Optical anisotropy of a worm-like chain and its application to the determination of the persistence length in an aromatic polyamide

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The optical anisotropy, as obtained from the depolarization of light scattering, has been evaluated for a worm-like chain as a function of the segment anisotropy δ_0 and of the ratio of the contour length L to the persistence length q. The comparison between the theoretical curves and the experimental data obtained for an aromatic polyamide [poly(*para*-phenylene terephthalamide)] in a range of *DP* from 7 to 30 leads to a value of q in good agreement with that calculated from other methods requiring a wider range of molecular weights.

The possibility of obtaining nematic phases from concentrated solutions of semi-flexible polymers and their use in the spinning of high modulus fibres has made the characterization of the flexibility of these molecules more interesting. Because of limitations in their molecular weight range and solubility, direct measurements from diffraction methods is often difficult and one is restricted to hydrodynamic measurements where the interpretation raises some theoretical problems[1]. We show here that the optical anisotropy as measured from the depolarization of light scattering offers a new alternative, requiring only a limited range of degree of polymerization in the low molecular weight range.

THEORY

The experimental quantity directly available from the depolarization ratio of the excess intensity scattered by a solution, eventually extrapolated at zero angle, is the 'optical anisotropy' Δ^2 of the solute particle, a dimensionless quantity defined as[2]:

$$\Delta^2 = \frac{(\alpha - \beta)^2}{9(\overline{\Delta\alpha})^2} \tag{1}$$

where α and β are the principal polarizabilities of the particle and $\overline{\Delta\alpha}$ its mean excess polarizability which can be calculated from the solvent index of refraction, the solute index of refraction increment d*n*/d*c* and molecular weight, using the Gladstone–Dale relation:

$$\frac{2n_0\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)}{n_0^2 + 2} = \frac{4\pi}{3}\frac{N}{M}\overline{\Delta\alpha} \tag{2}$$

For a chain molecule made of N segments, the optical properties which are represented by a Langevin polarizability ellipsoid, with principal values α_0 and β_0 one has:

$$\Delta^2 = \frac{\delta_0^2}{N^2}\sum_i\sum_j \frac{3\,\overline{\cos^2\alpha_{ij}} - 1}{2} \tag{3}$$

or

$$(\alpha - \beta)^2 = (\alpha_0 - \beta_0)^2 \sum_i\sum_j \frac{3\,\overline{\cos^2\alpha_{ij}} - 1}{2} \tag{3a}$$

where α_{ij} is the angle between the axes of the optical ellipsoids associated with segments i and j, the average being taken over the chain conformation, and δ_0 is defined, as above, as a dimensionless quantity $\overline{\Delta\alpha_0} = \overline{\Delta\alpha}/N$.

For the extreme cases of a chain with no correlation in orientation $\Delta^2 = \delta_0^2/N$ or $(\alpha - \beta) = N^{1/2}(\alpha_0 - \beta_0)$, and of a rigid rod with polarizability ellipsoids aligned along the axis $\Delta^2 = \delta_0^2$ or $(\alpha - \beta) = N(\alpha_0 - \beta_0)$.

For a free rotating chain with a valency angle $\pi - \theta$, Benoit has calculated[3]:

$$\Delta^2 = \delta_0^2\left[\frac{1}{N} + \frac{1}{2}(3\cos^2\phi - 1)(3\cos^2\psi - 1) \times \frac{N(1-p) - 1 + p^N}{N^2(1-p)^2}\right] \tag{4}$$

where $p = (3\cos^2\theta - 1)/2$, and ϕ and ψ specify the orientation of the ellipsoid axis of segment i with the direction of bonds i and $i+1$.

Semi-flexible chains can be described using the worm-like chain model or chain with persistence length introduced by Porod and Kratky[4]. The properties of such a chain can be derived from those of the free rotating chain with a valency angle, by making θ and the bond length tend to zero while increasing N to maintain the contour length $L = Na$ constant. One obtains then a limiting value $\cos\theta = \exp(-a/q) = \exp(-2\lambda a)$, where q is the persistence length and λ^{-1} the length of the statistical element.

