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Depolarization of Light Scattered in Nematic Liquid Crystals

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Some investigations indicate that molecular aggregates appear near the isotropic liquid-mesophase transition on cooling the isotropic liquid.

There is a short range order in these formations as the orientations of the swarms are not correlated.[1] The length of these aggregates ξ called "coherent length" changes with the temperature and close to the clearing temperature T_c are of the order of a few hundred Angstroms.[1] Johnson[2] has measured the Kerr response of seven nematics just above their nematic—isotropic ($n - i$) transition temperature in their isotropic state. The author has found that in *p*-metoxybenzylidene-*p,n*-butylaniline (MBBA) there are molecular aggregates with a form of rigid rods 170 Å long. The rest of the substance has a calculated rod length which agrees with the actual molecular length of approximately 20 Å. This leads to the conclusion that no aggregation of molecules into larger groups is taking place. Tolstoy[3] has measured the temperature dependence of double refraction and the angle of extinguishing in a stream of isotropic liquid *p*-azoxyanisole at 135°C. The experimental data obtained are explained by the molecules uniting into groups which are orientated as whole units under the action of external forces. According to the authors these groups have the shape of a rotational ellipsoid.

In the nematic phase when the liquid crystal is not submitted to external forces (i.e., electric and/or magnetic field) and to rubbing the molecules are also arranged in aggregates according to a number of authors. Wang and Leu[4] have investigated the depolarization ratio of the band 1145 cm^{-1} from the Raman spectrum of *p*-(*p*-ethoxyphenylazophenyl undecylenate (PPU) and have concluded that the size of the single domain PPU in the nematic phase is less than the wavelength of He—Ne laser used by them.

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By means of a polarizing microscope Rosen and Shen[5] have observed domains with length of approximately 30 microns in a mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride. Durand and Rao[6] have extended the investigations of the mesophase to the hypersonic frequencies. They have found that in a transparent bulk the domain length is of the order of 2000 Å. de Vries[7] has shown that in the nematic phase of *bis*-(4'-*n*-octyloxybenzol)-2-chloro-1-phenylendiamine the molecules are organized in small aggregates—cybotactic groups and these groups appear to be fairly rigid.

The aim of the present short communication is to investigate the degree of the depolarization of scattered light at 90° and to check:

1) Whether this scattering is caused by aggregates in which the molecules are equally oriented and, if so,

2) to determine their sizes and the dependence of their lengths on temperature.

Two fundamental factors of depolarization of scattered light may be introduced:[8] the first $-\Delta_h$, when the incident light is linearly polarized with horizontal vibrations of the electric vector E_y and secondly $-\Delta_v$, with vertical vibrations of incident light electric vector E_z.

If the incident beam proceeds along the horizontal axis "x" and the scattered light is observed in the "y" direction perpendicular to "x" and lying in the "xy" plane, the following formula can be derived[8]

$$\Delta_v = \frac{Y_{zx}}{Y_{zz}} \qquad \Delta_h = \frac{Y_{yx}}{Y_{yz}}$$

where Y is the intensity of the scattered light. The first index denotes the direction of polarization of incident light and the second one the polarization of scattered light. According to theory[9] Δ_h characterizes the dimensions of the scattering particles. In the case when their size is comparable to the wavelength of incident light λ, Δ_h is bigger than one. If $\Delta_h = 1$ the scattering particles are much smaller than the wavelength.

On the other hand Δ_v gives information about the anisotropy of the polarizability of these particles. Δ_h and Δ_v have been widely used for the investigations of molecular aggregates in proteins,[10] plastics,[11] rubber,[12] colloidal gold,[13] glasses[14] and hydrocarbons of the paraffin series.[15] To our knowledge no determinations of Δ_h and Δ_v in liquid crystals have been made up to now.

Figure 1 shows our experimental setup. A He—Ne laser (6328 Å) with approximately 30 mW output was used as a light source. The sample cell was surrounded by a metal block which acted as a thermal reservoir. The

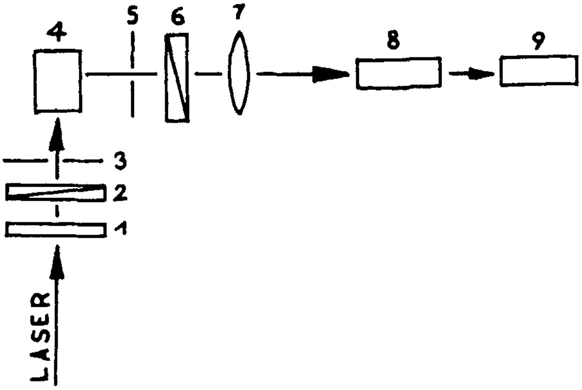

FIGURE 1 Schematic of experimental setup. 1. $\lambda/2$ plate, reversing the polarization of the laser beam when Δ_v is determined; 2,6: polarizers; 3: 1 mm entrance pinhole; 4: sample cell; 7: lens; 8: photomultiplier FEU-28; 9: galvanometer.

temperature of the sample was read and maintained automatically with a precision of $\pm 0.2°$. A 1 mm pinhole was put in front of the entrance window of the cell which allowed a narrow parallel beam to fall on the sample.

With a view to ascertain the precision and the reliability of our experimental setup we determined Δ_h for a 28 % solution of phenol in water at the temperature of mixing (65°C) and Δ_v of benzene at room temperature. For the system "phenol-water" and for pure benzene our results coincide well with those obtained by other authors[8]—the deviations are less than 4 %.

