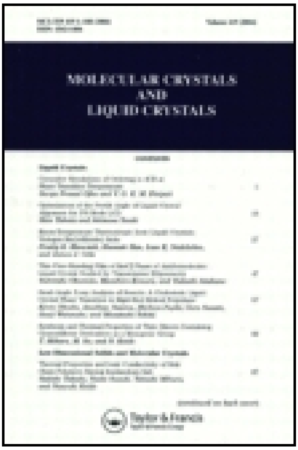

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Light Scattering from Poly (Acrylate)/E7 Mixtures

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A Light Scattering (LS) study of Poly(acrylate)/E7 mixtures is presented. The polarized component Ivv is measured as a function of the scattering angle for several compositions. The data are compared with the theoretical predictions of the scattering intensity in the case of isotropic and anisotropic spheres in the Rayleigh-Gans Approximation (RGA) and in the Anomalous Diffraction Approximation (ADA). Information on the size and optical symmetry of the droplets is obtained neglecting interparticle correlations and multiple scattering effects. Possible correlations between the present data and previous transmission measurements on these systems are discussed.

Keywords: Light scattering; polymer dispersed liquid crystals; Rayleigh-Gans approximation; Anomalous diffraction approximation

INTRODUCTION

Mixtures of polymers and liquid crystals (LCs) under certain conditions present structures showing nematic LC droplets dispersed in a polymer matrix[1-3]. These structures scatter light with intensities controlled by an external electric field. The droplets are birefringent with an ordinary and an extraordinary refractive index n_0 and n_e, respectively, while the polymer matrix has its own refractive index denoted n_p. The polymer is usually selected such that $n_p=n_o$. In the absence of an external field, the droplet directors are randomly oriented giving rise to strong scattering of light.

The purpose of the present paper is to analyze the intensity as a function of the scattering angle for Poly(acrylate)/E7 at different compositions and compare the data with theoretical predictions. These mixtures are prepared in our laboratory by the method of polymerization induced phase separation (PIPS)[4-7]. Reactive solutions made of mixtures of monomers, oligomers and nematic LCs are exposed to electron beam radiation. Crosslinking-polymerization takes place simultaneously and leads to phase separation of the polymer and the LC.

The structure and size of the LC droplets dispersed in the polymer matrix can be investigated by LS which consists of illuminating the sample with linearly polarized light, and examining the scattered intensity after the light has passed through an analyzer placed with its plane normal to the incident beam. Here only the VV mode where the analyzer axis is parallel to the polarization direction of the incident beam is considered. LS from nematic droplets is a relatively new topic and the associated theories use in general the Rayleigh-Gans (RGA)[8,9] or the Anomalous Diffraction (ADA)[10] approximations.

The experimental ratio $I_{VV}(q)/I_{VV}(q=0)$ is compared with the calculated quantity in both the RGA and the ADA models. This enables us to study the morphology of the mixture and extract the mean size of LC droplets; q is the amplitude of the wave vector and is related to the scattering angle θ and $k=\frac{2\pi}{\lambda}$ by $q=2k\sin(\theta/2)$, where λ is the optical wavelength of the incident beam.

EXPERIMENTAL PART

Materials

The LC mixture E7 (Merck Ltd, GB) was used during this work. The refractive indices of this mixture are $n_o=1.5183$ and $n_e=1.7378$ (T=20°C, $\lambda=632.8$ nm, values given by Merck). Although these values characterize E7 in the pure state, they will be adopted assuming that they remain unchanged for the phase separated systems. The prepolymer chosen consists of an aromatic polyester acrylate (Rahn AG, Switzerland) diluted in additional monomers including Tripropyleneglycoldiacrylate (UCB, Belgium). The refractive index of the polymer matrix (saturated by dissolved LC molecules) is $n_p=1.5269$ (T=20°C, $\lambda=632.8$ nm)[11].

