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## The Measurement of the Nematic Order Parameter by X-ray Scattering Reconsidered

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**Abstract.** — This paper reviews and extends the procedure used to measure the nematic order parameter by X-ray scattering. We show that the well-known integral equation derived by Leadbetter and coworkers, relating the scattered intensity  $I(\theta)$  to the orientational distribution function  $f(\beta)$ , can be analytically simplified both in the general case and in the case of the Maier-Saupe distribution function. The Maier-Saupe distribution leads to a particularly simple analytical result previously obtained by Paranjpe and Kelkar. This result is extensively discussed here and tested on a large variety of thermotropic liquid crystals. In most cases, this very simple and practical approach provides a good description of the data. This supports at the same time the analysis of the scattering leading to Leadbetter's integral equation and the Maier-Saupe distribution. We also discuss the validity and accuracy of this simple method compared to other ones.

### 1. Introduction

The determination by X-ray scattering of the orientational distribution function of crystallites or molecules with respect to a fiber axis is a recurring problem met in many domains of condensed matter physics. Powerful methods, such as the exploitation of pole figures [1, 2], first devised for classical metallurgy have later been successfully applied to the study of polymers [3, 4]. This question is also of particular importance in the case of liquid crystals and has therefore been addressed very early. Falgueirettes and Delord [5], De Vries [6] and Leadbetter and coworkers [7] have thus discussed methods of measuring the nematic order parameter of classical mesophases of simple rod-like molecules. The simplest approach is that of Leadbetter *et al.* and it was widely applied (with different variants) to many mesogenic compounds [8, 9]. This method consists in the exploitation of the so-called “wide angle diffuse ring” corresponding to the lateral mean distance between first neighbour molecules and is based on several quite drastic assumptions which it is useful to recall here:

- i) the molecules are considered as rod-like homogeneous particles of revolution symmetry;

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(\*) associé au CNRS

- ii) the wide angle diffuse ring is only due to the lateral interferences between these particles; therefore, a diffuse ring of scattering centered at the origin of reciprocal space is attached to each particle;
- iii) the previous assumption also implies that the orientational distribution function of a single particle is obtained by treatment of the intensity scattered by a cluster of interfering particles instead of a single one. This is more or less comparable to a kind of mean field approximation and tends to overestimate the order parameter;
- iv) the form factor of the particle and the nematic longitudinal correlation length are not taken into account though they strongly affect the scattering of highly oriented phases. This results in a systematic underestimation of the order parameter

The last two assumptions were fully discussed in reference [7].

A geometrical analysis then leads to the now classical formula [7] relating the intensity  $I(\theta)$  scattered in a direction at an angle  $\theta$  with the director, to the orientational distribution function  $f(\beta)$  of the rod axis:

$$I(\theta) = \int_{\beta=\theta}^{\pi/2} \frac{f(\beta) \sin \beta}{\cos^2 \theta \sqrt{\text{tg}^2 \beta - \text{tg}^2 \theta}} d\beta \quad (1)$$

where  $\beta$  is the angle between the rod axis and the director (Fig. 1).

This integral equation is usually numerically inverted by assuming, in most cases, a more or less specific expansion of  $I(\theta)$  and  $f(\beta)$ . However, this equation can also be analytically inverted

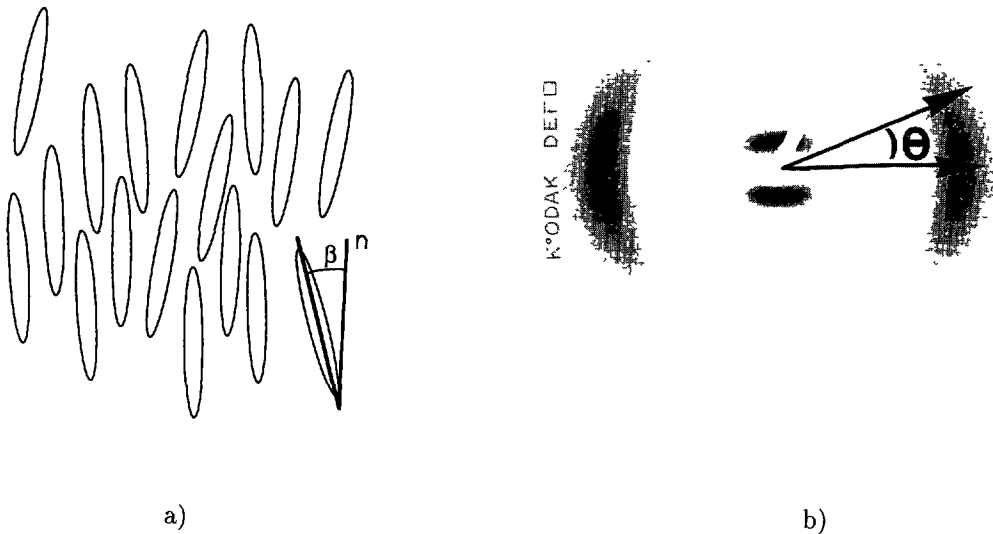


Fig. 1. — a) Definition of the angle  $\beta$  between a rod and the nematic director  $\mathbf{n}$ . The ellipses represent the molecules. b) Definition of the polar angle  $\theta$  describing the scattering in the wide angle diffuse ring (4O.8 at 66 °C).

[10, 11] but this calculation gives  $f(\beta)$  through a somewhat complicated integral formula also involving derivation of the data sets. Furthermore, such a process does not provide any means of estimating the validity of the distribution function thus derived.

Recently, Deutsch [11] has also shown that the order parameter  $S$  can be calculated with the formula:

$$S = \bar{P}_2 = 1 - N^{-1} \frac{3}{2} \int_0^{\pi/2} I(\theta) \left[ \sin^2 \theta + (\sin \theta \cos^2 \theta) \text{Log} \left( \frac{1 + \sin \theta}{\cos \theta} \right) \right] d\theta \quad (2)$$

where

$$N = \int_0^{\pi/2} I(\theta) d\theta$$

We present here very simple analytical calculations of equation (1) both in the general case and with use of the Maier-Saupe orientational distribution function and we compare the results of these calculations with X-ray scattering experiments on different compounds. This will give us the opportunity to check at the same time the validity of equation (1) and of the Maier-Saupe orientational distribution function.

