

EFFECT OF SOLVENT IN THE EVALUATION OF THE EXPERIMENTAL DATA ON THE FLOW BIREFRINGENCE OF POLYMER SOLUTIONS

J.KOVÁŘ, I.FORTELNÝ and M.BOHDANECKÝ

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

Received April 10th, 1972

Calculations of the flow birefringence of a solution of an anisotropic low-molecular weight compound in an isotropic solvent have shown that the method of evaluation of the birefringence data used so far will not give the anisotropy of intrinsic molecular polarizability but a quantity which also contains terms depending on the geometrical shape of the molecule of the dissolved compound and on the polarizability of the molecule of the solvent. It is probable that this factor also plays a role in polymer solutions and contributes to the so far unexplained influence of the solvent on the birefringence properties of these systems.

The magnitude of the flow birefringence of polymer solutions is influenced by the hydrodynamic, thermodynamic, and optical properties of the system. The relationships used for the evaluation of the experimental data have been derived on the basis of theories neglecting some possible physical phenomena. In these theories there appear frictional and conformational properties of the polymer molecule, excluded volume and the optical interaction between the distant and adjacent parts of the polymer chain; however, the solvent is regarded as a continuum.

Such an approach has as its consequence that the theory does not in any way include the distribution of the solvent molecules in the vicinity of the polymer chain. Although such simplifications were roughly warranted by an agreement between theory and experiment, a gradual extension and deepening of the experimental material led to the discovery of such effects of the solvent which could not be explained satisfactorily in terms of the existing theories. According to some authors¹⁻¹², the main cause of the effect of the molecular character of the solvent lies in the orientation of solvent molecules near the polymer chain. These authors have arrived at a conclusion that the existing relationships used for interpretation can be employed only for those solvents in which the orientational effects cannot appear, that is, in the solvents with geometrically and optically isotropic molecules.

It has been an aim of this paper to show theoretically that the effect of the optically and geometrically isotropic molecules of the solvent should also be taken into account when interpreting the flow birefringence measurements. This effect has not as yet been investigated theoretically.

THEORETICAL

Our conception of the effect of the solvent on the flow birefringence of polymer solutions is based in Kirkwood's¹³ approach to the calculation of the polarizability of nonpolar dielectrics. This approach was also used by Čopič¹⁴ and Koyama^{15,16}, who however took into account only the mutual optical interaction of the individual parts of the polymer chain. We shall show here that the optical interaction of the solvent molecules with the polymer must also be borne in mind, even in the case of a solvent with geometrically and optically isotropic molecules. This is given by the fact that parts of the polymer chain (segments) are generally geometrically anisotropic. This leads to an anisotropy of the distribution of positions of the solvent molecules with respect to the geometrical centre of the part of the polymer chain under consideration. Then the dipoles on the solvent molecules induced by the light wave form in this centre an additional field not described by the Lorenz-Lorentz field. Such effect of the solvent can also be shown for solutions of low-molecular weight compounds with geometrically and optically anisotropic and nonpolar molecules, in a solvent consisting of optically isotropic spherical molecules. The solution is simpler than for polymer solutions and quite sufficient for qualitative illustration. This system is considered further in this paper. The problem will also be simplified by regarding the molecules of the dissolved compound as having the form of a rotational ellipsoid, and assuming that the main axes of the tensor of the polarizability of the molecule are identical with the geometrical ones.

A component notation of tensors and Einstein's summation symbolics are used throughout this paper. All calculations are carried out in the CGS system.

From a relationship for intrinsic birefringence used by Nagai¹⁷ we have:

$$\Gamma = \frac{135nkT}{2\pi(n^2 + 2)^2 (f_{zz} - f_{xx}) N_p} \lim_{G \rightarrow 0} \frac{n_{\parallel} - n_{\perp}}{G}, \quad (1)$$

where Γ is the difference between the main polarizabilities of a molecule of the dissolved compound, if the effect of the solvent is absent, n is the refractive index of the solvent, f_{zz} and f_{xx} are main components of the tensor of the frictional moment of the molecule of the dissolved compound ($f_{xx} = f_{yy}$), N_p is the number of molecules of the dissolved compound in 1 cm³ of solution at infinite dilution, G is the only one non-zero component of the tensor of the velocity gradient for the plane simple shear in a system connected with the flow x' , y' , z' ($G = G_{x'y'}$), n_{\parallel} and n_{\perp} are refractive indexes of the solution in the direction of the optical axis of the solution and perpendicular to it. An infinitely dilute solution can be represented by a system where one molecule of the dissolved compound in a unit volume is surrounded by $N - 1$ solvent molecules. For such system it holds, after Buckingham and Raab¹⁸:

