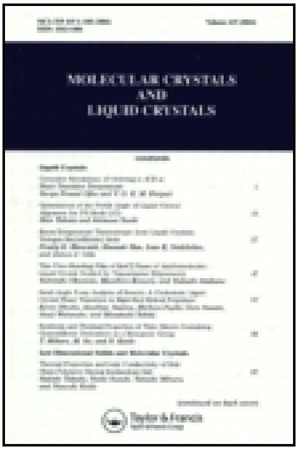

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Static Light Scattering from Tripropyleneglycoldiacrylate/E7 Mixtures: Theorie and Experiments

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STATIC LIGHT SCATTERING FROM TRIPROPYLENEGLYCOLDIACRYLATE/E7 MIXTURES: THEORIE AND EXPERIMENTS

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Experimental static Small Angle Light Scattering (SALS) data obtained from a selected monomer – liquid crystal system are presented. A blend involving the eutectic nematic mixture of low molecular weight liquid crystals (E7) and a difunctional monomer (tripropyleneglycoldiacrylate or TPGDA) was choosen to highlight the variations of the light scattering intensity in terms of scattering and azimuthal angles. Measurements of SALS were made in the VH mode under cross-polarized optical alignments.

The experimental results were compared to a theory developed originally for bulk semi-crystalline polymers showing an anisotropic behavior and adapted to liquid crystalline systems. Depolarized light scattering intensities were calculated for isolated spherical droplets of liquid crystal molecules exhibiting a radial configuration. In particular, the characteristic anisotropic features of radial droplets in the VH mode were obtained both experimentally and theoretically. A good agreement between theoretical results and experimental findings was found for droplet radii of 5 μm.

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Keywords: liquid crystal; monomer; Rayleigh Gans Approximation; small angle light scattering

1. INTRODUCTION

The performance of Polymer Dispersed Liquid Crystals (PDLCs) in electro-optic applications depends crucially on the capacity of these systems to scatter light under the off-state conditions (no electric field applied) [1,2]. The random distribution of liquid crystal (LC) director orientation within the droplets generates enhanced variations in the refractive indices and leads to a strong scattering of the incident light. Under normal mode conditions for compounds with a positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp} > 0$), initially the system is opaque but when an electric field is applied, the LC molecules orient along its direction leading to a high film transparency. A characteristic parameter of the electro-optic response is the ratio of transmitted intensities in the on and off-states. Therefore, optical properties of the system under on and off states are important. In particular we are interested here in the depolarized light scattering components in the absence of an electric field denoted I_{VH}.

Small Angle Light Scattering (SALS) measurements were performed using a mixture of a low molecular weight LC and a monomer. A mixture composed of 30 weight percent (wt%) TPGDA and 70 wt% E7 is considered representing an interesting model system known to have good electro-optical response functions in its polymerized/crosslinked state [3].

The experimental results obtained from SALS measurements are compared to calculations of the light scattering intensities as a function of scattering and azimuthal angles. The formalism presented here is based on the van de Hulst [4,5] scattering matrix whose elements depend on the geometry of the system considered and the configuration of the LC within droplets. The calculation of the van de Hulst matrix elements is made under the Rayleigh-Gans Approximation (RGA) [6,7].

2. EXPERIMENTAL PART

a. Materials and Sample Preparation

The nematic LC used in this study was the eutectic mixture E7 from Merck Eurolab (Darmstadt,Germany), composed of 51 weight percent (wt%) of 4-cyano-4′-*n*-pentyl-biphenyl(5CB), 25 wt% of 4-cyano-4′-*n*-heptyl-biphenyl (7CB), 16 wt% of 4-cyano-4′-*n*-octyloxy-biphenyl (8OCB), and 8 wt% of 4-cyano-4″-*n*-pentyl-p-terphenyl (5CT). Nevertheless, E7 exhibits a single nematic-isotropic transition temperature ($T_{\mathrm{NI}} = 61°\mathrm{C}$) and its glass transition is at $-61°\mathrm{C}$. The ordinary, extraordinary and mean effective refractive indices of E7 at $\lambda = 632.8\,\text{nm}$ and $T = 25^\circ\text{C}$ are $n_o = 1.5183$, $n_e = 1.7378$ and $n_{LC} = 1.5948$, respectively. The latter quantity is defined in terms of the refractive indices n_o and n_e as follows $\text{n}_{\text{LC}} = \left(\frac{\text{n}_\text{e}^2 + 2\text{n}_\text{o}^2}{3}\right)^{1/2}$.