## 2. Calculation of Equation (1)

2.1. CALCULATION IN A GENERAL FRAME. — The orientational distribution function  $f(\beta)$  can be expanded without any loss of generality either in a series of Legendre polynomials of even degrees or also in a series of circular functions:

$$f(\beta) = \sum_{i=0}^{\infty} f_{2i} \cos^{2i} \beta \quad (3)$$

Inserting this in equation (1) leads to:

$$I(\theta) = \sum_{i=0}^{\infty} \int_{\beta=\theta}^{\pi/2} \frac{f_{2i} \cos^{2i} \beta \sin \beta}{\cos^2 \theta \sqrt{\text{tg}^2 \beta - \text{tg}^2 \theta}} d\beta$$

using  $x = \cos^2 \beta$ , we obtain:

$$I(\theta) = \sum_{i=0}^{\infty} \frac{f_{2i}}{2 \cos \theta} \int_0^{\cos^2 \theta} \frac{x^i}{\sqrt{\cos^2 \theta - x}} dx$$

This integral is tabulated [12] in the form:

$$\int_0^{\cos^2 \theta} x^{\nu-1} (\cos^2 \theta - x)^{\mu-1} dx = (\cos^2 \theta)^{\mu+\nu-1} B(\mu, \nu)$$

where  $B(\mu, \nu)$  is the Beta function. Here, we have  $\nu = i + 1$  and  $\mu = 1/2$  resulting in:

$$I(\theta) = \sum_{i=0}^{\infty} \frac{f_{2i}}{2 \cos \theta} (\cos^2 \theta)^{i+\frac{1}{2}} B\left(\frac{1}{2}, i+1\right)$$

but  $B(1/2, i+1)$  can be expressed with  $\Gamma$  functions:

$$B\left(\frac{1}{2}, i+1\right) = \frac{\Gamma\left(\frac{1}{2}\right) \Gamma(i+1)}{\Gamma\left(i+1+\frac{1}{2}\right)}$$

and using the relations:

$$\Gamma\left(\nu + 1 + \frac{1}{2}\right) = \frac{(2\nu + 1)!!}{2^{\nu+1}} \Gamma\left(\frac{1}{2}\right)$$

where

$$(2\nu + 1)!! = 1.3.5.7. \dots (2\nu + 1) \text{ and } \Gamma(\nu + 1) = \nu!,$$

one finally obtains the equation:

$$I(\theta) = \sum_{\nu=0}^{\infty} f_{2\nu} \frac{2^{\nu}!}{(2\nu + 1)!!} \cos^{2\nu} \theta \quad (4)$$

$$I(\theta) = f_0 + \frac{2}{3} f_2 \cos^2 \theta + \frac{8}{15} f_4 \cos^4 \theta + \frac{16}{35} f_6 \cos^6 \theta + \frac{128}{315} f_8 \cos^8 \theta + \frac{256}{693} f_{10} \cos^{10} \theta + \dots \quad (4')$$

Equations (4, 4') show that, within the model proposed by Leadbetter and coworkers, the intensity scattered can be expanded in a series of  $\cos^{2\nu} \theta$ , the coefficients of which give directly those of the expansion of  $f(\beta)$  in equation (3). This remark means that no numerical inversion of equation (1) is needed but the mere fit of  $I(\theta)$  in the series expansion (4') gives immediately access to  $f(\beta)$ . Note that for  $\theta = \pi/2$ , the intensity is not zero but equal to  $f_0$ . However,  $f_0$  may be negligible in front of the other  $f_{\nu}$  coefficients in the case of a very oriented phase and only in that case.

From a different point of view, it would seem that expanding  $f(\beta)$  in a series of Legendre polynomials  $P_{2\nu}$  would be more elegant and practical to calculate the order parameters. Unfortunately, such an expansion did not yet seem to lead to simple results.

We can now calculate the order parameters: the most important order parameter is  $S = \frac{1}{2} (3\langle \cos^2 \beta \rangle - 1)$  with:

$$\langle \cos^2 \beta \rangle = \frac{\int_0^{\pi/2} f(\beta) \cos^2 \beta \sin \beta \, d\beta}{\int_0^{\pi/2} f(\beta) \sin \beta \, d\beta} \quad (5)$$

using the series expansion (3) and  $x = \cos \beta$ , we easily obtain

$$\langle \cos^2 \beta \rangle = \frac{\sum_{\nu=0}^{\infty} \frac{f_{2\nu}}{2\nu + 3}}{\sum_{\nu=0}^{\infty} \frac{f_{2\nu}}{2\nu + 1}} \quad (6)$$

and hence  $S$ . The isotropic state is described by  $f_{2\nu} = 0$  except for  $f_0 \neq 0$ , which correctly gives  $\langle \cos^2 \beta \rangle = 1/3$  and  $S = 0$ . The perfectly oriented state is described by  $f_{2\nu} = 0$  except when  $f_{2\nu} \rightarrow \infty$ , which correctly gives  $\langle \cos^2 \beta \rangle = 1$  and  $S = 1$ . Note that the denominator is equal to  $1/4\pi$  if the distribution function is normalized.

Other order parameters  $\langle P_{2k}(\cos \beta) \rangle$  can also be calculated in this way.

Finally, the integrated intensity  $\int_0^{\pi/2} I(\theta) d\theta = \frac{1}{8}$  is a constant. (As already implicitly noted in reference [11], no solid angle correction of the form  $\sin \theta$  needs to be made to calculate the

integrated intensity because it is directly included in  $I(\theta)$  by the solid angle of the detector itself.) Actually, this property is always valid for any form of  $f(\beta)$  since it derives mathematically from the general form of equation (1).

2.2. CALCULATION IN THE FRAME OF THE MAIER-SAUPE ORIENTATIONAL DISTRIBUTION FUNCTION. — We now consider the Maier-Saupe distribution function [13] because it is a simple and widely used particular case. This distribution function is of the form

$$f(\beta) = \frac{1}{Z} e^{m \cos^2 \beta} \quad (7)$$

where  $Z$  is a normalization constant given by:

$$Z = 4\pi \int_0^1 e^{mx^2} dx \quad (8)$$

and  $m$  is a parameter describing the strength of the nematic interaction compared to the effects of temperature. The scattered intensity is expressed as

$$I(\theta) = \int_{\beta=\theta}^{\pi/2} \frac{1}{Z} \frac{e^{m \cos^2 \beta} \sin \beta}{\cos^2 \theta \sqrt{\operatorname{tg}^2 \beta - \operatorname{tg}^2 \theta}} d\beta.$$

Substituting successively  $x = \cos^2 \beta$ ,  $t = (\cos^2 \theta - x)^{1/2}$  and  $y = m^{1/2} t$ , we obtain:

$$I(\theta) = \frac{e^{m \cos^2 \theta}}{\sqrt{m} Z \cos \theta} \frac{\sqrt{\pi}}{2} \operatorname{erf}(\sqrt{m} \cos \theta) \quad (9)$$

where  $\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-y^2} dy$  is the error function [12].

This result was first obtained and discussed by Paranjpe and Kelkar in reference [14]. It shows that equation (1) combined with the Maier-Saupe distribution function implies that the scattered intensity should be fitted to the simple form (9).