Preparation of PDLC films

(100-x) weight percent (wt%) of the prepolymer (x=30, 40, 50) and x wt% of the LCs were mixed together at room temperature until the mixtures became homogeneous. Several samples were prepared for each composition by sandwiching the initial reactive mixture between a glass plate (Balzers, Liechtenstein) and a 100 μm thick poly(ethylene-terephthalate) sheet (Renker, Germany), both coated with a thin layer of conducting indium/tin oxide. The thickness of the composite films was controlled by using 25 μm thick spacers (double face adhesive strips, 3M, France).

Electron Beam Curing

An electron beam generator (Electrocurtain Model CB 150 from Energy Sciences Inc., USA) operating at a high voltage of 175 kV was used to prepare the PDLC samples. This value was increased to 190 kV to allow an uniform penetration of the applied dose in the depth of the samples. The sandwiched composite materials were placed in a sample tray, which was passed under an inert atmosphere under the accelerated electron curtain on a conveyor belt. The applied dose of 60 kGy was achieved by using a beam current of 4 mA and a conveyor speed of 0.22 m·s^{-1}. No temperature control during the irradiation process was applied.

Light Scattering (LS)

Light scattering measurements were performed at room temperature using a classical setup. The He-Ne Laser (λ=632.8 nm) was polarized perpendicular to the scattering plane. An analyzer was kept parallel to the polarizer to measure the scattering component I_{VV}. A beam stop prevented the transmitted beam from reaching the screen. The scattering pattern was recorded by a CCD camera. For I_{VV} a ϕ-independent circular intensity pattern was found allowing to perform radial averages of the scattered intensity. ϕ represents the azimuthal angle.

THEORETICAL SCATTERING INTENSITY I_{VV}

The polarized scattering intensity takes a simple form for spherical droplets in terms of S_1 and S_2, the diagonal elements of the van de Hulst scattering matrix[12,13]

$$I_{VV}=\frac{I_0}{k^2r^2}\left|S_1\sin^2\phi+S_2\cos^2\phi\right|^2 \qquad (1)$$

where I_0 is the intensity of incident beam and r the distance between sample and detector. The matrix elements S_1 and S_2 depend on the optical symmetry and the approximation chosen to describe the system. The RGA provides a model of LS under the following conditions

$$\left|\frac{n_{LC}}{n_P}-1\right|<<1 \qquad 2kR\left|\frac{n_{LC}}{n_P}-1\right|<<1 \qquad (2)$$

where R is the radius of the droplet and n_{LC} the effective refractive index of the LC

$$n_{LC}=\sqrt{\frac{n_e^2+2n_o^2}{3}} \tag{3}$$

The first condition in Eq.(2) means that the average refractive indices n_P and n_{LC} should remain close to each other. The second condition means that the droplet radius must be much smaller than the wavelength λ. Valuable information can be inferred on structure and size of droplets by examining scattering data of Poly(acrylate)/E7 mixtures in the framework of the theoretical predictions made for anisotropic spheres. From the theoretical point of view, Meeten et al[13,14] applied the method of Stein and Rhodes[15] representing the scattering objects by homogeneous spheres with radial and tangential refractive indices. In the general case where anisotropic contributions are taken into account, they obtained the following expressions for the elements of the van de Hulst matrix

$$S_1=\frac{2ik^3R^3}{3}\left[3(\mu-1)f_1+\Delta\mu f_2\right] \tag{4}$$

$$S_2=\frac{2ik^3R^3}{3}\left[3(\mu-1)f_1\cos\theta-\Delta\mu f_2(1+\cos^2\frac{\theta}{2})\right] \tag{5}$$

where $\mu=\frac{n_r+2n_t}{3n_P}$ is the mean refractive index of the LC droplet relative to n_P, $\Delta\mu=\frac{n_r-n_t}{n_P}$ is the optical anisotropy relative to n_P, n_r and n_t are the radial and tangential refractive indices of the sphere, respectively. Under the conditions chosen in this work, the refractive indices are related by $n_t=n_0$ and $n_r=n_e$. The quantities u, f_1, and f_2 introduced here are

$$u=qR \qquad f_1=\frac{\sin u-u\cos u}{u^3} \qquad f_2=\frac{u\cos u-4\sin u+3\int_0^u\frac{\sin t}{t}dt}{u^3} \tag{6}$$

Combining these results, they obtained the scattering intensity

$$I_{VV}(q)=I_0\left(\frac{2k^2R^3}{r}\right)^2$$

$$\left((\mu-1)f_1+\frac{\Delta\mu}{3}f_2-\left\{2(\mu-1)f_1\sin^2\frac{\theta}{2}+\frac{\Delta\mu}{3}f_2(2+\cos^2\frac{\theta}{2})\right\}\cos^2\phi\right)^2 \quad (7)$$

It is worth noting that the original theory of Stein and Rhodes[15] gives different results for $I_{VV}(q)$.

