In the method of Gulari *et al.* $G(\Gamma)$ is approximated by a histogram and the ordinates evaluated at equal intervals in Γ from experimental values of $g^{(2)}(\tau)$ of extremely high signal-to-noise ratio. Further progress with the method depended inherently on the assumption that equation 1 can be applied to a polydisperse system, which is not appropriate. Their equations 15 and 17 were developed for monodisperse systems but applied to solutions of narrow fractions.

The best that might be achieved with the histogram method is to obtain a measure of $\bar{k}_D^\theta$ from the shift in the maximum of the histogram, but its location is subject to considerable uncertainty. Thus, despite the considerable and complex calculations required by the method, and its demands on high quality data, it offers no advantages over simpler fitting procedures for investigations of the concentration dependence and is not as accurate. Preliminary results[8] on computer studies of simulated data for narrow fractions indicate that the simpler direct procedures, such as the cumulants method or force-fitted single exponential, give reliable results for $\bar{k}_D^\theta$.

Another way of appreciating the difference between equations 1 and 2 is to consider the effect on $G(\Gamma)$ of a change in c for each case. $G(\Gamma)$ should, more properly, be written $G(\Gamma,c)$, and we shall write $G(\Gamma_0)$ for $G(\Gamma,0)$ where $\Gamma = \Gamma_0(1+k_Dc)$; no distinction is made at this stage between $k_D^\theta(M)$ and $\bar{k}_D^\theta$. $G(\Gamma,c)$ can be expressed entirely in terms of the static properties of the system, and can easily be related to $G(\Gamma_0)$ by transforming equation 3 into Γ_0 space:

$$|g^{(1)}(\tau)| = \int G(\Gamma_0) \exp\left(-\Gamma_0(1+k_Dc)\tau\right) d\Gamma_0$$

Thus $G(\Gamma)d\Gamma = G(\Gamma_0)d\Gamma_0$, or $G(\Gamma) = G(\Gamma_0)/(d\Gamma/d\Gamma_0)$.

If equation 1 were applicable, $(d\Gamma_0/d\Gamma) = 1$ since $k_D^\theta(M)\Gamma_0$ is a constant. Thus $G(\Gamma)$ is identical in shape to $G(\Gamma_0)$, but shifted an amount $k_D^\theta(M)\Gamma_0c$ from the origin; in fact the shift is towards the origin since $k_D^\theta(M)$ is negative. This clearly presents some difficulties near $\Gamma = 0$.

However, equation 2 results in a compression of $G(\Gamma)$ towards the origin, with a resulting uniform scaling of $G(\Gamma)$, as c is increased. This follows since $(d\Gamma/d\Gamma_0) = (1+\bar{k}_D^\theta c)$, and thus $G(\Gamma,c) = G(\Gamma_0)/(1+\bar{k}_D^\theta c)$.

In conclusion, it has to be emphasized that the histogram method in photon-correlation spectroscopy is not a definitive test of the concentration dependence of the diffusion coefficient in dilute solution.

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Orientation of nematic liquid crystalline polymer in a magnetic field. Evaluation of magnetic susceptibility*

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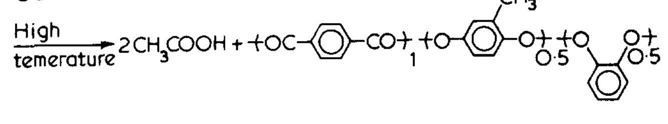
Introduction

In the last few years, studies concerning liquid crystal (LC) polymers have been of increasing interest because of the development of ultra high strength fibres spun from nematic solutions of polyamides and polyesters[1]. The synthesis of thermotropic LC polymers characterized by the alternating sequence along the chain of substantially rigid aromatic groups and flexible segments has already been reported[2-8]. So far, most of the work has focused on aromatic polyazomethines and polyesters and has been stimulated by the interest in relating the type and the thermal stability range of the thermotropic mesophases exhibited by these polymers to the nature of the mesogenic moieties contained in the main chain. However, relatively little work has been devoted to the study of the physical properties of these polymeric mesophases[9-11].

