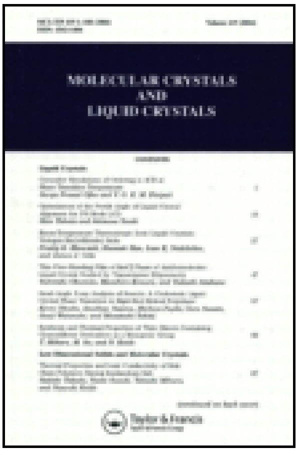

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Small-Angle Scattering of Polarised Light. V: Liquid Crystalline Droplets in an Isotropic Polymer

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SMALL-ANGLE SCATTERING OF POLARISED LIGHT. V: LIQUID CRYSTALLINE DROPLETS IN AN ISOTROPIC POLYMER

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Abstract The light scattering properties of spherical droplets of a nematic low molar mass liquid crystal dispersed either in a polymer matrix or in water have been investigated. The size of the droplets varied from 0.5μm to 100μm. Only a radial arrangement of the director in spherical droplets was considered. Up to ten orders HV scattering patterns were experimentally measured. Calculations have been conducted using the anomalous diffraction and Rayleigh-Gans-Debye theories. Particles larger then 2μm show an extremely good agreement with the anomalous diffraction theory. Particles smaller than 2μm show no agreement with either theory. This may be due to a more complex director arrangement than the radial distribution assumed here.

INTRODUCTION

Thin films based on the dispersion of nematic liquid crystals (LC) in a polymer matrix or vice versa, (Polymer Dispersed Liquid Crystals or PDLC)[1, 2] are new opto-electronic materials with a large range of applications for displays, temperature sensors, and light shutters. PDLC materials can be prepared from different methods: The liquid crystal can be dissolved in a prepolymer followed by a polymerization induces a phase separation, in the polymer melt followed by cooling or, as an emulsion in a polymer solution, solvent evaporation. The resulting structure of the materials depend on many parameters, particularly the relative concentration and the preparation procedure. Some of the structures consist of spherical droplets of one component in a matrix of the other.

The principal of using PDLC films is based on the fact that when there is no applied voltage the director orientation inside the liquid crystal varies from place to place. The incoming light is scattered because of the difference in refractive index between the liquid crystal and the polymer, because of the variation in the liquid crystal director orientation, and because of strong multiple scattering[3]. The films are milky white in this "off-stage". The degree of "off-stage" scattering is then a complex function of domain size, director orientation and concentration of the liquid crystalline domains. Under an electric field, the liquid crystal director within each domain becomes uniformly oriented and if the polymer matrix refractive index matches the ordinary refractive index of the liquid crystal, the film becomes highly transparent.

Here we consider the most simple structure which can be formed, that is droplets of the liquid crystal in a polymer matrix. Before undertaking any light scattering modelling, it is first necessary to establish how the director can be arranged inside the droplet. Two main factors play a role, the anchoring at the droplet wall and the size of the droplet[4]. Four main textures can be found, an axial one and a radial one when the anchoring is homeotropic (perpendicular to the wall) and bipolar and concentric ones when the anchoring is tangential.

Recently, several studies discussing experimental results and theoretical predictions of the light scattered by nematic spheres have been published[4-11]. None of them present an extended comparison between experiments and theory. In other related papers, the dependence of the PDLC light scattering performance and/or optical transmittance on various film parameters[12-17], applied voltage[18-20], cure or cooling temperature[21-25] was investigated.

The aim of this study is to conduct a basic investigation into the light scattered by nematic droplets. The objectives are to find a suitable theory and to compare it to experiments. The experiment and the theoretical predictions will be compared only in the HV conditions (when the sample is placed between crossed polars), where the effect of director orientation will be predominant.

EXPERIMENTAL PART

Two types of liquid crystal dispersions were prepared, both with the E7 liquid crystal manufactured by Merck. The first material was prepared using the classic PDLC technique: E7 was mixed with the prepolymer Norland-65 in the proportion of four parts of polymer to one part of the liquid crystal. This mixture was homogenized by stirring with a magnetic bar, placed on a glass plate and polymerized under UV light

(UVITERNO AG lamp). The stirring intensity and time were varied and so was the UV exposure time. The final size of the liquid crystal droplets was strongly dependent on the stirring intensity and time of the mixture. For example, stirring at 700rpm during 20-30s gave a final size of 100-300μm while stirring at 1300rpm during 5min gives a final size of 1-5μm. The size of the droplets was measured by optical microscopy.

A second preparation procedure was used in order to produce well-controlled droplets in terms of size, director orientation and concentration. The E7 liquid crystal was mixed with water and gently stirred. Well isolated droplets were prepared in this way, with sizes depending on stirring velocity (typically the sizes were in the range between 2 and 30μm).

The light scattering experiment was performed on a vertical bench on which were mounted a He-Ne laser, (wavelength in vacuum 0.633 μm, beam diameter 1.5mm), a polariser, the sample placed between two glass slides, an analyzer placed at 90° to the analyzer (HV conditions) and either a photographic plate or a CCD camera. Light scattering patterns were recorded over small angles, (0.5°-10°), depending on the size of the droplets. The HV light scattering patterns were analyzed by image analysis in order to obtain the polar and azimuthal dependence of the scattered light intensity. The scattering angles measured in the air were corrected to scattering angles in the material by applying Snell's law of refraction at the material-glass-air interfaces of the scattering cell.

