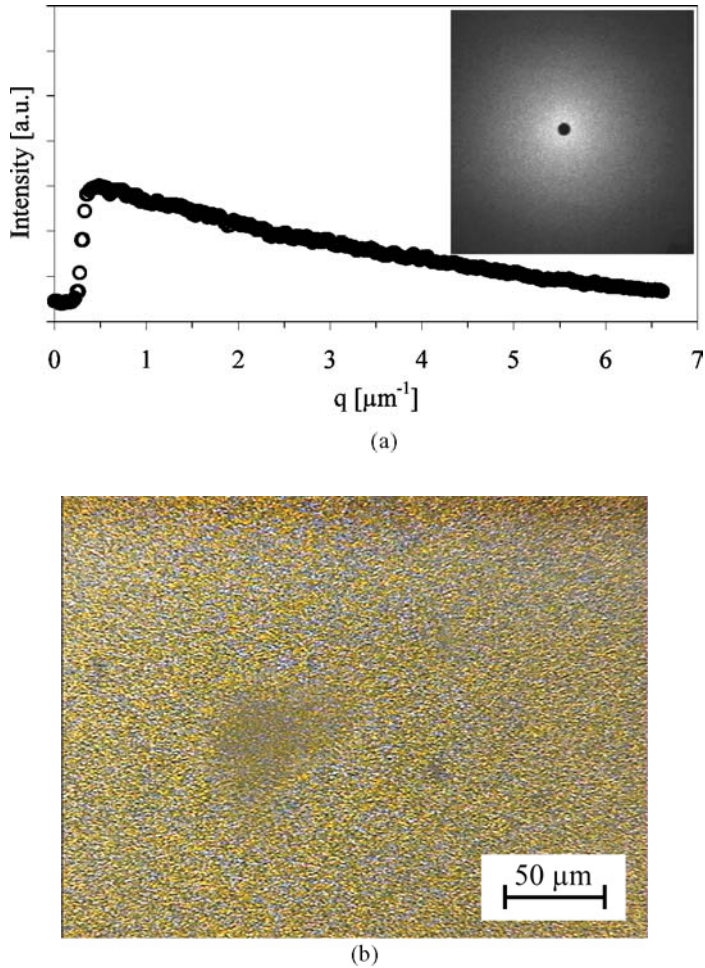


FIGURE 2. (a) HV light-scattering intensity versus q (EB-cured 30 wt-% TPGDA/70 wt-% E7 mixture at -10°C. The figure insert is typical of isotropic scattering objects. (b) Typical POM micrograph (EB-cured 30 wt-% TPGDA/70 wt-% E7 blend, $T = -10^{\circ}$C). Note the much smaller droplets compared to Figure 1b. (See COLOR PLATE IX)

samples with the same film thickness. Polymerization induced phase separation process governs the sample morphology leading to the possibility to control the number density, size, form, and director configuration of the LC molecules. Multiple scattering effects might also contribute to the scattered intensity. Optical Microscopy reveals much smaller droplets in the

case of EB-cured samples as one can see from the micrograph of Figure 2b. Adaptation of models developed in the literature for crystalline polymers is currently under progress. We hope to be able to rationalize the present results using reasonable conditions for the system TPGDA/E7.

CONCLUSIONS

A comparative study of light scattering by monomeric and EB-cured TPGDA/E7 mixtures has been performed. The scattered intensity was measured as a function of q, the amplitude of the wave vector. Polarized Microscopy observations have shown that changes in the scattering pattern after EB-curing are due to changes in the size distribution of the scattering objects. Further theoretical work is in progress to rationalize these results and correlate the light scattering envelop with the sample morphology of the films.

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