Tripropyleneglycoldiacrylate (TPGDA) as monomer was obtained from Cray Valley (France). The refractive index of this monomer is 1.4485 at $\lambda = 589\,\text{nm}$ and 25°C. A blend made of 30 wt% TPGDA and 70 wt% E7 was mechanically stirred at room temperature until the mixture became homogeneous.

The samples were prepared by sandwiching a drop of the mixture between two round glass slides. They 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, using a sample stage (Linkam THMS 600) coupled with a programmable temperature control unit (Linkam 90). Then they were cooled at a rate of −1°C/min. The SALS measurements were made at a temperature of 0°C during the cooling ramp in the above thermal process.

b. Small Angle Light Scattering (SALS)

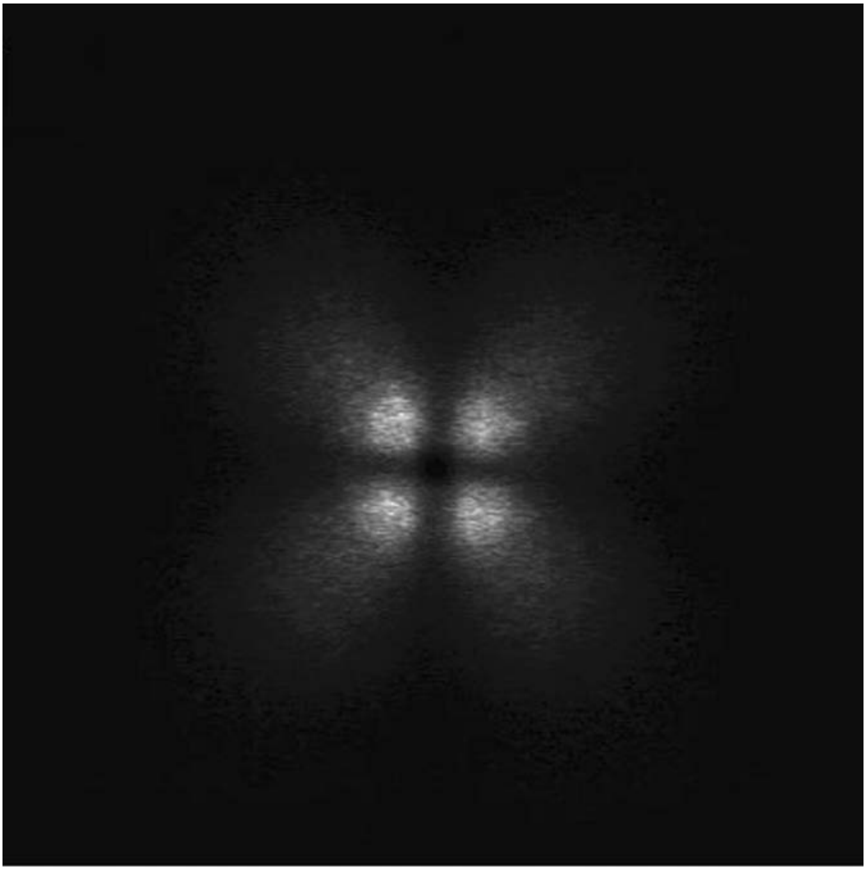
SALS experiments were conducted by using a vertically polarized He-Ne laser ($\lambda = 632.8\,\text{nm}$, power 10 mW), and a Hamamatsu C3077 CDD video camera. The I_{VH} component was obtained by putting the analyzer axis perpendicular to the polarization of the incident beam. The signal was analyzed with the help of an adapted small angle scattering software commercialized by Bruker Analytical X-Ray System (Wisconsin, USA).

c. Polarized Optical Microscopy

The thermo-optical study was performed on a POM Zeiss (Germany), coupled to a color digital camera (Hitachi KP-D50). The optical micrograph was taken at $T = 0^\circ\text{C}$ and recorded on the computer to illustrate the sample morphology under crossed polarizers.