The refractive indices of the studied materials are given in Table 1.

TABLE 1: Refractive indices of the materials. m_r, m_t and m_l are defined in the text

material	m_r	m_t	m_l
E7	1.7462	1.5216	
Norland-65			1.524
water			1.3317

RESULTS AND DISCUSSION

Theory

The objects which are scattering light are of comparable size or larger than the wavelength of the light. As will be seen later, they are either disks or spheres. These objects are in a nematic state, therefore anisotropic, but embedded into an isotropic medium. The Mie theory is obviously not applicable here, since it is strictly limited to isotropic spheres. Two theories can then be used, the Rayleigh-Gans-Debye approximation (RGD) and Anomalous Diffraction approximation (AD). A complete description of the basis of these two theories can be found in refs.26-34. As seen below, only large spheres will be studied in detail, in which case the light is scattered at small angles. Small-angle light scattering, (SALS), by anisotropic spheres with a radial symmetry has been studied for a long time, mainly due to its application to polymer spherulites[27]. The light scattering intensity under crossed polarization have been calculated for radial spheres with the RGD[28] and AD[29] approximations. The comparison with experiments has only been performed for the first scattering order[35] in the case of anisotropic spheres, due to the lack of "perfect" spheres. Here perfect refers to the difficulty in finding spheres with very good radial orientation. The light scattering intensity I_{HV} in these two approximations is given by the following[30]:

for RGD:

$$I_{HV} = (2ik^2a^3)^2[2(\bar{\mu}-1)f_1\sin^2(\theta/2) + r_0^2 + \Delta\mu f_2(2+\cos^2(\theta/2)1/3]^2\sin^2\tau\cos^2\tau$$

for AD:

$$I_{HV} = |S_{is}\sin^2(\theta/2)+S_{am}\cos^2(\theta/2)|^2\sin^2(2\tau)\, k^2r_0^2$$

where $k=2\pi/\lambda$, λ being the wavelength of the light in the medium, a is the sphere radius, r_0 is the distance between the sample and the photographic plate, $\bar{\mu}=(m_r+2m_t)/(3m_1)$, $\Delta\mu=(m_r-m_t)/m_1$, $f_1=(\sin u-u\cos u)/u^3$, $f_2=(u\cos u-4\sin u+3\mathrm{Si}u)/u^3$, $u=2ka\sin(\theta/2)$, θ and τ are the polar and azimuthal scattering angles, $\mathrm{Si}u=\int(\sin x/x)dx$, $S_{is} = k^2\int\{1 - 0.5[\exp(-iF_e) + \exp(-iF_0)]\}J_0(u/a)\rho d\rho$, $S_{an} = k^2\int 0.5[\exp(-iF_0) - \exp(-iF_e)]J_2(u/a)\rho d\rho$, J_0 and J_2 are integer-order Bessel functions, ρ is the radius for the considered light ray and F_e and F_0 are the phase differences for the extraordinary ray and the ordinary ray, respectively:

$$F_0=2k(\mu_t-1)(a^2-\rho^2)^{1/2}$$

$$F_e=2k[(\mu_t-1)(a^2-\rho^2)^{1/2}+\Delta\mu \arctan(a^2/\rho^2-1)^{1/2}+0(\Delta\mu^2)+...]$$

The RGD and AD approximations have different domains of validity[26]:

RGD: $|\bar{\mu}-1|<<1$

$2ka|\bar{\mu}-1|<<1$

AD: $|\bar{\mu}-1|<<1$

$ka >> 1$

Experimental Results and Comparison with Theories.

For the studied systems (E7+Norland-65 and E7+water) the ranges over which the sphere radius is valid are given in Table 2, taking into consideration the data of Table 1.

TABLE 2: Range of validity of the RDG and AD theories for the two mixtures. $\bar{\mu}$ is the relative refractive index, a is the radius of the sphere.

	$\lvert\bar{\mu}-1\rvert$	a (RGD)	a (AD)
E7+Norland-65	0.01	a<<5μm	a>>0.1μm
E7+water	0.16	a<<0.3μm	a>>0.1μm

Figure 1 is an example of a E7 droplet in Norland-65. The micrographs are taken between crossed polars. The size of the droplet allows a good resolution of the texture. All the droplets larger than 2μm in diameter have a clearly spherical shape. It is not possible to precisely describe the shape of the smaller droplets due to the resolution limit of the microscope. The texture inside the droplets is very variable. Most of them have an extinction cross when observed between crossed polars, showing that the director is in a radial position. The concentric director arrangement can be ruled out since no droplet seen off-axis was found. In some cases droplets with a more complex defect structure were observed. We will now focus only on the case of axial droplets.