At this point, it is instructive to use the series expansion of the error function:

$$\operatorname{erf}(u) = \frac{2}{\sqrt{\pi}} e^{-u^2} \sum_{k=0}^{\infty} \frac{2^k}{(2k+1)!!} u^{2k+1}$$

to obtain an alternative form for  $I(\theta)$ :

$$I(\theta) = \frac{1}{Z} \sum_{i=0}^{\infty} \frac{2^i m^i \cos^{2i} \theta}{(2i+1)!!} \quad (9')$$

$$I(\theta) = \frac{1}{Z} \left[ 1 + \frac{2m}{3} \cos^2 \theta + \frac{4m^2}{15} \cos^4 \theta + \frac{8m^3}{105} \cos^6 \theta + \frac{16m^4}{945} \cos^8 \theta + \dots \right] \quad (9'')$$

which should be compared to the general form (4). It appears that in the frame of the Maier-Saupe distribution function, all the coefficients of the series are related so that there remains only one independent parameter,  $m$ . Indeed, the Maier-Saupe distribution is obtained by only considering the quadrupolar term of the multipole development of the interaction which is a severe restriction.

Here also, we can calculate the main order parameter  $S$ . Starting from equation (5) and substituting  $x = \cos \beta$  leads to:

$$\langle \cos^2 \beta \rangle = \frac{\int_0^1 x^2 e^{mx^2} dx}{\int_0^1 e^{mx^2} dx} = \frac{J_2(m)}{J_0(m)}$$

The integral  $J_2(m)$  can be integrated by parts and related to  $J_0(m)$ :  $J_2 = \frac{1}{2m} [e^m - J_0]$ . Now, it can be recognized that  $J_0 = \frac{1}{\sqrt{m}} \int_0^{\sqrt{m}} e^{x^2} dx$  is actually Dawson's integral [12, 13]. So that  $J_0$  can be expressed as a series:  $J_0 = \sum_{k=0}^{\infty} \frac{m^k}{k!(2k+1)}$ . Finally,  $S$  is given by  $S = \frac{1}{2} \langle 3 \cos^2 \beta \rangle - 1$ . Table I shows the values of  $S$  as a function of  $m$ . Higher order parameters can be calculated in exactly the same way. Here also, it can easily be checked that the integrated intensity remains equal to 1/8.

Now, we would like to compare the description given here with the experimental data. Actually, two hypotheses should be separately checked: first, the validity of equation (1) obtained by Leadbetter *et al.* [7], then the validity of the Maier-Saupe orientational distribution function. However, the expansion of  $I(\theta)$  in the form of a series of circular functions as predicted by equation (4) in the general case is a result always valid as soon as  $I(\theta)$  has the cylindrical symmetry. Therefore, the fit of  $I(\theta)$  with expansion (4) is actually not by itself a proof of the validity of equation (1). To test the validity of equation (1) we would therefore need an independent way of determining the  $f_{2i}$  coefficients of expansion (4). In the absence of such an independent means of deriving  $f(\beta)$ , we could only try to compare the values of  $S$  obtained in this way with those of the literature. Altogether, in this respect, the situation is quite the same as that of the analytical inversion method of reference [11]. Furthermore, expansion (4) (and (9') too) converges only very slowly, especially in the case of large order parameters. This

Table I — Relation between the Maier-Saupe coefficient  $m$  and the order parameter  $S$ .

$m$	$J_0$	$\langle \cos^2 \beta \rangle$	$S$
1	1.46	0.43	0.15
2	2.37	0.53	0.30
3	4.22	0.63	0.45
4	8.23	0.70	0.55
5	17.17	0.76	0.65
6	37.73	0.81	0.71
7	86.03	0.84	0.76
8	201.51	0.86	0.79
9	481.52	0.88	0.82
10	1168.23	0.89	0.84

makes the use of this expansion extremely awkward and inefficient so that we did not really try to apply it. The fundamental interests in expansion (4) lie in the following points:

- it shows the direct relation (so far unknown) between the development of  $I(\theta)$  and that of  $f(\beta)$ ;
- it shows the constraints imposed on such a type of development by the choice of the Maier-Saupe orientational distribution function instead of a general one.

However, practically speaking, expansion (4) is very hard to use. Fortunately, we will show in the next section that, in most cases, the Maier-Saupe distribution function is valid so that equation (9) can safely be applied. Moreover, we have indications that when equation (9) does not describe the scattering quite well, this is not due to the Maier-Saupe distribution but rather because one of the underlying assumptions i-iv is not valid.

### 3. Experiments

We have studied several mesogenic compounds ranging from classical rod-like molecules to phasmidic molecules and mesomorphic polymers in order to try to define the domain of validity of the previous results. We have considered SmA phases as well as nematic ones since the nematic order can be followed in the SmA phase too. The case of SmC phases is more complicated but can be addressed in a similar way as shown in reference [7]. The X-ray scattering experiments were performed with already described classical set-ups using a focussing monochromator ( $\lambda\text{CuK}\alpha = 1.541 \text{ \AA}$ ), point collimation, a magnetic field to orient the sample and an air-evacuated camera [15]. The scattered intensity was recorded on photographic X-ray films and special care was taken to use them in their properly linear dynamic range. The scattered intensity (Fig. 1) was then digitalized with a scanner previously standardized with Kodak photographic step tablets of calibrated optical densities. The experimental scattered intensity  $I_{\text{exp}}(\theta)$  needs to be corrected in order to obtain the normalized intensity  $I(\theta)$  scattered by the sample:

$$I_{\text{exp}}(\theta) = k \cdot I(\theta) + I_{\text{BG}}$$

$I_{\text{BG}}$  represents all the background intensity such as inelastic scattering from the sample and residual instrumental noise. This term of course depends on the scattering angle and also slightly on the temperature but we assume that it does not depend on the polar angle  $\theta$ . We estimated  $I_{\text{BG}}$  by averaging its values measured in different areas around the diffuse ring.  $I_{\text{BG}}$  is rather difficult to appreciate and since it has a crucial influence on the subsequent data treatment especially at low order parameters, its influence is one of the flaws of the whole procedure.

The Lorentz-polarization and absorption corrections proved to be negligible at these scattering angles.

The multiplicative constant  $k$  gathers various factors such as the intrinsic scattering power [1] of the sample, the exposure time, the sample volume, etc. This term has to be very accurately determined when absolute measurements are needed, which is a rather tedious work. For our purpose, fortunately, there is no real need to perform absolute measurements and this constant will remain as a fit parameter of not much significance.