3. RESULTS AND DISCUSSION

Panel a of Figure 1 represents the pattern of the depolarized component I_{VH} of light scattering, recorded during cooling of the precursor mixture TPGDA(30)/E7(70) at 0°C. This is a typical example of the light scattering pattern which depends upon temperature and composition. One sees the characteristic dependence with the azimuthal angle φ giving the four-lobe pattern and maximum scattering at odd multiple of $\varphi = \pi/4$. Figure 1b exhibits the sample morphology of the TPGDA(30)/E7(70) mixture at



(a)

FIGURE 1 a) Scattering pattern of I_{VH} obtained by SALS from the 30 wt% TPGDA/70 wt% E7 system at a temperature of 0°C. b) Micrograph obtained by POM of the same mixture under similar conditions.

T = 0°C, obtained by polarized optical microscopy. The observations were made under crossed polarizers revealing a radial configuration of the droplet directors, thus confirming the result shown in Figure 1a. The average droplet diameter could be deduced from magnified views of the POM picture and was estimated to roughly 10 μm.

These experimental results will be discussed by means of the theories developed for semi-crystalline polymers and adapted to liquid crystalline compounds. Using the general Van de Hulst matrix [5], the depolarized scattering intensity can be expressed in terms of matrix elements S_1, S_2,

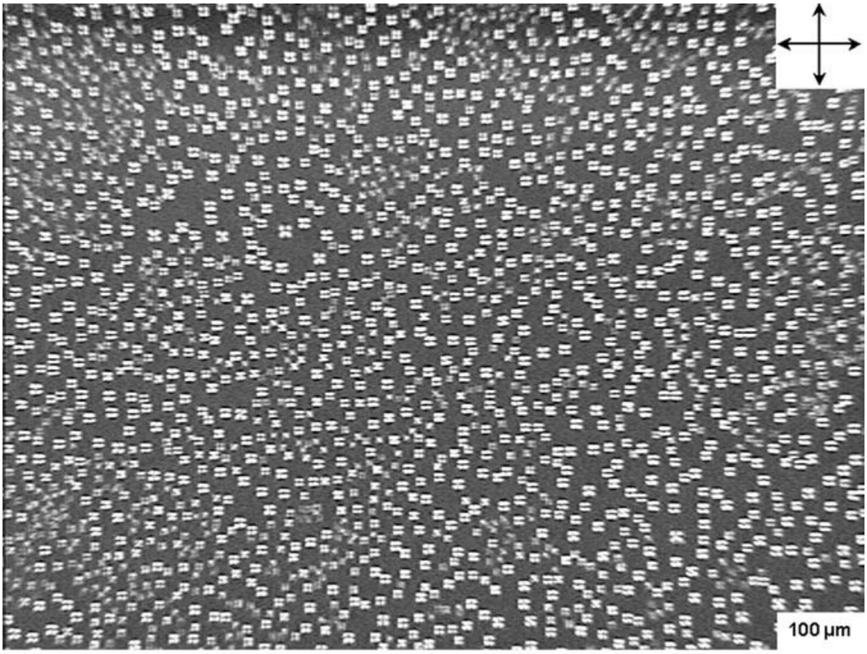


FIGURE 1 Continued.

S_3 and S_4. One finds [8,9]

$$I_{VH} = C\left[\frac{S_3 \ \sin^2\varphi - S_4 \ \cos^2\varphi \ \cos\theta + (S_2 - S_1 \ \cos\theta) \ \sin\varphi\cos\varphi}{\sqrt{1-\sin^2\theta \ \cos^2\varphi}}\right]^2$$

where θ is the scattering angle and C is a constant depending on the incident light intensity, the wavelength of the incident light, and the distance between the sample and the detector.

The matrix elements S_i (i = 1 to 4) depend on the droplet shape (spherical, ellipsoidal), LC configuration (radial, axial) and the working approximation (Rayleigh-Gans RGA or Anomalous Diffraction ADA). A detailed analysis of the scattering under all those conditions is straightforward but lengthy. It is beyond the scope of the present paper. Due to a lack of space, we will limit ourselves with the above general expressions and give the graphical results for a spherical droplet in the RGA scheme.

Following the equation above, the depolarized component of the SALS, I_{VH}, was calculated for a large number of droplet radii and the theoretical curves were confronted with the experimental data given below.