The application of this procedure to relation (4) requires a separate calculation of the limiting value of p, which due to the statistical nature of the process, cannot be found by replacing $\overline{\cos^2\theta}$ by $(\overline{\cos\theta})^2$. One can then use the theory of the worm-like chain initiated by Saito[5] in which the chain is considered as the trajectory of a quantum particle. The solution of a propagation equation leads to a Green's function giving the probability that the angle between the tangents at two points of curvilinear abcissae S and S' is θ:

$$G(\theta, \phi, S'|0, 0, S) = \frac{1}{4\pi} \sum_n (2n + 1) \times$$

$$\exp[-n(n+1)\lambda|S' - S|]\, P_n(\cos\theta) P_n(1) \qquad (5)$$

Taking in account the orthogonality of the Legendre polynomials $[P_1(\cos\theta) = \cos\theta; P_2(\cos\theta) = (3\cos^2\theta - 1)/2]$ one obtains for the average of interest in the calculation of relations (3) and (4):

$$\overline{\frac{3\cos^2\theta - 1}{2}} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \frac{3\cos^2\theta - 1}{2} \times$$

$$\left[5\exp(-6\lambda|S' - S|)\frac{3\cos^2\theta - 1}{2}\right] \sin\theta\, d\theta\, d\phi$$

$$= \exp(-6\lambda|S' - S|) \qquad (6)$$

while:

$$\cos\theta = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \cos\theta\, [3\exp(-2\lambda|S' - S|)\cos\theta] \times$$

$$\sin\theta\, d\theta\, d\phi = \exp(-2\lambda|S' - S|) \qquad (7)$$

For the case where the optical ellipsoids are oriented along the segment direction ($\alpha_{ij} = \theta_{ij}$) one can directly replace the summation over the segments in relation (3) by an integration over the contour length:

$$\Delta^2 = \frac{\delta_0^2}{L^2}\, 2 \int_0^{S'} \int_0^{L} \exp(-6\lambda|S - S'|) ds\, ds'$$

which gives, introducing the quantity $x' = 6\lambda L = 3L/q$

$$\Delta^2 = \delta_0^2 \left\{\frac{2}{x'} - \frac{2}{x'^2}[1 - \exp(-x')]\right\} \qquad (8)$$

or

$$(\alpha - \beta)^2 = N^2(\alpha_0 - \beta_0)^2 \left\{\frac{2}{x'} - \frac{2}{x'^2}[1 - \exp(-x')]\right\} \qquad (8a)$$

For the case where the ellipsoid is at an angle with the segment direction, but assuming free rotation, one can simply replace p in relation (4) by its value[6]:

$$\Delta^2 = \delta_0^2 \left(\frac{3\cos^2\phi - 1}{2}\right) \left(\frac{3\cos^2\psi - 1}{2}\right) \times$$

$$\left\{\frac{2}{x'} - \frac{2}{x'^2}[1 - \exp(-x')]\right\} \qquad (9)$$

or

$$(\alpha - \beta)^2 = N^2(\alpha_0 - \beta_0)^2 \left(\frac{3\cos^2\phi - 1}{2}\right) \left(\frac{3\cos^2\psi - 1}{2}\right) \times$$

$$\left\{\frac{2}{x'} - \frac{2}{x'^2}[1 - \exp(-x')]\right\} \qquad (9a)$$

analogous to equation (8) but for a geometrical factor depending on ϕ and ψ in the apparent segment anisotropy $\delta_{0\,\mathrm{app}}^2$. Δ^2 or $(\alpha - \beta)$ is then shown to vary in a way very similar to the mean square distance $\langle r^2 \rangle$[6]:

$$\langle r^2 \rangle = L^2 \left\{\frac{2}{x} - \frac{2}{x^2}[1 - \exp(-x)]\right\}$$

$$x = 2\lambda L = \frac{L}{q} \qquad (10)$$

but with an apparent persistence length three times smaller.

