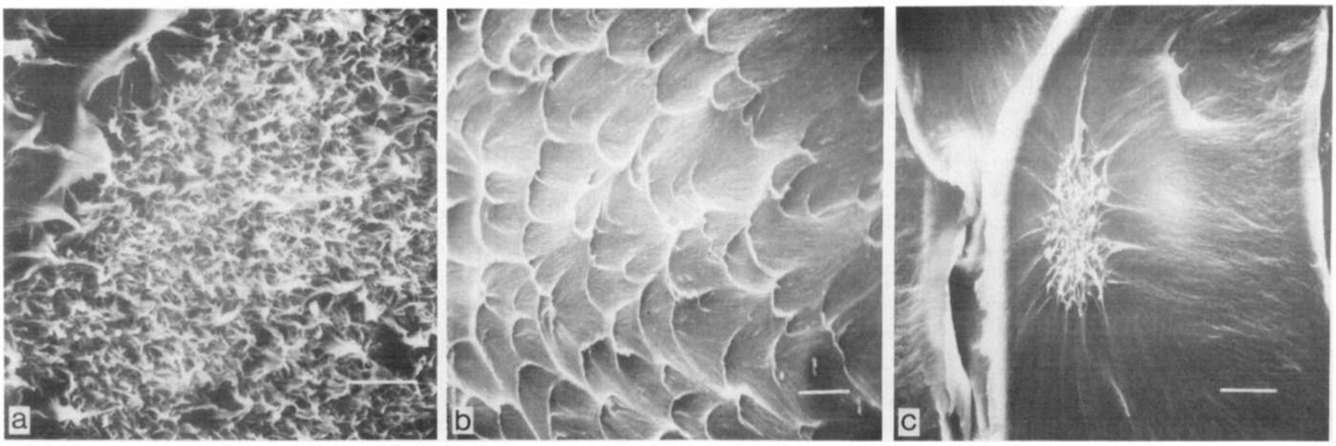


Figure 2 Void coalescence mechanism in LDPE: (a) very fine voids at $\Delta K = 0.45$ MPa m$^{1/2}$, scale bar = 20 μm; (b) coarse voids at ΔK = 1.0 MPa m$^{1/2}$, scale bar = 0.5 mm; (c) centre of coarse void showing texture similar to that shown in (a), scale bar = 30 μm. Crack propagation direction from left to right; frequency, 10 Hz

respectively). It is believed that both of these fracture surfaces were produced by a void growth mechanism. Above $\Delta K = 0.6$ MPa m$^{1/2}$, though, there seems to have been a dramatic decrease in the nucleation rate of these voids and an enhanced opportunity for pronounced void growth. Curiously, these large voids appear to have been nucleated by local void clusters whose appearance was quite similar to the smaller voids seen at low ΔK levels (*Figure 2c*). The discontinuity in *FCP* behaviour reported by Andrews and Walker also was accompanied by a change in fracture morphology but was described differently, based on alternative microscopic techniques. Nevertheless, the phenomenological similarity of the two studies is confirmed. Unfortunately, while the correlation between crack growth rate behaviour and fracture mode transition in LDPE is striking, the fundamental reason for this behaviour remains unknown.

It is not clear why LDPE exhibits *FCP* discontinuities and high density polyethylene (HDPE) does not[3]. In the latter study, fatigue crack growth rates increased continuously with increasing ΔK values for several molecular weights and thermal histories. Additional complexities become apparent when comparisons are made with regard to fracture surface markings. For example, ultrahigh molecular weight polyethylene[4] and HDPE[3] reveal various groupings of parallel fatigue fracture surface lines. Though White and Teh[5] reported similar features in LDPE, none were identified in this investigation. Clearly, much additional research on the fatigue behaviour of polyethylene is needed.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research.

REFERENCES

1 Andrews, E. H. and Walker, B. J. *Proc. R. Soc. London* (*A*) 1971, **325**, 57
2 Hertzberg, R. W., Nordberg, H. and Manson, J. A. *J. Mater. Sci.* 1970, **5**, 521
3 de Charentenay, F. X., Laghouati, F. and Dewas, J. in 'Deformation, Yield and Fracture of Polymers,' Plastics and Rubber Institute, London 1979, p 6.1
4 Salvati, E. A., Wright, T. M., Burstein, A. H. and Jacobs, B. *J. Bone and Joint Surgery* 1979, **61-A**, 1239
5 White, J. R. and Teh, J. W. *Polymer* 1979, **20**, 764

A comment on the histogram method in photon correlation spectroscopy applied to dilute polymer solutions

David Caroline
School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd, LL57 2UW, UK
(*Received* 3 *November* 1980)

Photon-correlation spectroscopy[1] is now routinely used to measure diffusion coefficients of macromolecules in dilute solution since rapid and accurate determinations can be made. It is usual to measure the diffusion coefficient D as a function of the solute concentration c, principally to obtain D_0, the value of D at infinite dilution, from an extrapolation of the data. Thus, although the main purpose of these investigations is often to determine D_0, it is also possible to study the concentration dependence, and this has been a popular area of investigation in the study of dilute polymer solutions.