In liquid crystal samples of limited thickness multiple scattering causes spurious depolarization of incident and scattered light. This effect was eliminated by measuring Δ_h and Δ_v as a function of various thicknesses and extrapolating to zero thickness according to Shen, *et al.*[16]

The depolarization of light scattered in four nematic-*p*,*p*′-dimethyloxyazoxybenzene (PAA), *p*-methoxybenzylidene-*p*,*n*-butylaniline (MBBA), *p*-ethoxybenzylidene-*p*,*n*-butylaniline (EBBA) and Merk 5 was investigated. The Δ_h and Δ_v values are summarized in Table I.

As our results indicate Δ_h for the isotropic phase at temperature $T = T_c + 1°$, $\Delta_h = 1$ for all investigated liquid crystals but for the mesophase $\Delta_h > 1$. This implies that the dimensions of scattering "particles" existing in the liquid crystal phase are comparable to the wavelength of incident light.

To evaluate more precisely the dimensions of molecular formations in the investigated nematic we determined Δ_h for standard patterns with a known size of scattering particles. According to Gans,[9] Δ_h depends on the shape and dimensions of scattering particles but not on their optical anisotropy. As standard patterns we used diluted water solutions of bentonites with a

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TABLE I

Factors of depolarization of scattered light

	MBBA				PAA			
	$T°$	Δ_h	ξ[Å]	Δ_v	$T°$	Δ_h	ξ[Å]	Δ_v
Mesophase	293	1.46	1760	0.73	391	1.39	1600	0.69
	303	1.45	1700	0.73	397	1.39	1600	0.69
	313	1.45	1700	0.72	403	1.38	1550	0.69
	317	1.43	1600	0.71	405	1.34	1500	0.67
	319	1.38	1500	0.67	406	1.29	1350	0.64
Isotropic liquid	320	1.08	600	0.63	407	1.05	450	0.59
	321	1.00	—	0.59	409	0.99	—	0.52
	323	0.99	—	0.54	413	1.00	—	0.50
	328	1.00	—	0.54	418	1.00	—	0.50
	EBBA				Merk 5			
	$T°$	Δ_h	ξ[Å]	Δ_v	$T°$	Δ_h	ξ[Å]	Δ_v
Mesophase	313	1.45	1750	0.72	293	1.49	1900	0.76
	323	1.45	1750	0.72	303	1.40	1900	0.76
	333	1.45	1750	0.72	313	1.49	1900	0.76
	338	1.45	1750	0.72	323	1.48	1900	0.74
	343	1.44	1700	0.72	333	1.48	1850	0.74
	345	1.42	1600	0.70	338	1.48	1850	0.74
	347	1.37	1500	0.66	343	1.47	1800	0.73
					345	1.45	1700	0.71
					347	1.39	1550	0.67
Isotropic liquid	348	1.08	600	0.63	348	1.06	500	0.62
	350	0.99	—	0.59	350	0.99	—	0.58
	353	1.00	—	0.55	353	1.00	—	0.59
	358	1.00	—	0.55	358	1,00	—	0.53

cylindrical shape and the ratio of the long to the short axis is 4 : 1, their length being determined by electron microscopic analysis as follows: 2500 Å, 2200 Å, 1800 Å and 1400 Å. The values obtained for Δ_h are respectively: 1.80, 1.60, 1.47 and 1.33. Making use of the dependence of Δ_h on the length of scattering particles in the bentonite solutions we determined ξ the molecular formations in the investigated nematics at different temperature. The results are given in Table I as well. The average error in determining of Δ_h was about 7%.

Our experimental results indicate that within the limits of the error Δ_h depends slightly on the temperature. This shows that the length of the molecular formations changes very little with the temperature. Several degrees before the clearing temperature T_c, Δ_h and consequently ξ begins

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significantly to decrease. Thus, for instance, ξ for MBBA of 1700 Å at 40°C falls to 1500 Å at 46°C.

Immediately after T_c in the isotropic liquid at the interval $T = T_c + 1$°C the length of the molecular aggregates is still significant—about 600 Å. At further increase of the temperature they are quickly destroyed. From our data it is obvious that at the phase transition liquid crystal—isotropic liquid the dimensions of the scattering formations decreases more than twice. One degree above T_c, $\Delta_h = 1$ which indicates that in the isotropic liquid the light is scattered by particles much smaller than the wavelength of the incident beam.

Δ_v for all investigated substances in the isotropic phase is considerably large. This shows that the scattering molecules are strongly anisotropic. At the phase transition $i - n$ Δ_v slightly increases. Unfortunately, at this moment we are not yet able to give precise data for the form of the molecular aggregates but comparing the Δ_v values for the investigated liquid crystals and those for bentonite solutions ($\Delta_v = 0.60$) we can infer that the ratio of the short to the long axis for the molecular formations existing in the studied nematics is approximately 1 : 4.

CONCLUSION

Our results lead to the following conclusions:

1) In bulk samples of the investigated nematic liquid crystals, where the orientational influence of the walls is staying away and without magnetic and electric fields molecular aggregates with length of about 1500–1800 Å exist.

2) The length ξ of these molecular formations changes very little with the temperature. 5–6°C before T_c, ξ begins significantly to decrease.

3) Immediately after T_c in the isotropic liquid at the interval $T = T_c + 1$°C the length of molecular aggregates is still significant—about 500–600 Å. One degree above T_c they are destroyed.

To throw more light on these problems investigations of whole homologous series of liquid crystals with molecules of different structure properties and degree of anisotropy, as well as the influence of electric and magnetic fields on the sizes of aggregates, are currently in progress. The results obtained will be the subject of a future publication.

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