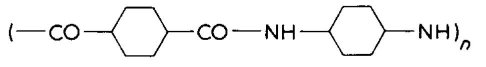
For large values of L/q one obtains from equation (9a):

$$(\alpha - \beta)^2 = N \left[(\alpha_0 - \beta_0)^2 \left(\frac{3\cos^2\phi - 1}{2}\right) \times \left(\frac{3\cos^2\psi - 1}{2}\right) \frac{2q}{3b}\right] \qquad (11)$$

where b is the length of the repeat unit ($L = Nb$). The square root of the quantity in brackets can be defined as the difference of polarizability of the statistical element.

APPLICATION TO THE CASE OF AROMATIC POLYAMIDES

We have recently started the study of some aromatic polyamides, such as poly(*para*-phenylene terephthalamide):



in 96% sulphuric acid. Light scattering, viscosity and flow birefringence experiments show that their properties are well interpreted by a worm-like chain model[7,8]. Moreover, in the course of the light scattering studies, low molecular weight samples (either raw or fractionated) were shown to exhibit large depolarization ratios ρ_u up to 0.25.

Values of Δ^2 have been calculated and plotted as a function of the weight-average number of repeat units n_w, as deduced from the measured molecular weight. A rough extrapolation to $n_w = 1$ gives a first value of $\delta^2_{0\mathrm{app}}$. Plots of the quantity

$$\frac{2}{x'} - \frac{2}{x'^2}\,[1 - \exp(-x')]$$

as a function of N are then constructed for different values of the persistence length q using $b = 12$Å as the length of the repeat unit[10]. Values of $\Delta^2/\delta^2_{0\mathrm{app}}$, according to relation (8), are reported on these plots using slightly varying figures for $\delta^2_{0\mathrm{app}}$. The results are given in *Figure 1*, where one sees that a most satisfactory agreement is obtained for $\delta^2_{0\mathrm{app}} = 0.40$ and $q = 150$ Å. This last value is in good agreement with that derived from viscosity ($q = 150$ Å), radii of gyration ($q = 200$ Å) and rotatory diffusion constants from flow birefringence ($q = 185$ Å)[7–9].

From $\delta^2_{0\mathrm{app}}$ one calculates the apparent difference of polarizability of the repeat unit using relation (2); with $n_0 = 1.43$, $\mathrm{d}n/\mathrm{d}c = 0.309$ and $M = 238$ one finds:

$$(\alpha_0 - \beta_0)\left(\frac{3\cos^2\psi - 1}{2}\right)\left(\frac{3\cos^2\phi - 1}{2}\right)$$

$$= 2.06 \times 10^{-24}\ \mathrm{cm}^3$$

This is a consistent result if one considers that most of the anisotropy arises from the two benzene rings, each with a difference of principal polarizabilities of 6×10^{-24} cm^3, the axes of their polarizability ellipsoid being essentially perpendicular to the segment direction ($\phi = \psi = \pi/2$), from which one calculates a contribution of $2 \times 6 \times 10^{-24} \times 1/4 = 3 \times 10^{-24}$ cm^3.