$$\frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2} - \frac{n_{\perp}^2 - 1}{n_{\perp}^2 + 2} = \frac{4\pi}{3} \overline{\Pi}(\tau, G), \quad (2)$$

where $\overline{\Pi}(\tau, G)$ is the mean value of $\Pi(\tau, G)$ defined as:

$$\begin{aligned} \Pi(\tau, G) &= \sum_{i=1}^N \Pi^{(i)}(\tau, G) \\ \Pi^{(i)}(\tau, G) &= \frac{\partial p_{\alpha}^{(i)}}{\partial E_{\beta}} (e_{\alpha}^{\parallel} e_{\beta}^{\parallel} - e_{\alpha}^{\perp} e_{\beta}^{\perp}), \end{aligned} \quad (3)$$

where $p_{\alpha}^{(i)}$ is the dipole moment of the i -th molecule, E_{α} is the electric vector of the incident light wave, e_{α}^{\parallel} and e_{α}^{\perp} are unit vectors in the directions of the measurement, τ denotes the configuration of the assembly of molecules under investigation. The change in the dipole moment of the molecule can be expressed by¹⁹:

$$\begin{aligned} \frac{\partial p_{\alpha}^{(1)}}{\partial E_{\beta}} &= a_{\alpha\gamma}^{(1)} \left(\delta_{\gamma\beta} + \frac{\partial F_{\gamma}^{(1)}}{\partial E_{\beta}} \right), \\ \frac{\partial p_{\alpha}^{(i)}}{\partial E_{\beta}} &= a^{(2)} \left(\delta_{\alpha\beta} + \frac{\partial F_{\alpha}^{(i)}}{\partial E_{\beta}} \right) \quad \text{for } i \neq 1, \end{aligned} \quad (4)$$

where $a_{\alpha\beta}^{(1)}$ and $a^{(2)}$ are polarizabilities of an anisotropic molecule of the dissolved compound and of an isotropic molecule of the solvent, $F_{\alpha}^{(i)}$ is the field in the centre of the i -th molecule due to the other molecules of the system, and $\delta_{\alpha\beta}$ is the unit tensor. In an approximation of the point dipoles it holds:

$$F_{\alpha}^{(i)} = \sum_{\substack{j=1 \\ j \neq i}}^N T_{\alpha\beta}^{(ij)} p_{\beta}^{(j)} = \sum_{\substack{j=1 \\ j \neq i}}^N \left(\frac{1}{r^{(ij)}} \right)^5 (3r_{\alpha}^{(ij)} r_{\beta}^{(ij)} - (r^{(ij)})^2 \delta_{\alpha\beta}) p_{\beta}^{(j)}, \quad (5)$$

where $r^{(ij)}$ is the distance of the centres of the i -th and j -th molecules. By substituting from Eq. (5) and (4) into Eq. (3) we obtain

$$\begin{aligned} \overline{\Pi}(\tau, G) &= (a_{\alpha\beta}^{(1)} + (N-1)a^{(2)} + 2a^{(2)}a_{\alpha\gamma}^{(1)}T_{\gamma\beta}^{(1)}) + \\ &+ (a^{(2)})^2 T_{\alpha\beta} + \dots (e_{\alpha}^{\parallel} e_{\beta}^{\parallel} - e_{\alpha}^{\perp} e_{\beta}^{\perp}), \end{aligned} \quad (6)$$

where

$$T_{\alpha\beta}^{(1)} = \sum_{i=2}^N T_{\alpha\beta}^{(1i)} = \sum_{i=2}^N T_{\alpha\beta}^{(i1)}, \quad T_{\alpha\beta} = \sum_{i=2}^N \sum_{\substack{j=2 \\ j \neq i}}^N T_{\alpha\beta}^{(ij)}.$$

Since $n_{\parallel} - n_{\perp}$ is very small compared to the refractive index of the solution, we obtain by rearrangement of Eq. (2):

$$\lim_{G \rightarrow 0} \frac{n_{\parallel} - n_{\perp}}{G} = \frac{2\pi(n^2 + 2)^2}{9n} \left(\frac{\partial \bar{\Pi}(\tau, G)}{\partial G} \right)_{G=0}. \quad (7)$$