Figures 2 a-d show the experimental scattered intensity  $I_{\text{exp}}(\theta)$  and its fit (smooth solid line) by equation (9) for compound 4O.8 (N-(4-n-butyl oxybenzylidene)-4-n-octylaniline) at different temperatures in the nematic and SmA phases. There are only two fit parameters:



the multiplicative factor  $k$  and the parameter  $m$  of the Maier-Saupe distribution function. In the nematic phase, the fit is very good whereas it is only fair in the SmA phase. This is most probably due to the fact that, in the latter phase, we observe a series of diffuse lines in the diffraction pattern. These diffuse lines arise from longitudinal correlations enhanced in the SmA phase, and alter the measures of  $I_{\text{exp}}(\theta)$ . This good agreement between the observed and predicted shapes of the scattered intensity means that both the procedure of Leadbetter *et al* leading to equation (1) and the Maier-Saupe distribution function, in spite of all their drastic assumptions, do describe the wide angle scattering by 4O.8. Moreover, the order parameters (Tab. II) obtained by the fit are quite comparable to those obtained in [7] through numerical

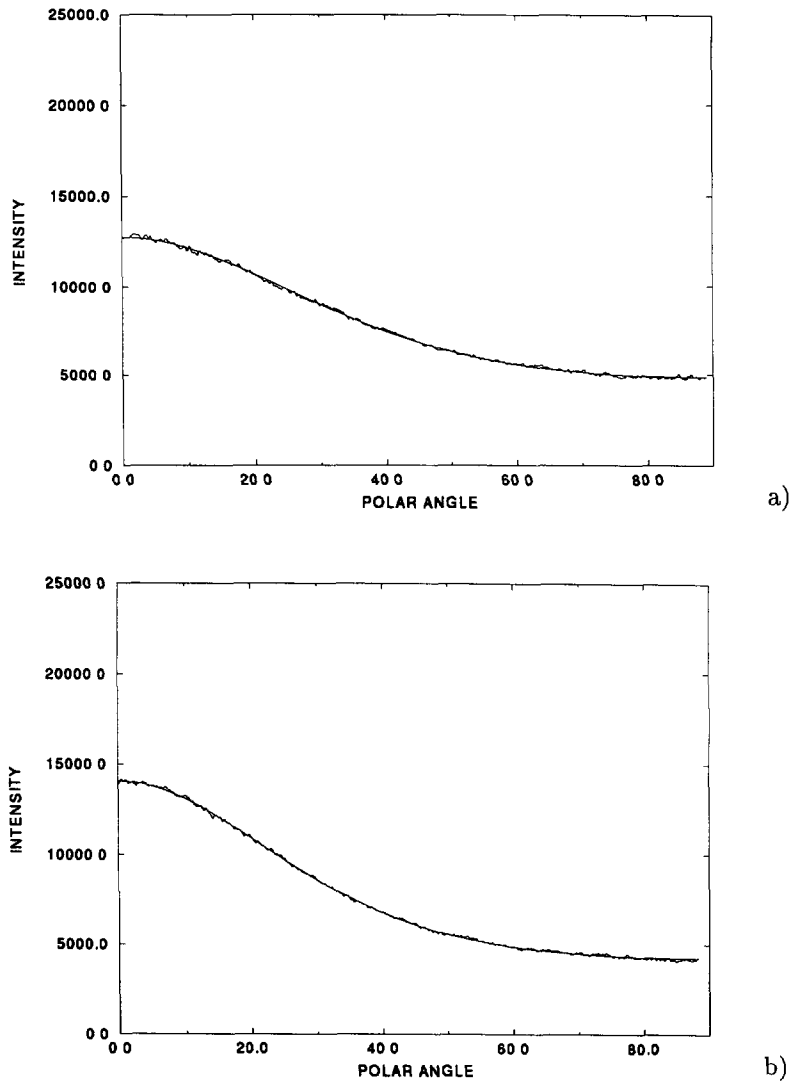


Fig. 2. — Scattered intensity  $I_{\text{exp}}(\theta)$  versus polar angle for compound 4O.8 at: a)  $T = 78\text{ }^{\circ}\text{C}$  (nematic),  $S = 0.40$ . b)  $T = 74\text{ }^{\circ}\text{C}$  (nematic),  $S = 0.50$ . c)  $T = 66\text{ }^{\circ}\text{C}$  (nematic),  $S = 0.65$ . d)  $T = 56\text{ }^{\circ}\text{C}$  (smectic A),  $S = 0.78$

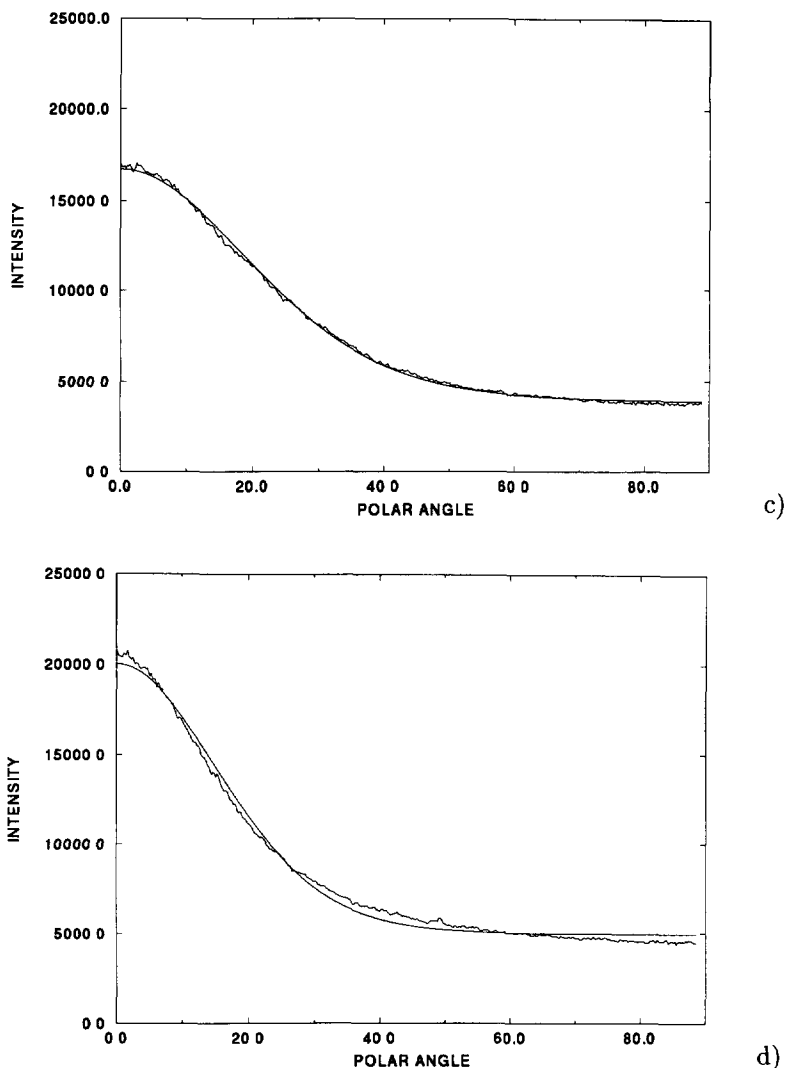


Fig. 2. — (Continued)

inversion, except at high temperatures close to  $T_c$ . This discrepancy may come from the lower signal/noise ratio which may have hampered one or the other method. More surprisingly, the values of the order parameters obtained with use of formula (2) are about 20% larger than the previous ones. Formula (2) derives mathematically from equation (1) without use of the Maier-Saupe distribution function and should therefore be equivalent to the numerical inversion performed in [7]. We do not understand at this time the origin of this discrepancy. We have also considered other classical rod-like molecules of the  $nO\cdot m$  series and of the series of Schiff bases (Fig. 3). These various compounds essentially led to the same conclusions as those obtained from the study of 4O.8. We have then chosen “phasmidic” molecules which considerably depart from the classical structure of rod-like mesogens since they are made from an unusually long rigid core grafted with several aliphatic chains at its extremities [16]. The

Table II. — Comparison between the order parameter estimations made by use of equation (9), after reference [7b] and by use of equation (2) obtained in reference [11].