For an ideally monodisperse polymer sample in dilute solution, D varies linearly with c:

$$D(M,c) = D_0(M)\,(1 + k_D(M)c) \text{ (monodisperse)} \qquad (1)$$

(The M-dependence has been indicated for completeness.) The coefficient k_D depends on the particular system and is

0032-3861/81/050576-03$02.00

a function of the polymer molecular weight M and temperature T.

However, the variation of k_D with M often shows considerably more scatter than one would expect from a technique capable of high-precision[2], and it has been suggested that the polydispersity of the sample, even for narrow fractions, has a dominant effect on the value obtained for k_D when simple data-fitting procedures appropriate to ideally monodisperse samples are used.

In an attempt to cirumvent this problem, Gulari *et al.*[3] have used their histogram method of data analysis specifically to test the concentration dependence in a theta system (polystyrene in cyclohexane). They maintain that observations at two concentrations on a single polymer sample are all that is necessary to make a definitive decision amongst the theories. The purpose of this communication is to point out a conceptual oversight in their argument that renders their particular procedure invalid; as a result, their conclusions may need revising.

The point at issue is what is the appropriate value to use for k_D in a polydisperse sample. Gulari *et al.* assume that each molecular-weight species takes on the value of k_D it would have in a monodisperse solution, but this is unlikely since it implies that each polymer molecule behaves as if it were in a monodisperse solution of the same overall concentration. Their application of equation 1 to each species in a polydisperse solution is inappropriate, though it forms a central link in their argument. We propose to show that in a theta system the concentration dependence is governed by a collective coefficient $\bar{k}_D$ which is the same for all species in the solution.

The theoretical expressions for k_D take the form[4]

$$k_D = (2-\lambda)A_2M - pv_h - v$$

where A_2 is the second virial coefficient of the solution and v the specific volume of the bulk polymer ($=0.92\ \mathrm{cm^3\ g^{-1}}$ for polystyrene). The specific hydrodynamic volume v_h equals $(4\pi/3)R_h^3N/M$ where N is Avogadro's number and R_h the hydrodynamic radius. (R_h can be found from D_0 through the Stokes–Einstein equation, $D_0 = kT/6\pi\eta R_h$ where k is Boltzmann's constant and η the solvent viscosity). For polystyrene at the theta point $v_h = 0.030\ M^{1/2}\ \mathrm{cm^3\ g^{-1}}$. The coefficient λ appears only in Yamakawa's theory[5], where it has a value of 1.345 at the theta point and decreases slightly for an expanded coil in a good solvent. The coefficient p is unity in the theories of Yamakawa[5] and Imai[6]. However, Pyun and Fixman[7] obtain a value of 7.16 for p in their 'hard-sphere' model; in their 'soft-sphere' model p is 2.23 at the theta point but increases to the hard-sphere value as the coil expands.

The present discussion will be restricted to theta systems (as was the histogram analysis) since the expression for k_D simplifies considerably on account of A_2 becoming zero: $k_D^\theta = -pv_h - v$. Physically, the reduction of D with c is a direct result of the polymer molecules effectively occupying a fraction ($k_D^\theta c$) of the total volume, with a consequent restriction in their motion. The theories differ in predicting the exact value of the volume which becomes inaccessible, but agree that it is proportional to v_hc (plus the small vc term).

This physical picture is helpful in determining the correct value to choose for k_D^θ in a polydisperse solution. It seems clear that in this case the concentration dependence of D for a particular species M is governed not by $k_D^\theta(M)$, the value appropriate to a monodisperse sample of the species, but by a value $\bar{k}_D^\theta$ which is determined by $\bar{v}_h$, the aggregate hydrodynamic volume occupied by unit mass of the polydisperse sample. If $f(M)$ is the molecular-weight distribution function of the sample and $V_h(M)$ the hydrodynamic volume of a single molecule of species M, then

$$\bar{v}_h = \int f(M)NV_h\,\mathrm{d}M/\int f(M)M\,\mathrm{d}M$$

$$= \int f(M)Mv_h\,\mathrm{d}M/\int f(M)M\,\mathrm{d}M$$

Thus $\bar{v}_h$, the weight-average specific hydrodynamic volume, is the value which determines $\bar{k}_D^\theta$ and governs the concentration dependence of all the polymer molecules in the solution, whatever their species:

$$D(M) = D_0(M)(1+\bar{k}_D^\theta c)\ \text{(polydisperse)} \qquad (2)$$

and

$$\bar{k}_D^\theta = -p\bar{v}_h - v$$

One interesting result of the existence of $\bar{k}_D^\theta$ is that the concentration dependence of D for a particular species M is different in polydisperse and monodisperse solutions. In a polydisperse system, with a common $\bar{k}_D^\theta$, each species M suffers the same fractional change in the diffusion coefficient, $\Delta D/D_0$, for a given overall concentration change Δc. In contrast, for a series of monodisperse solutions, a given change Δc produces the same absolute change ΔD, since in equation 1 $k_D(M) \propto M^{\frac{1}{2}}$ and $D_0 \propto M^{-\frac{1}{2}}$.

The normalized intensity autocorrelation function $g^{(2)}(\tau)$ of the light scattered from a dilute polymer solution is related to the first-order (optical) correlation function $g^{(1)}(\tau)$ through the Siegert relation[1]:

$$g^{(2)}(\tau) = 1 + \beta|g^{(1)}(\tau)|^2$$

where β is a factor less than unity which depends on the optical arrangement. For a perfectly monodisperse sample of small molecular size,

$$|g^{(1)}(\tau)| = \exp(-\Gamma\tau)$$

where $\Gamma = DK^2$ and K is the scattering vector ($=(2\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the light in the solution and θ the scattering angle). The radius of gyration R_g has to be sufficiently small so that $x = K^2R_g^2 < 0.1$, otherwise intramolecular motion will distort $g^{(1)}(\tau)$ in a complicated way[2]. Except for the highest molecular weights ($M > 10^7$) or the broadest distributions with substantial tails in this region, the condition can be met by carrying out the experiment at sufficiently low angle.

Even for narrow fractions, $|g^{(1)}(\tau)|$ should be represented by a distribution of exponentials:

$$|g^{(1)}(\tau)| = \int G(\Gamma)\exp(-\Gamma\tau)\,\mathrm{d}\Gamma \qquad (3)$$

$G(\Gamma)$ is a distribution function which depends on the distribution of molecular weights $f(M)$ and some function of the polarizability of the molecule $\mu(M)$ as well as the Debye scattering factor $P(x)$ $[=(2/x^2)(e^{-x}-1+x)]$; the latter can be written as $P(K,M)$ since $R_g = R_g(M)$.

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:

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

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

If equation 1 were applicable, $(\mathrm{d}\Gamma_0/\mathrm{d}\Gamma) = 1$ 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 $(\mathrm{d}\Gamma/\mathrm{d}\Gamma_0) = (1+\bar{k}_D^\theta c)$, 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.

References

1 See, for example, 'Photon Correlation and Light Beating Spectroscopy', Eds, Cummins, H. Z. and Pike, E. R., Plenum Press, New York, 1974, and Berne, B. J. and Pecora, R., 'Dynamic Light Scattering' Wiley-Interscience, New York, 1976
2 Jones, G. and Caroline, D. *Chem. Phys.* 1979, **37**, 187
3 Gulari, E., Gulari, E., Tsunashima, Y. and Chu, B. *Polymer* 1979, **20**, 347
4 Yamakawa, H. 'Modern Theory of Polymer Solutions' Harper and Row, New York, 1971
5 Yamakawa, H. *J. Chem. Phys.* 1962, **36**, 2995
6 Imai, S. *J. Chem. Phys.* 1969, **50**, 2116
7 Pyun, C. W. and Fixman, M. 1964, **41**, 937
8 Caroline, D. to be submitted for publication

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

C. Noel and L. Monnerie
Laboratoire de Physicochimie Structurale et Macromoléculaire, ESPCI 10, *rue Vauquelin,* 75231
Paris Cedex 05, *France*

M. F. Achard, F. Hardouin, G. Sigaud and H. Gasparoux
Centre de Recherche Paul Pascal, 33405 *Talence, France*

(*Received* 31 *December* 1980)

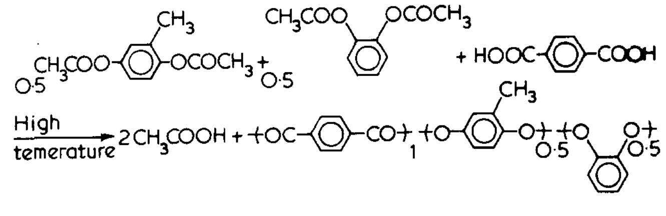
Introduction

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:



---

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

0032–3861/81/050578–03$02.00