To calculate $(\partial \bar{\Pi}(\tau, G)/\partial G)_{G=0}$ in Eq. (7), we shall use the distribution function of the molecules in the form:

$$\varrho(\tau, G) = \varrho_1(\tau_1, G) \varrho_2(\tau_2), \quad (8)$$

where τ_1 denotes the orientation of the anisotropic molecule with respect to the flow, and τ_2 determines the position of the molecules of the solvent. If we described the interaction of a molecule of the dissolved compound with the molecules of the solvent in flow in a purely hydrodynamic way, we could employ the Gotlib and Svetlov orientational distribution function²⁰:

$$\varrho_1 = 1 + \frac{Gf_{x'y'}}{2kT}, \quad (9)$$

where $f_{x'y'}$ is the component of the frictional moment of the molecule of the dissolved compound in a system connected with the flow. Formally it can be written

$$\varrho_1 = \exp(-U/kT), \quad \text{where } U = -kT \ln(1 + Gf_{x'y'}/2kT). \quad (10)$$

The calculation of $(\partial \bar{\Pi}(\tau, G)/\partial G)_{G=0}$ is based on the relationship

$$\frac{\partial \bar{\Pi}}{\partial G} = \frac{\partial}{\partial G} \left(\frac{\int \pi \exp(-U/kT) \varrho_2 \, d\tau}{\int \exp(-U/kT) \varrho_2 \, d\tau} \right). \quad (11)$$

By differentiating in Eq. (11) and limit transition for $G \rightarrow 0$ we get:

$$(\partial \bar{\Pi}/\partial G)_{G=0} = (1/kT) (\langle \Pi \rangle \langle \partial U/\partial G \rangle - \langle \Pi \partial U/\partial G \rangle),$$

where $\langle \rangle$ means averaging over $\varrho(\tau, 0)$. Since for $G = 0$ the directions e_{α}^{\parallel} and e_{α}^{\perp} are equivalent, it holds $\langle \Pi \rangle = 0$. Hence,

$$(\partial \bar{\Pi}/\partial G)_{G=0} = -(1/kT) \langle \Pi \partial U/\partial G \rangle. \quad (12)$$

Bearing in mind that for $G \rightarrow 0$ the angles of the directions of measurement with the x' axis are 45° and 135° and that $f_{\alpha\beta}$ is a symmetrical tensor, we obtain

$$(\partial U/\partial G)_{G=0} = -(1/4) f_{\alpha\beta} (e_{\alpha}^{\parallel} e_{\beta}^{\parallel} - e_{\alpha}^{\perp} e_{\beta}^{\perp}). \quad (13)$$

In Eq. (12) $(\partial U/\partial G)_{G=0}$ is substituted from Eq. (13) and Π is substituted by using Eq. (6); $(\partial \Pi/\partial G)_{G=0}$ is introduced into Eq. (7). The expression for $\lim_{G \rightarrow 0} ((n_{\parallel} - n_{\perp})/G)$ thus calculated is substituted into (1), which after algebraic rearrangement gives eventually

$$\Gamma = (a_{zz}^{(1)} - a_{xx}^{(1)}) + a^{(2)}(2a_{zz}^{(1)} + a_{xx}^{(1)}) \langle T_{zz}^{(1)} \rangle + (3/2)(a^{(2)})^2 \langle T_{zz} \rangle + \dots \quad (14)$$

if expressions $\langle T_{zz}^{(1)} \rangle = -2\langle T_{xx}^{(1)} \rangle$ and $\langle T_{zz} \rangle = -2\langle T_{xx} \rangle$ are used¹⁹.

DISCUSSION

We have demonstrated that an evaluation of the optical anisotropy of small anisotropic molecules of the dissolved compound based on the flow birefringence measurements will yield, even for a solvent with optically and geometrically isotropic molecules, Γ values which besides the own optical anisotropy of the molecule contain contributions caused by the solvent (second and third term in Eq. (14)). These contributions are due to the distribution anisotropy of the positions of the molecules of the solvent around the centre of the molecule of the dissolved compound. They disappear only for solvents with unpolarizable molecules ($a^{(2)} = 0$). Contrary to Fukuda and coworkers¹⁰, we believe that a contribution to Γ could be important even in the case of a solvent with optically and geometrically isotropic molecules. According to data given in a survey by Buckingham and co-authors¹⁹, remarkable differences were found between Kerr's and Mouton-Cotton's constants for benzene and carbon disulphide depending on whether they were determined from measurements in the gaseous phase or in solution, with tetrachloromethane as solvent. Kerr's constants determined in the gaseous phase were even twice as high as those in solvent. Buckingham and coworkers attribute these differences to the effect of the distribution of the positions of the solvent molecules with respect to the centre of the molecule of the dissolved compound.