$T/T_c$	$S$ (this work)	$S$ (after Ref [7])	$S$ (by use of Eq. (2))
0.997	0.40	—	0.67
0.991	0.50	—	0.74
0.989	—	0.60	—
0.986	0.50	—	0.74
0.980	—	0.61	—
0.974	0.60	0.63	0.79
0.963	0.65	—	0.82
0.960	—	0.67	—
0.952	0.71	—	0.87
0.946	—	0.73	—
0.935	0.78	0.75	0.91
0.920	—	0.76	—

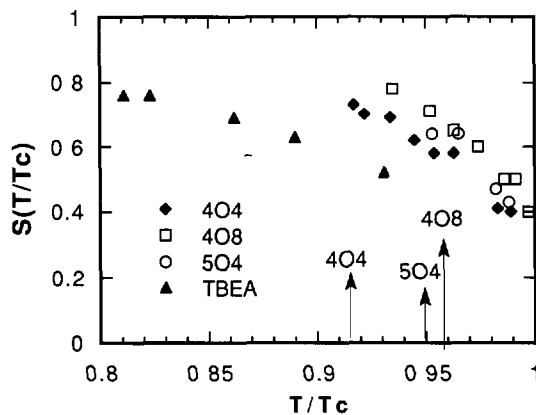


Fig. 3. — Order parameter variation *versus* reduced temperature in the nematic phase and smectic A phase of some compounds of the  $nOm$  series (the arrows point the transition between the two mesophases), and in the nematic phase of the terephthal-bis-ethylaniline (TBEA).

chemical formula of the phasmidic compound is:  $(H_{15}C_7O)_2\phi CO_2\phi NCH\phi CHN\phi O_2C\phi (OC_7H_{15})_2$ .

The wide angle scattering is still well described by equation (9) either for a pure phasmidic compound or for its mixtures in various parts with classical rod-like molecules. Thus, the phasmidic mesogen in no way differs from the conventional ones in this respect. However the exact signification of the resulting  $S$  values is questionable. In fact an assembly of phasmidic molecules contains two sets of chains oriented at  $60^\circ$  one to each other, and it is clear that the

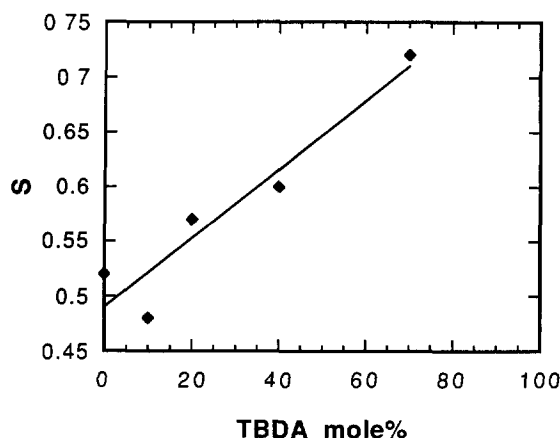
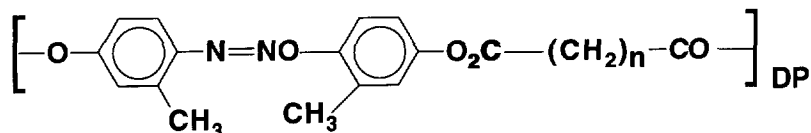


Fig. 4. — Order parameter variation *versus* composition for mixtures of a phasmidic compound with terephthal-bis-decyylaniline (TBDA).

angular extension of the wide angle scattering arc depends both of cores and chains orientational distributions. Therefore the  $S$  values reported in Figure 4 are partly representative of the distribution of the chain long axes which depends of the molecular architecture. Indeed the addition of a rod-like molecule, the terephthal-bis-decyylaniline, to the phasmidic compound, though does not significantly modify the stability range of the nematic phase, increases the order parameter.

In general, the validity of the assumptions leading to the description of the scattering is essentially assured by the disorder of the phase: the disorder indeed tends to average the molecular conformations so that the molecules can effectively be described as homogeneous cylindrical rods. Besides, in a highly disordered phase there will be little enough short range-order for the cluster approximation to be correct. Moreover, the more disordered the phase, the smaller the influence of the other features of the diffraction pattern. The influence of these features such as the diffuse lines, perpendicular to the meridian depends on the form factor of the considered molecule, as it appears in Figures 5a-c where different experimental curves around  $S = 0.7$  are compared: the fit is less good for the compounds of the terephthal-bis-alkylaniline than for the  $nO$   $m$  series. In addition, the effects of the finite nematic correlation length is small when the order parameter is not too large (i.e.  $S < 0.8$ ) [7]. In order to examine to which extent equation (9) can be applied to the case of large order parameters, we have considered very oriented nematic phases, namely those of mesomorphic polymers.

We first selected a well-known series of main-chain polyesters of the following chemical formula



which was studied by a large variety of techniques [17]. For polymer PE-11 ( $n = 11$ ), we observed that equation (9) still provides a fairly good description. In contrast, in the case of polymer PE-10 ( $n = 10$ ) some discrepancy occurs at low temperatures. Indeed, the fit is not as good and gives order parameter values  $S \approx 0.7$  (Fig. 5d) which are too low compared to what could be inferred ( $S \geq 0.8$ ) by inspecting the diffraction pattern. In this case, the small-angle

diffuse ring looks more like a small diffuse line than a diffuse ring. This means that the phase is highly ordered so that assumption iv) clearly breaks down. The fact that we observe this discrepancy for PE-10 rather than for PE-11 comes from a classical odd-even effect [17]. The spacers of PE-11 present many more gauche conformations than those of PE-10 and therefore decrease both the nematic longitudinal correlation length and the nematic order parameter (Fig. 6).

We have also selected several side-chain polymers of another well-known series [18].