The Anomalous Diffraction Approximation (ADA) replaces the three dimensional object by a two dimensional platelike object which collects the phase information of the light passing through the scattering particle[12]. Two conditions must be satisfied in the ADA:

$$kR>>1 \qquad \left|\frac{n_{LC}}{n_m}-1\right|<<1 \qquad (8)$$

The first condition tells us that the droplet radius is much larger than the wavelength λ while the second condition insures that the refraction and reflection at the nematic/polymer interface can be neglected. In the case of isotropic spheres, the ADA has been worked out by Meeten et al[13] who reported the following results:

$$S_1=k^2R^2\int_0^1\{1-\exp(-2i\Delta)\}J_0(ux)x\,dx \qquad \Delta=kR(\mu-1)\sqrt{1-x^2} \qquad S_2=S_1\cos\theta \qquad (9)$$

Δ is the phase shift, $J_0(x)$ the zeroth order Bessel function.

RESULTS AND DISCUSSIONS

Figure 1 shows the scattering data representing Ivv (q)/Ivv (q=0) as a function of q for the sample of 70% LC weight fraction. Theoretical predictions of Meeten et al. for 0° azimuthal angle are included in different conditions. The thick and dashed curves represent isotropic spheres of radius R=0.5 μm within the RGA and ADA, respectively. Both approximations give reasonable descriptions of the data although the ADA seems slightly better. The thin curve is hardly visible in this figure because it goes practically through all the data points. This curve is obtained for an anisotropic sphere of radius R=0.3 μm within the RGA at the same azimuthal angle of 0°. The agreement between the latter curve and data is much better than the other theoretical curves included in this figure. Nonetheless, it is difficult to conclude, on the basis of these data only, that the RGA for anisotropic spheres of radius R=0.3 μm is the unique possibility.

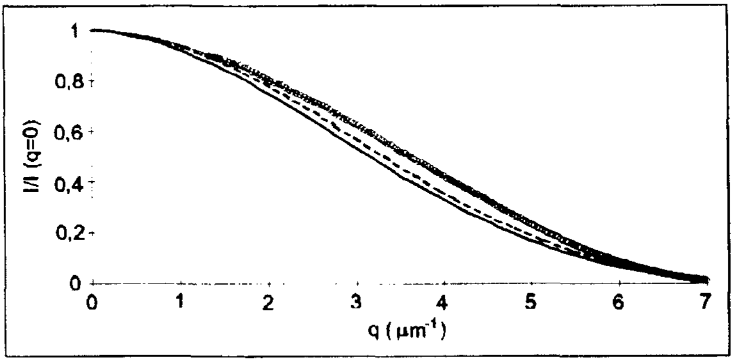

FIGURE 1 Variations of the polarized component of the light scattering intensity normalized at q=0, Ivv (q)/Ivv (q=0) as a function of the amplitude of wave vector q for Poly(acrylate)/E7 system at 70 wt% LC (symbol O). The other curves represent theoretical predictions using the theory of Meeten et al. for spheres of radius R at an azimuthal angle ϕ=0°. Continuous thick line —— RGA+isotropic sphere with R=0.5 μm; dashed line ---- ADA+isotropic sphere with R=0.5 μm; continuous thin line —— RGA+anisotropic sphere with R=0.3 μm. The last curve represents the best fit to the data.