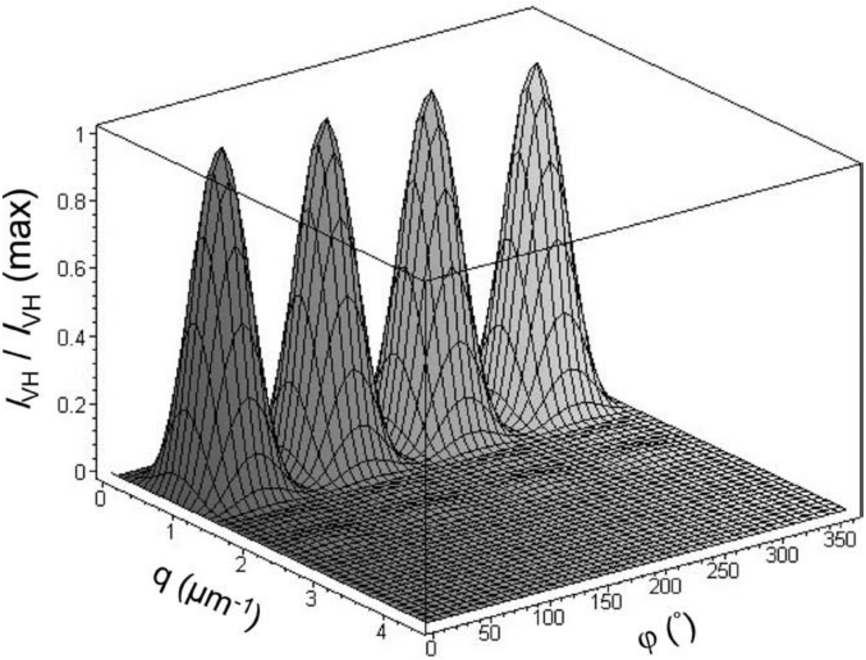


FIGURE 2 $I_{\rm VH}$ as a function of the wave vector $q(q = 4\pi \sin(\theta/2)/\lambda)$ and the azimuthal angle φ. This case corresponds to a spherical droplet with a radius of 5 μm and a radial configuration using the RGA.

Figure 2 shows a tri-dimensional plot of the calculated depolarized scattered intensity in terms of the wave vector $q = (4\pi/\lambda) \sin(\theta/2)$ and φ. The calculations were made in the RGA approximation for the case of spherical droplets with a radial configuration of the liquid crystal directors. A droplet radius of 5 μm was used to calculate the variation of $I_{\rm VH}$ presented in Figure 2, following the experimental results from microscopy observations.

Figure 3 shows the normalized depolarized scattering intensity $I_{\rm VH}$ in terms of the azimuthal angle φ at a constant q value of $1\,\mu m^{-1}$, which corresponds roughly to the maximum intensity observed. The theoretical curve shows the expected oscillatory trend of $I_{\rm VH}$ in terms of φ, with maxima located at odd multiple of $\varphi = \pi/4$. A good agreement was reached between the calculated curve compared with the experimental result.

Complementary observations can be made in the case of the q-dependence of the depolarized component $I_{\rm VH}$ for $\varphi = 45^\circ$ as illustrated in Figure 4. The experimental data obtained under the same conditions show an intensity maximum around $I_{\rm VH} = 0.8\,\mu m^{-1}$ and a slow decrease of the intensity with the wave vector q. Theoretical curves are given for three