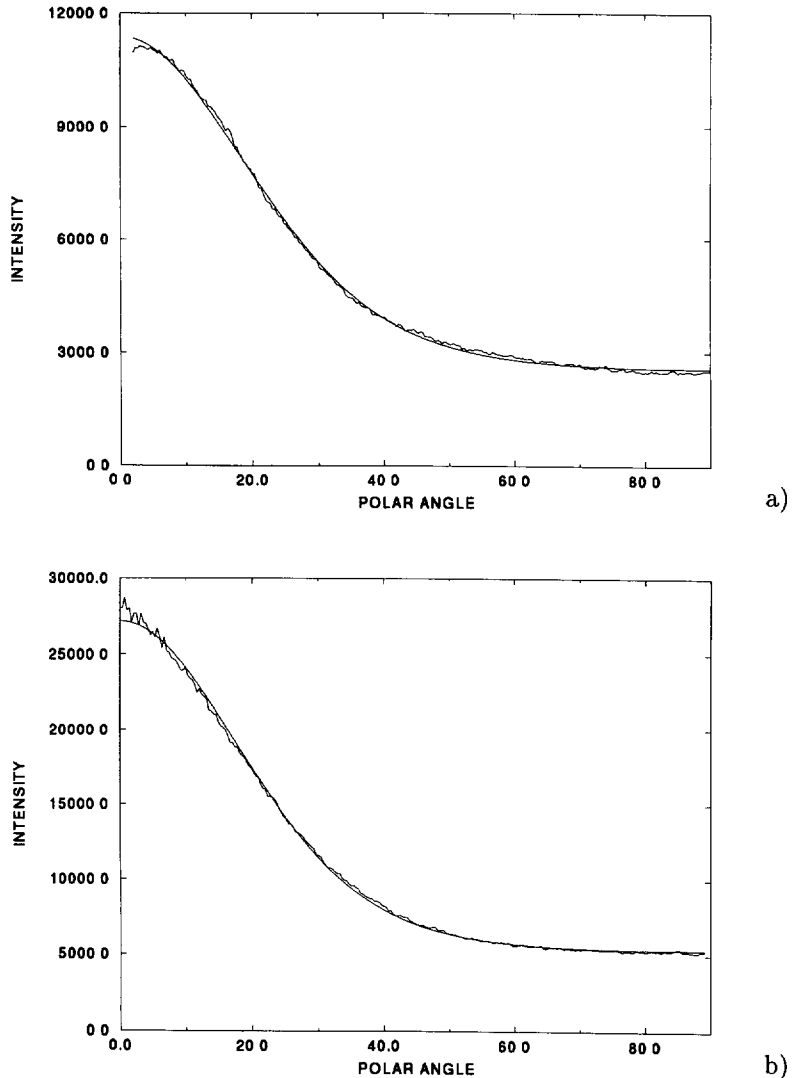


Fig. 5. — Scattered intensity  $I_{\text{exp}}(\theta)$  versus polar angle for  $S \approx 0.7$ . Comparison of different compounds a) 4O.4,  $T = 48^\circ\text{C}$  (nematic),  $S = 0.70$ . b) TBEA,  $T = 176^\circ\text{C}$  (nematic),  $S = 0.69$ . c) 30% phasimidic compound, 70% TBDA,  $T = 180^\circ\text{C}$  (nematic)  $S = 0.72$ . d) Polymer PE10,  $T = 123^\circ\text{C}$  (nematic),  $S = 0.74$ . e) Polymer PMAOCH<sub>3</sub>,  $T = 63^\circ\text{C}$  (smectic A),  $S = 0.70$ .

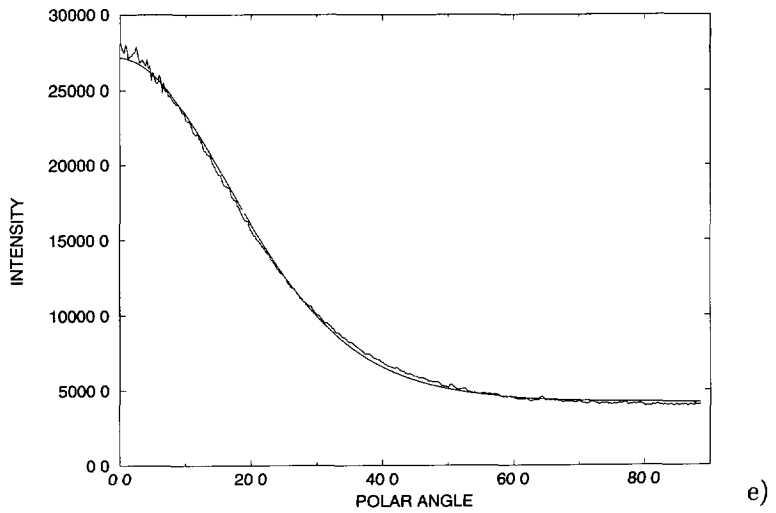
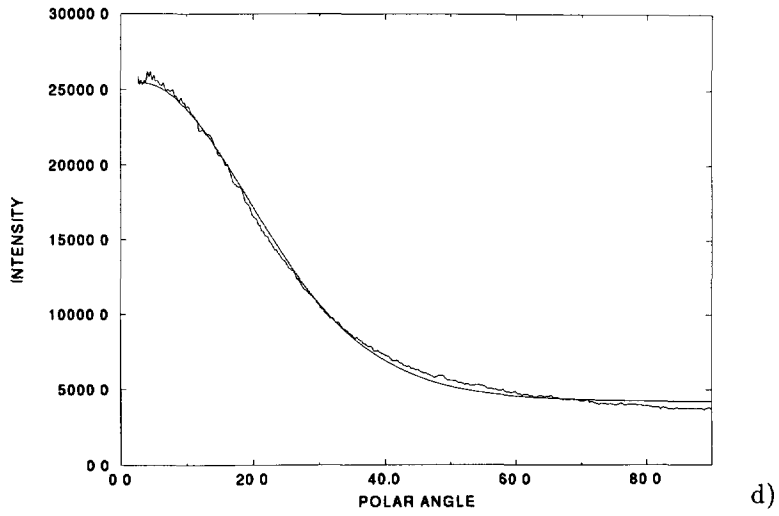
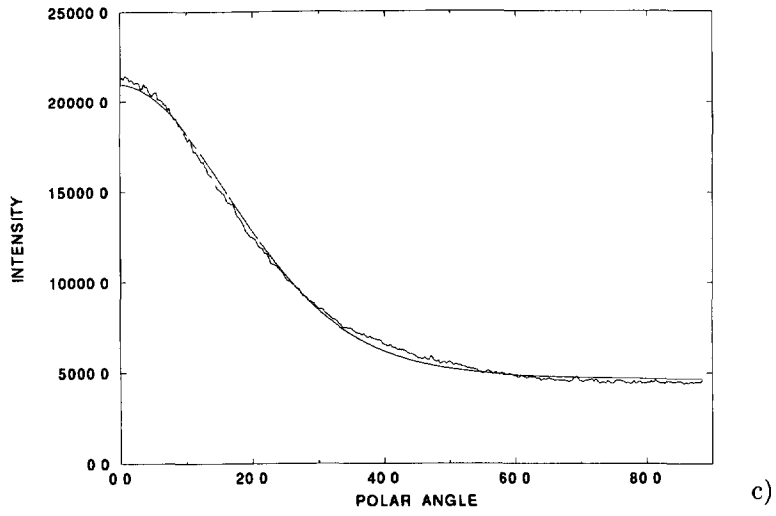


Fig. 5 — (Continued)