We have not explored in this figure all possibilities offered by the theoretical formalism. For example, we have not considered models originally developed by Stein, Rhodes and coworkers for spherulites of cristalline polymers which give different results. Moreover, scattering curves with other azimuthal angles may give better fits in some cases in particular using ϕ=45° but are not shown here. A more detailed comparative study of data and theoretical predictions is presented elsewhere[16].

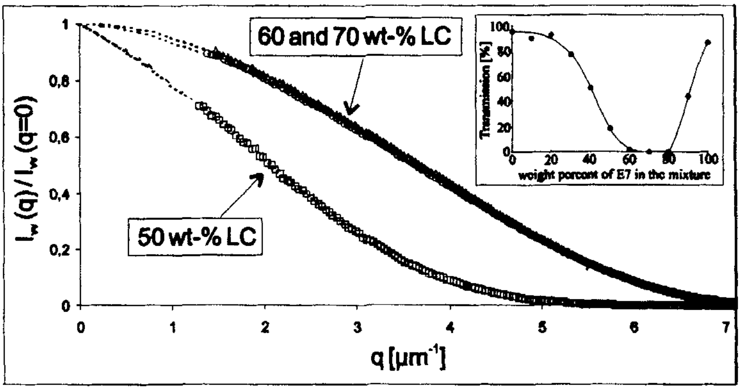

FIGURE 2 Variations of the polarized component of the light scattering intensity normalized at q=0, Ivv (q)/Ivv (q=0) as a function of the amplitude of wave vector q for Poly(acrylate)/E7 system and three different LC weight fractions. □ : 50 wt% LC; Δ : 60 wt% LC; O : 70 wt% LC; the figure insert represents transmission data for the same mixture[6]. Discontinuous curves are extrapolations of data using least square fit.

Figure 2 shows the scattering data for three samples with the LC compositions 70, 60 and 50 wt%. The polarized component of the normalized intensity is practically the same for 70 and 60 wt% but for 50 wt%, the scattering is much more reduced. It is interesting to correlate these results with those of the transmitted light for the same samples shown on the figure insert[6]. The intensity of transmitted light is practically zero for the PDLC films containing 70 and 60 wt% LC while for the 50 wt% sample the signal is much more significant. This observation is consistent with the fact that the relative scattering is the same for the former two samples; while for the latter sample the scattering is lower. Recent scattering data obtained on similar systems under the influence of an external electric field (on state) confirm these observations. A detailed discussion of correlations between scattering and transmission data will be presented in the near future[17].

The fact that the signal of the scattering intensity changes with the composition may be an indication that the interdroplet correlations are not negligible as it is assumed in the present work.

Scanning electron microscopy (SEM) measurements are currently in progress in order to correlate these results with the observed morphology. First results from samples containing 50 wt-% LC revealed droplets presenting an ellipsoidal form with an axial ratio of 0.7 ± 0.1 (ratio of the length of the minor to the major axis) and a major axis of 0.5 ± 0.2 μm[5]. The overall range of major length axis values was found in a monomodal distribution between 0.1 and 1.4 μm. Analysis of recent data indicated that droplet size and shape do not change significantly by increasing the LC concentration, and only their number density increases. The results obtained from SEM are within experimental error in good correlation with the theoretical predictions derived for the droplet size, especially with the calculations obtained from the RGA model for anisotropic spheres of diameter 0.6 μm (radius 0.3 μm). These findings have to be confirmed by further investigations in order to clarify the relationship between data from SEM and LS.

CONCLUSIONS

Variations of the scattering intensity with the amplitude of wavevector q are calculated using the RGA and the ADA. The results are compared with the LS data obtained PDLC systems made of Polyacrylate / E7 mixtures prepared in our laboratory by electron beam radiation and PIPS process. Comparison of data and theoretical results show different possibilities. The RGA and the ADA models for isotropic spheres of radius of 0.5 μm provide reasonable fit with the data and the ADA is slightly better. The RGA gives the best fit for anisotropic spheres of radius 0.3 μm. Consistency between LS data for different LC compositions and transmission data provides an encouraging result for undergoing more systematic studies on other PDLC systems under various conditions. This could help making a more decisive conclusion on the appropriate model for nematic droplets and the correlations between LS and transmission experiments.

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