A typical small-angle HV light scattering pattern for an axial droplet for E7 in Norland-65 is shown in Fig.2. It consists of a weak central intensity and a typical clover-leaf pattern. A series of intensity minima and maxima are found along the 45°axis. Such a result is similar to what is known for polymer spherulites. The major difference here is that higher orders of scattering can be clearly seen, up to the 5^{th} order in Norland-65 and up to the 10^{th} order in water. This opens the way for an extended comparison with theories.

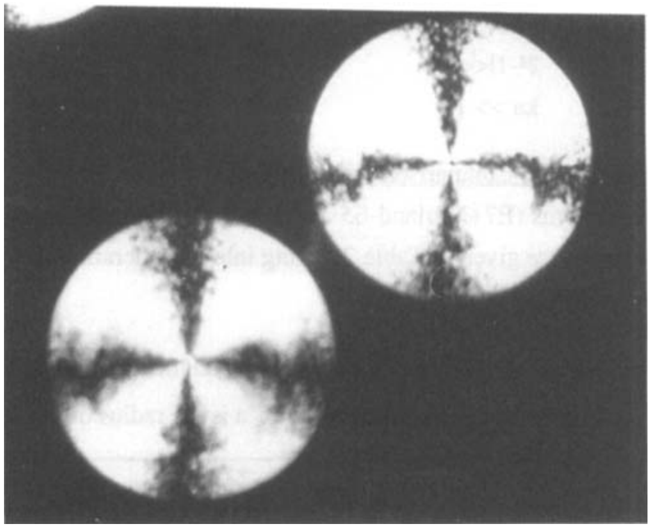

FIGURE 1: Micrograph of a E7 droplet in Norland-65, seen between crossed polarisers. The droplet diameter is 120 μm

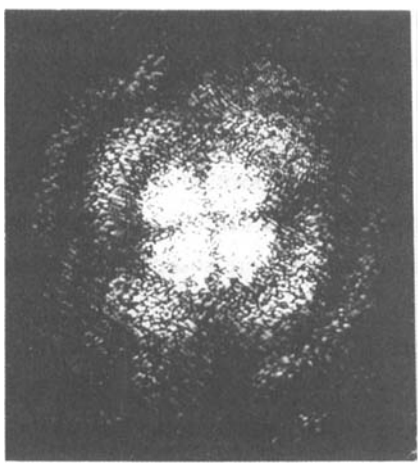

FIGURE 2: Small-angle HV light scattering pattern for the droplet shown in Figure 1.

The light scattering patterns for droplets of different sizes of E7 in Norland-65, (from 1 to 100μm), were recorded and the scattering angle of each intensity maximum was measured. For the same sizes the scattering maxima were calculated using the refractive index data given in Table 1 for the RGD and AD approximations. The comparison between experiment and theories are given in Table 3.

TABLE 3: E7 in Norland-65. Comparison between experiments, RDG and AD theories for different droplet diameters. a is the radius of the sphere, θ_e is the experimental scattering angle, θ_{RGD} is the theoretical angle calculated with the RGD theory and θ_{AD} is the theoretical angle calculated with the AD theory. Angles are in degrees.

2a		θ_e	θ_{RGD}	θ_{AD}
2μm	first max	5.4	7.7	5.7
	second max	17.0	14.2	
10μm	first max	1.4	1.6	1.1
	second max	2.3	3.3	2.5
	third max	2.9	4.5	4.0
60μm	first max	0.3	0.2	0.3
	second max	0.7	0.6	0.8
	third max	1.3	0.8	1.3
	forth max	1.5	0.9	1.6
85μm	first max	0.2	0.2	0.2
	second max	0.7	0.4	0.7
	third max	0.9	0.5	0.9
	forth max	1.1		1.1

The results show that the larger the droplet size is, the more closely the AD approximation coincides with the experimental data. This confirms the theoretical validity range of the AD theory given above.

The RGD theory cannot correctly describe the experimental data. At large sphere diameters, it is not valid. At low sphere diameters, the director arrangement is probably not radial. The AD theory shows a relatively good agreement at large sphere diameter.

A much better comparison can be obtained from the E7 liquid crystal in water. Due to the simpler preparation method, single spheres can be isolated. The homeotropic anchorage of the nematic molecules at the wall gives very clear radial spheres, as observed by optical microscopy. The light scattering patterns confirm this since many scattering orders can be seen. Table 4 shows that the AD theory can perfectly describe the scattering by an anisotropic sphere, up to the tenth order, provided of course that the internal structure is well controlled.

TABLE 4: Comparison between the experimental scattering angle (in degree) θ_e of the first ten scattering maxima and the theoretical scattering angle θ_{AD} calculated with the AD theory for a E7 droplet in water (diameter of the droplet 20 μm).

Maximum	1	2	3	4	5	6	7	8	9	10
θ_e	0.76	2.3	3.2	4.0	4.8	5.8	6.8	7.7	8.5	9.9
θ_{AD}	0.76	2.3	3.2	4.0	4.9	5.7	6.9	7.7	8.8	10.1

CONCLUSIONS

Liquid crystalline droplets with an axial director orientation can be used for testing light scattering theories. The goal will now be to find good model systems for more complex PDLC samples, especially taking the scattering by defects into account.

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