Should a solvent with optically and geometrically anisotropic molecules be considered, the contribution of the solvent to Γ would of course also depend on the distribution of orientations of the solvent molecules. In the flow birefringence theory of polymer solutions it would be necessary, in order to include the effect of the solvent on the optical anisotropy of the polymer, to modify Nagai's relationship¹⁷:

$$\lim_{\substack{c \rightarrow 0 \\ G \rightarrow 0}} \frac{n_{\parallel} - n_{\perp}}{cG\eta_0} = \frac{\pi(n^2 + 2)^2}{135kTn\eta_0} \cdot (N/M) \langle 3\gamma_{\alpha\beta} f_{\beta\gamma} \delta_{\alpha\gamma} - \gamma_{\alpha\beta} \delta_{\alpha\beta} f_{\gamma\delta} \delta_{\gamma\delta} \rangle. \quad (15)$$

(c is the concentration of the solution, η_0 is the viscosity of the solvent, N is Avogadro's number and M is the molecular weight of the polymer), by replacing the momentary polarizability of the chain $\gamma_{\alpha\beta}$ by a total change of the dipole moment of the chain with respect to E_{α} , averaging not only over all conformations of the chain, but also over all mutual configurations of the solvent

molecules (including their orientations in a general case) and over the individual parts of the polymer chain. Such procedure would not necessitate to calculate the form effects^{14-16,21} (i.e. a mutual optical interaction of the individual parts of the polymer chain) by means of the so-called "excess anisotropy" as has been done up to now. Let it also be mentioned that in the preceding reasonings the possibility of influencing the anisotropies of the intrinsic polarizability of molecules by their own interactions has been neglected. In some cases, however, such neglecting can be problematic. Thus, for instance, even for tetrachloromethane, which is usually regarded as an inert compound, mixed enthalpies were found in the systems^{22,23} ethers- CCl_4 and polypropylene oxide- CCl_4 which indicated a specific interaction between the CCl_4 molecules and the ether oxygen. Such interaction can also be reflected in the optical polarizabilities of the interacting CCl_4 molecules and ether groups.

REFERENCES

1. Garmova T. I.: Vest. Leningrad. Univ. No 22, 72 (1962).
2. Frismanova E. V., Dadivanian A. K., Duzhev G. A.: Dokl. Akad. Nauk SSSR 153, 1062 (1963).
3. Frismanova E. V., Dadivanian A. K., Duzhev G. A., Kamenev U. G.: Ukrain. Fiz. Ž. 9, 521 (1964).
4. Frismanova E. V., Dadivanian A. K.: J. Polym. Sci. C16, 1001 (1967).
5. Frismanova E. V., Dadivanian A. K.: Vysokomolekularnyje Sojedinenija 8, 1359 (1966).
6. Penzel E., Debeauvais F., Gramain P., Benoît H.: J. Chim. Phys. 67, 471 (1970).
7. Gent A. N.: Macromolecules 2, 262 (1969).
8. Gent A. N.: Rubber Chem. Technol. 43, 829 (1970).
9. Gent A. N., Kuan T. H.: J. Polym. Sci. A2, 9, 927 (1971).
10. Fukuda M., Wilkes G. L., Stein R. S.: J. Polym. Sci. A2, 9, 1417 (1971).
11. Nagai K.: J. Chem. Phys. 47, 4690 (1967).
12. Nagai K.: J. Phys. Chem. 74, 3422 (1970).
13. Kirkwood J. G.: J. Chem. Phys. 4, 592 (1936).
14. Čopič M.: J. Chem. Phys. 26, 1382 (1957).
15. Koyama R.: J. Phys. Soc. Japan 16, 1366 (1961).
16. Koyama R.: J. Phys. Soc. Japan 19, 1709 (1964).
17. Nagai K.: J. Phys. Chem. 74, 3411 (1970).
18. Buckingham A. D., Raab R. E.: J. Chem. Soc. 1957, 2341.
19. Buckingham A. D., Stiles P. J., Ritchie G. L. D.: Trans. Faraday Soc. 67, 577 (1971).
20. Gotlib Yu. Ya., Svetlov Yu. E.: Vysokomolekularnyje Sojedinenija 8, 1517 (1966).
21. Cvetkov V. N. in the book: *Newer Methods of Polymer Characterisation*. (Bacon Ke, Ed.). Interscience, London 1964.
22. Beath L. A., Williamson A. G.: J. Chem. Thermodynam. 1, 51 (1969).
23. Kershaw R. W., Malcolm G. N.: Trans. Faraday Soc. 64, 323 (1968).

Translated by L. Kopecká.