Molecules apt to form a nematic phase are characterized by asymmetrical shape and, for this reason are expected to have anisotropic magnetic susceptibilities and a tendency to become aligned when placed in a magnetic field. Here, we report initial observations concerning the behaviour, in a magnetic field, of a copolymer which has been identified as nematic by using the contact method[8] and we present results for the magnetic susceptibility χ and the anisotropy in this property.

Experimental

The copolymer was prepared in the Centre de Recherches des Carrières de Rhône-Poulenc, Saint-Fons, France by acidolysis reaction from the appropriate hydroquinone bis-acetates and terephthalic acid:



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[*] Presented at the International Symposium on Liquid Crystal Polymers, Leeds, July 16–17, 1980

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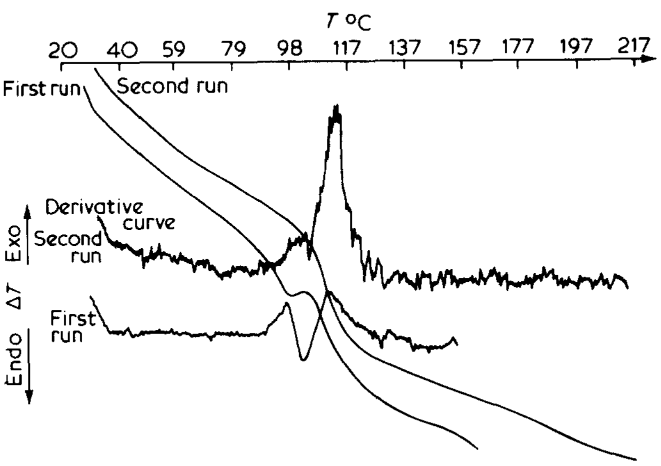

Figure 1 D.s.c. thermogram for copolymer obtained at a heating rate of 10°C/min

Bis-acetates of methylhydroquinone and pyrocatechol were synthesized by reaction of hydroquinones with excess acetic anhydride containing a trace of sulphuric acid catalyst, followed by recrystallization from ethanol.

Copolymer examined with a Du Pont 990 differential thermal analyzer, under a dry nitrogen atmosphere using a heating rate of 10°C/min, exhibits a glass transition at 109°C (*Figure 1*). No upper transition is observed up to 350°C. Observations with a polarizing microscope (Leitz, Panphot) equipped with a heating stage (Mettler FP 5) indicate a flow temperature of 180°–186°C. At this temperature, a small amount of polymer placed between glass slide and cover slip spontaneously gives rise to an anisotropic liquid that exhibits a typical threaded texture (*Figure 2*) and is isomorphic with the nematic phase of *N,N'*-bis(4-pentyloxybenzylidene)-*p*-phenylenediamine[8].

The magnetic susceptibility and the anisotropy in this property have been estimated using the Faraday method. The details of this method and the experimental set up have been described in references 12 and 13. The magnetic force is measured on a polymer sample suspended in a strong inhomogeneous field which provides the necessary magnetic induction gradient $B\,\partial B/\partial x$, where B is the magnetic induction and x the distance of the sample from the pole axis (*Figure 3*). Under these conditions, the magnetic force is related to the per-gram magnetic susceptibility χ of the sample by the following relation:

$$F=\frac{1}{2\mu_0}\frac{\partial B^2}{\partial x}\cdot m\cdot\chi$$

where m is the weight of the sample. The force F is recorded as an apparent change in the sample weight by means of a microelectrobalance. The sensitivity limit is $\Delta\chi$: 10^{-10} emu (or cgs u)g^{-1}. Glass cells of 5 mm diameter were employed. These small volumes permit the use of 100 milligram samples.

During the experiments, helium prevented extensive degradation of the polymer. A constant temperature of 280°C (within ±1°C) was maintained.