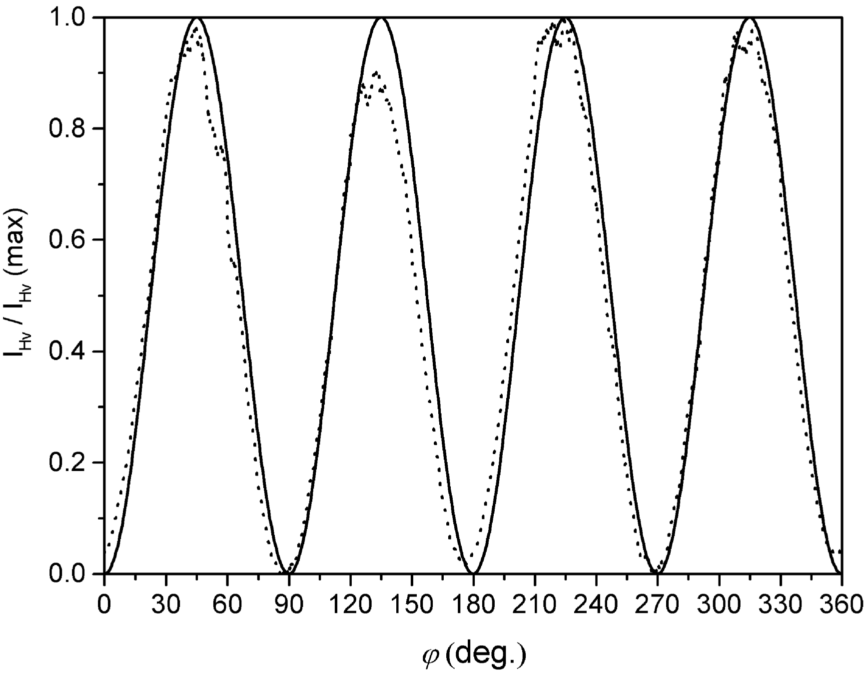


FIGURE 3 Variation of I_{VH} versus azimuthal angle φ at a wave vector $q = 1\,\mu m^{-1}$: The dotted line corresponds to experimental results obtained from the 30 wt% TPGDA/70 wt% E7 system at a temperature of 0°C. The continuous line represents the theoretical result using the same conditions as in Figure 2.

different droplet radii 4, 5, and 6 μm. Indeed, the calculated curve for a droplet radius of 5 μm shows a good qualitative agreement with the experiment but the width and the slope at high q-values are different. In particular, a value of $q = 0{,}8\,\mu m^{-1}$ was found for the position of the maxima of the calculated I_{VH} which is in good agreement with the experimental result. However, a slow decrease of I_{VH} for higher q values was observed experimentally which has not been found in the calculated curves. Indeed, the theory predicts no scattering at q values higher than $2{,}5\,\mu m^{-1}$ where still considerable values for I_{VH} were measured. The presence of anisotropic objects with radii smaller than 5 μm might be responsible for the slow decrease of I_{VH}. In order to illustrate this hypothesis, two theoretical curves for droplet radii of 4 μm and 6 μm were included in Figure 4. One clearly observes that the scattering curves tend to higher q-values with decreasing size of the scattering objects thus confirming the above mentioned assumption.

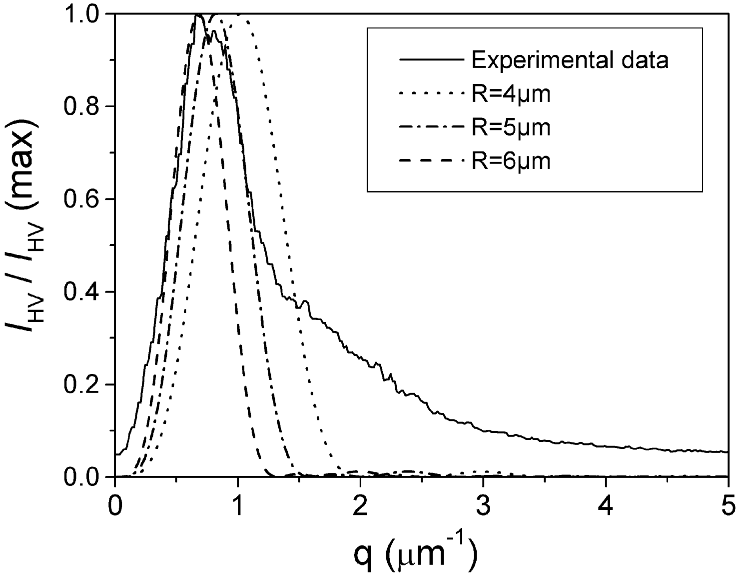


FIGURE 4 Variation of I_{VH} versus scattering wave vector q at an azimuthal angle $\varphi = 45°$. Experimental data and theoretical results are displayed. The latter correspond to droplet radii of 4, 5, and 6 μm obtained using the same conditions as in Figure 2.

4. CONCLUSION

The light scattering intensities from a monomer/liquid crystal system was investigated in terms of scattering and azimuthal angles. Experiments were performed on a mixture of difunctional acrylate (TPGDA) and nematic liquid crystal E7 at a composition of 30 wt% TPGDA and 70 wt% E7. The theoretical calculations were based on a general scheme developed for semi-crystalline polymers using the Van de Hulst matrix formalism. Plots of the depolarized scattered intensity versus scattering wave vector and azimuthal angle showed a good agreement with experimental data in the case of spherical droplets with radial configuration and a radius of 5 μm.

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