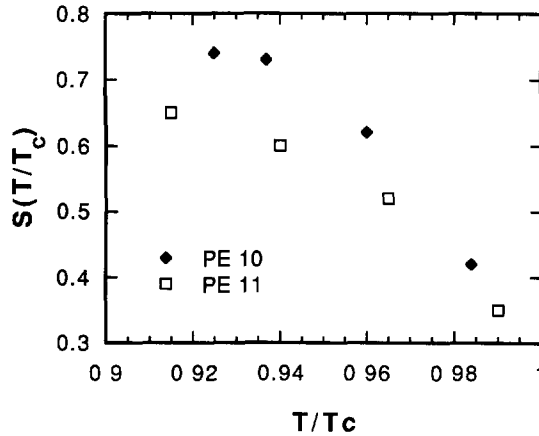
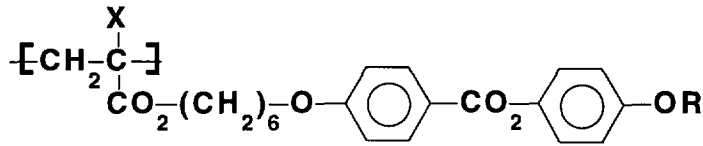


Fig. 6. — Order parameter variation *versus* reduced temperature for main chain polymers PE10 and PE11 in the nematic phase.

These polymers have the following chemical formula



where X = H (polyacrylate) or CH<sub>3</sub> (polymethacrylate) and R = CH<sub>3</sub> or OC<sub>4</sub>H<sub>9</sub>.

Figure 7 shows the fits of  $I_{\text{exp}}(\theta)$  with equation (9) for X = CH<sub>3</sub> and R = OC<sub>4</sub>H<sub>9</sub>. Here also, it appears that equation (9) provides a quite satisfactory fit to the data except for very large order parameters  $S \approx 0.8-0.9$ . The results on polymer PA-OCH<sub>3</sub> are quite comparable to those obtained in reference [9c], with the same value of  $S$  in the nematic phase, the same jump at the N/SmA transition but a slightly larger value at room temperature (0.85 instead of 0.75). This larger value is in good agreement with that obtained (0.88) from NMR measurements on the same compound [18]. Altogether, side chain polymers behave in the same way as conventional mesogens as far as the validity of equation (9) is concerned (Fig. 5e).

#### 4. Discussion

The variety of compounds presented in the previous section demonstrates that, in most cases, the curve of scattered intensity  $I(\theta)$  *versus* polar angle can be well described by equation (9). This seems to ensure the validity of both the scattering formula proposed by Leadbetter *et al.* [7] and the Maier-Saupe orientational distribution function. From a technical point of view, a fit of the data to equation (9) is clearly much easier to perform than the analytical or numerical inversion of the integral equation (1). Furthermore, when the background is properly subtracted, equation (9) only involves two unknown parameters (i.e. the multiplicative constant  $k$  and the parameter  $m$  related to  $S$ ). Therefore two single measurements of the scattered intensity, for instance at  $\theta = 0^\circ$  and  $\theta = 45^\circ$ , are enough to determine the order parameter (and the whole distribution). Actually, if one takes the pain of performing absolute measurements, the multiplicative constant  $k$  would be known so that a single measure, at  $\theta = 0$  for instance,

would be enough to measure the order parameter. The most serious problems hampering this method lie in the estimation of the background intensity especially at low order parameters, and in the influence of other features such as additional diffuse lines or correlation length effects especially at large order parameter. Because of these problems, we altogether estimate the accuracy of our order parameter determinations to be around 10%, and the validity of the approach becomes highly questionable for order parameters larger than  $\approx 0.8$ , and sometimes 0.7. It was also pointed out in [14a] that SmC fluctuations in the nematic phase may involve molecular conformations very different from the rod-like model. In this case, equation (9) could be roughly extended by considering a contribution due to the rigid core and another due to

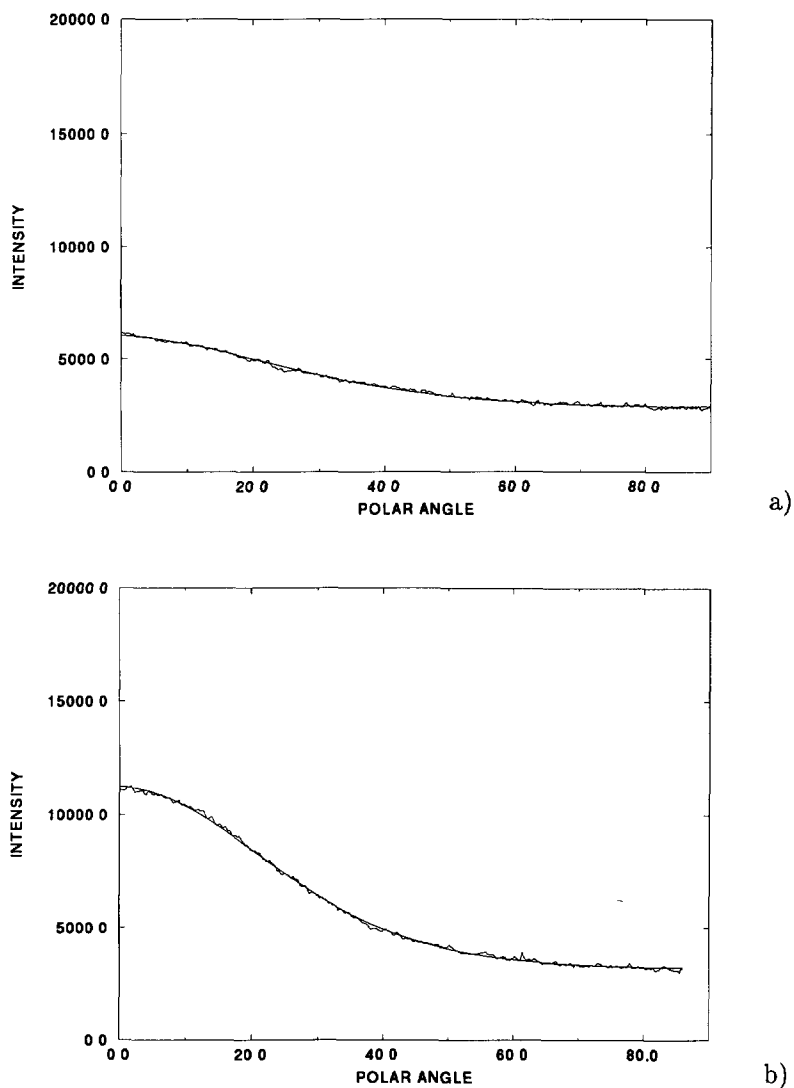


Fig. 7. — Scattered intensity  $I_{\text{exp}}(\theta)$  versus polar angle for polymer PMAOC<sub>4</sub>H<sub>9</sub> at: a)  $T = 115$  °C (nematic),  $S = 0.30$ . b)  $T = 101$  °C (smectic A),  $S = 0.54$ . c)  $T = 80$  °C (smectic A),  $S = 0.77$ . d)  $T = 25$  °C (smectic A glass),  $S = 0.85$ .