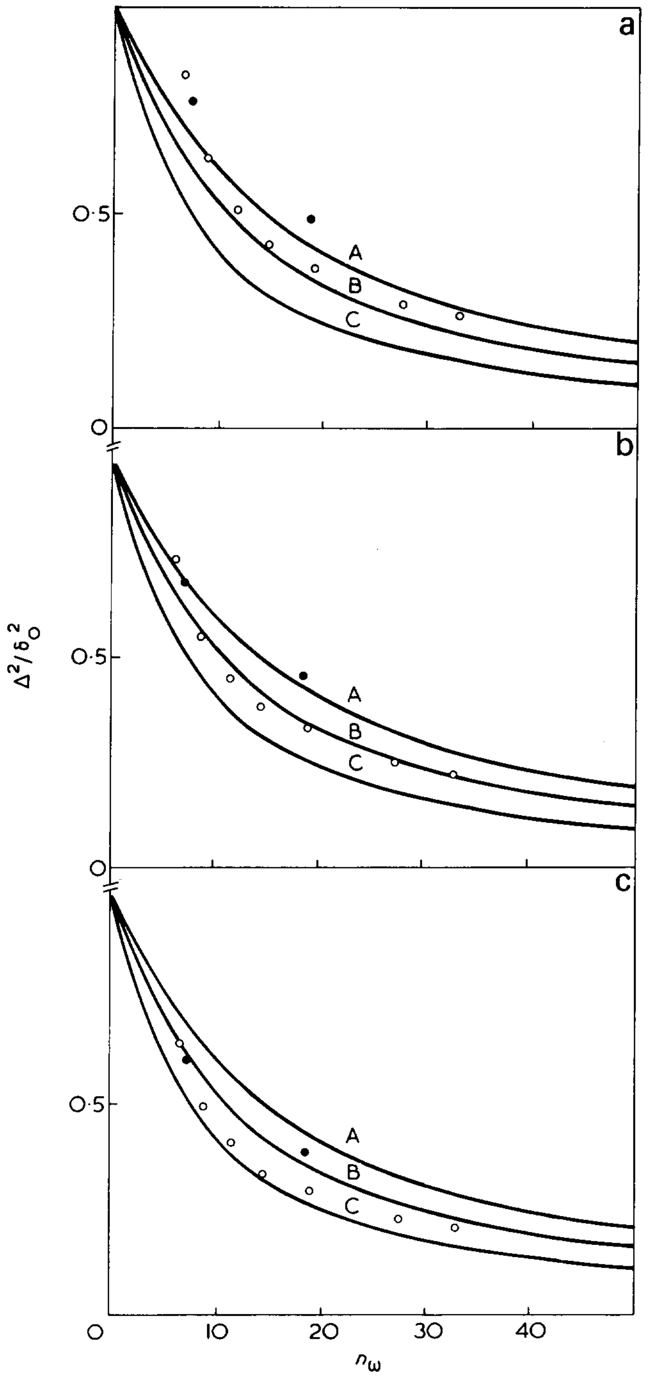


Figure 1 Optical anisotropy of aromatic polyamides as a function of the molecular weight. Experimental points have been normalized to slightly different values of the limiting anisotropy δ^2_0 and plotted on a family of theoretical curves, corresponding to different persistence lengths q (A, $q = 200$ Å; B, $q = 150$ Å; C, $q = 100$ Å) according to relation (8) (●, raw polymer; ○, fractions); (a) $\delta^2_0 = 0.35$; (b) $\delta^2_0 = 0.40$; (c) $\delta^2_0 = 0.45$. n_w is the weight-average number of elements in the chain

CONCLUSION

These results show clearly the relevance of the optical anisotropy as obtained from light scattering in the study of semi-flexible polymers. Due to the fact that it varies in a way similar to the ratio of the mean square end-to-end distance to the square of the contour length, but with an apparent persistence length three times smaller, the method applies in a range of molecular weight where radii of gyration cannot be obtained by light scattering.

REFERENCES

1 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971, Ch 2, 9
2 Weill, G. *Ann. Phys.* 1961, 6, 1063
3 Benoit, H. *C.R. Acad. Sci.* 1953, **236**, 687
4 Kratky, O. and Porod, G. *Rec. Trav. Chim.* 1949, **68**, 1166
5 Saito, N., Takahashi, K. and Yunoki, Y. *J. Phys. Soc. Japan* 1967, **22**, 217
6 Benoit, H. and Doty, P. *J. Phys. Chem.* 1953, **57**, 938
7 Arpin, M. and Strazielle, C. *Makromol. Chem.* 1976, **177**, 581
8 Arpin, M. and Strazielle, C. *Makromol. Chem.* 1976. **177**. 585
9 Arpin, M. *Thesis* Strasbourg (1976)
10 Northolt, M. G. and Van Aartsen, J. J. *J. Polym. Sci. (Polym. Lett. Edn)* 1973, **11**, 333