Results and discussion

Results summarized in *Figure 4* show the change of the diamagnetic susceptibility as a function of the magnetic field strength. As long as the magnetic field is too weak to cause complete orientation in the direction of the field, the measured magnetic susceptibility depends on the magnetic field strength and decreases (in absolute value) with increasing field strength. This is followed by a period of rapidly increasing alignment which appears as a sharp decrease of the magnetic susceptibility. Then, after a

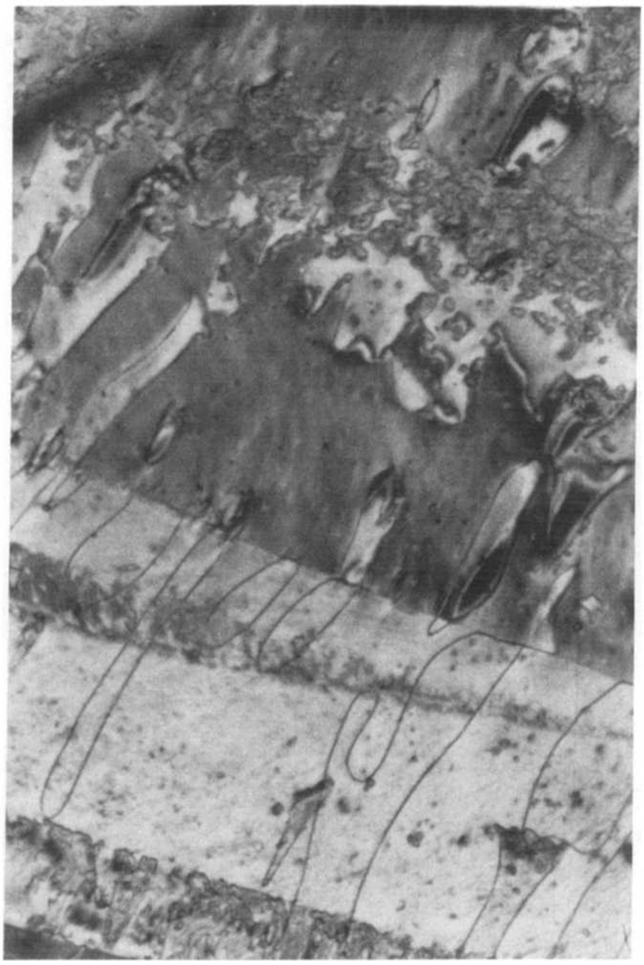

Figure 2 Photomicrograph of copolymer between crossed polarizers at 280°C

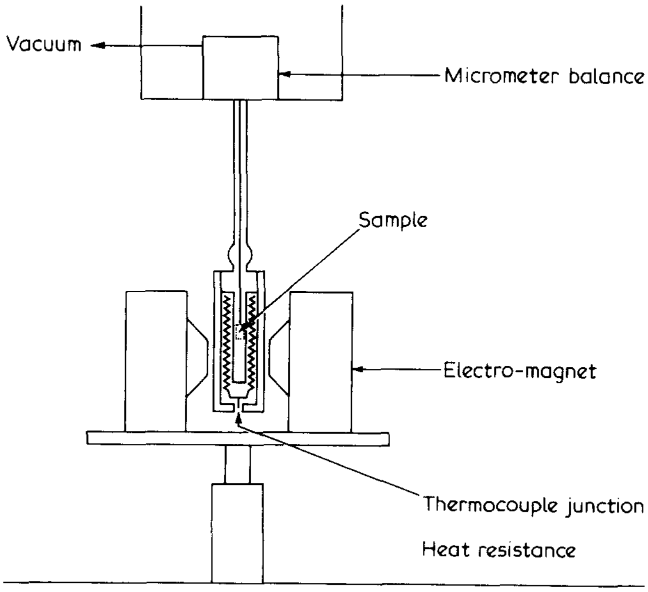

Figure 3 Faraday method: experimental set up

smaller decrease, the magnetic susceptibility approaches a nearly constant value. Practically complete orientation for copolymer in the nematic state ($T = 280°C$) is approximated at 6 kG. Above this threshold field, macromolecules arrange themselves parallel to the magnetic field and the sample becomes transluscent. It is of interest to note that, above the threshold field, orientation time is less than 2 min. At high electric field, Finkelmann *et al.*[11] have also determined short orientation times for copolymers with aromatic esters as mesogenic groups, separated by aliphatic spacers of variable length from the polymethacrylate chain.