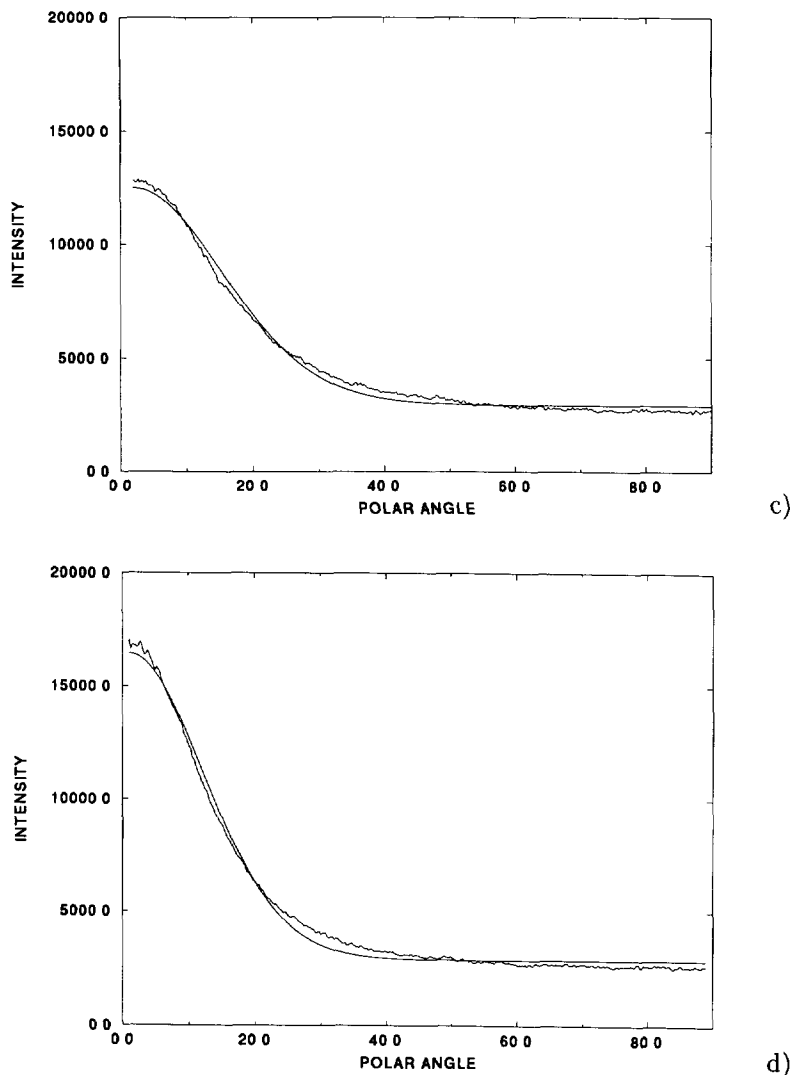


Fig. 7. — (Continued)

the chains.

As already noted in a large number of studies [7-9], the variation of the nematic order parameter with reduced temperature  $S(T/T_c)$  has a similar behaviour for a vast majority of compounds: it is the typical behaviour awaited for an order parameter at a first-order transition. Figure 8 summarizes this behaviour for both the classical rod-like molecules of the  $nO.m$  series and the mesomorphic side-chain polymers studied in this paper. This figure shows the very similar behaviour of all the compounds, be they of low or high molar mass.

Finally, let us briefly discuss the respective merits of the various experimental techniques most frequently used to measure the order parameter. Local spectroscopies such as NMR or ESR are also efficient methods, especially as they give local information more likely to describe the behaviour of a single molecule rather than a cluster of molecules. However, ESR usually

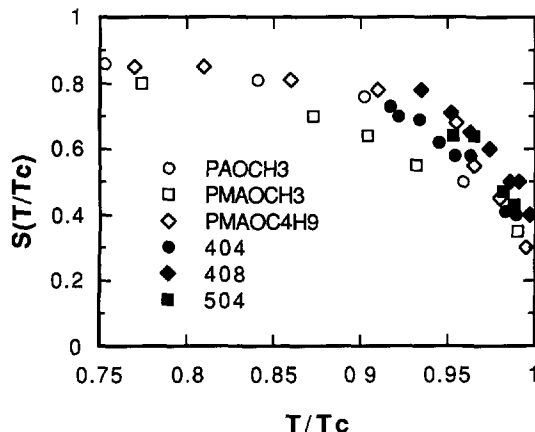


Fig. 8. — Order parameter variations *versus* reduced temperature for all studied compounds of the *nO.m* series and side-chain polymers.

requires the use of a probe which only partially follows the behaviour of the host molecules. Moreover, both techniques do not give access to the whole orientational distribution function  $f(\beta)$  but to a limited number of its moments. From another point of view, NMR gives very detailed information about the ordering of several (sometimes many) molecular sites but this wealth of information can become confusing when a more synthetic description is desired. In this case, macroscopic techniques such as magnetic anisotropy and optical birefringence may be more suitable. Both methods do not give the whole  $f(\beta)$  distribution but only its first moment,  $S$ . These global methods need perfectly aligned samples over large volumes. The order parameter is easily deduced from magnetic anisotropy measurements, the only difficulty arises in controlling the quality of alignment. Optical birefringence is a very simple and practical technique, in which the misalignments are easily checked, but it suffers from the fact that the relation between the macroscopic birefringence and the molecular polarizability is not as straightforward [19]. Furthermore, since the largest contribution to the polarizability comes from the  $\pi$  electrons of the rigid core, optical birefringence is more representative of the behaviour of mesogenic cores (similarly the magnetic anisotropy is mainly due to the aromatic moiety of the molecule). In this classification, the scattering techniques are in between the local and the macroscopic ones, so that the kind of information one wants to obtain should be carefully thought of before selecting a technique. Moreover the comparison between different techniques could provide a better idea of the degree of ordering of the different parts of molecules with complex shape such as phasmidic ones. Neutron scattering experiments have also recently been performed [20]. In this case, the use of mixtures of hydrogenated and perdeuterated molecules has allowed  $f(\beta)$  to be obtained in a way quite different from that of Leadbetter *et al.* [7]. The results were only in fair agreement with the Maier-Saupe distribution function in the nematic phase and partially disagreed in the SmA and SmC phases. This discrepancy was interpreted as the influence of local molecular biaxiality. An advantage of this technique is to get rid of many of the usual underlying assumptions i)-iv) such as the "cluster approximation" but obvious drawbacks are the need for a neutron beam, for deuteration and for a large sample quantity. Therefore, in the field of the scattering techniques, equation (9) first derived by Paranjpe and Kelkar, in spite of the shortcomings mentioned above and the drastic hypotheses leading to equation (1), still constitutes the most practical method of measuring the orientational distribution function and the nematic order parameter.

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