The anisotropy of the magnetic susceptibility $\Delta\chi$ will now be considered as the driving force for the orientation effect. $\Delta\chi$ is the difference between the susceptibilities parallel and perpendicular to the main axis of the uniaxial medium (the director $\vec{n}$):

$$\Delta\chi = \chi_{\parallel n} - \chi_{\perp n}$$

Concerning 'rod-like' liquid crystal systems, for positive magnetic anisotropy and high magnetic fields, the long molecular axis will tend to align with the applied field so that $\chi_{\parallel n}$ and $\chi_{\perp n}$ can be regarded as $\chi_{\parallel H}$, the susceptibility parallel to the magnetic field and $\chi_{\perp H}$, the corresponding value perpendicular to the field, respectively. Under these conditions, measurements of $\chi_{\parallel H}$ and $\bar{\chi}$, the isotropic susceptibility, allow determinations of the anisotropy of the magnetic susceptibility:

$$\Delta\chi = \chi_{\parallel H} - \chi_{\perp H} = \frac{3}{2}(\chi_{\parallel H} - \bar{\chi}) \qquad (1)$$

where $\bar{\chi}$ is given by the relation:

$$\bar{\chi} = \frac{1}{3}(\chi_1 + \chi_2 + \chi_3) = \frac{1}{3}\chi_{\parallel n} + \frac{2}{3}\chi_{\perp n}$$

Here χ_1, χ_2 and χ_3 are the principal susceptibilities of the molecules as derived from single crystals.

The Faraday method gives the value of $\bar{\chi} = -5.26 \times 10^{-7}$ emu cgs g^{-1} for the powdered polymer at room temperature and $\chi_{\parallel H} = -4.33 \times 10^{-7}$ emu cgs g^{-1} for the oriented nematic phase at 280°C. It is immediately apparent from *Figure 4* that the extrapolated value of the magnetic susceptibility at $H = 0$ is in good agreement with the isotropic susceptibility $\bar{\chi}$ determined for the powdered sample. Indeed, this extrapolated value corresponds to the zero state, i.e. no applied magnetic field, and, consequently, to randomly distributed single domains in the nematic phase. From the equation (1) for $\Delta\chi$, the anisotropy of the magnetic susceptibility is calculated as 1.4×10^{-7} emu cgs g^{-1} a slightly higher $\Delta\chi$ than that of the low molecular weight liquid crystals ($\Delta\chi = \sim 10^{-7}$)[14,15]. Such a difference may be attributed to a greater rigidity of the macromolecular chains as compared to the low molecular weight liquid crystals which contain two free terminal groups, usually alkyl groups.

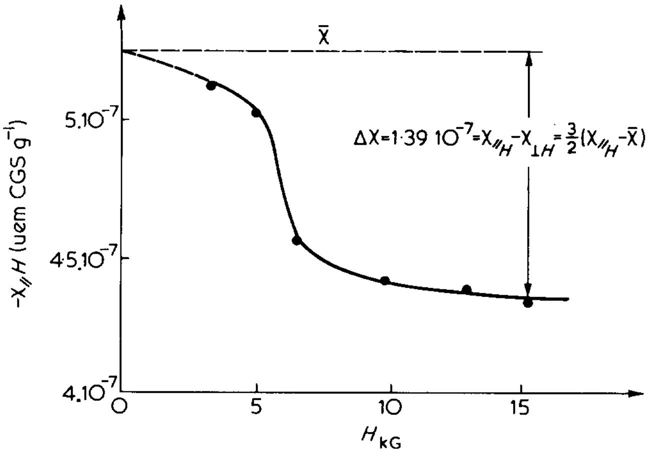

Figure 4 Magnetic susceptibility χ of copolymer vs. the magnetic field strength H at 280°C

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