Analysis of the Theoretical Methods of Calculations of Ideal Fiber Birefringences

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Synopsis

Based on the equation carried out previously, theoretical birefringence has been calculated for selected synthetic fibers, taking into account intermolecular interactions. The calculation has been carried out using bond polarizabilities given by Denbigh [*Trans. Faraday Soc.*, **36**, 936 (1940)] and Pietralla [*J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1117 (1984); **20**, 1193 (1982)]. Large discrepancies of Δn_{id} for polyamides between theoretical and experimental values have been found. The necessity for elaborating a new method of birefringence calculations has been pointed out.

INTRODUCTION

Fibers belong to the group of optically anisotropic solids. Quantitatively, the anisotropy of a birefringent body is characterized by the value of optical birefringence. This quantity is defined as a difference between refractive indexes by means of the following equation:

$$\Delta n \cong \varphi = n_\parallel - n_\perp \qquad (1)$$

where $n_\parallel$ = refractive index for a flat polarized light wave in which the vector of electric field vibrates in the plane parallel to the fiber axis and $n_\perp$ = refractive index for a flat polarized light wave in which the vector of electric field vibrates in the plane perpendicular to the fiber axis. Practically the index of optical birefringence for fibers is determined using both interference[1] and immersion[2] methods. Found value of birefringence is the base for general assessment of internal orientation (f_0) of the fiber (the Hermans–Platzek equation).[3] Moreover, it is necessary to know the value of birefringence for ideal crystalline fiber in order to determine the exact value of (f_0). Birefringence of such a fiber, Δn_{id}, can be determined experimentally[4] or analitically.[5] The values of Δn_{id}, which have been determined experimentally are usually found based on Stein's equation using data from the sonic method[7]:

$$\Delta n = \Delta n_c^0 \, f_c + \Delta n_a^0 \, (1 - \beta) \, f_a \qquad (2)$$

where Δn_c^0 = birefringence of ideal crystalline fiber, Δn_a^0 = birefringence of ideal amorphous fiber, β = degree of crystallinity of the fiber, f_c = orientation of crystalline regions, and f_a = orientation of amorphous regions. Application of the experimental method obliges us to know some

parameters of fine structure of the fiber, assessment of which is often complicated and unequivocal.[8] This can be the reason for significant discrepancies in the final Δn_{id} values. The analytical method of determination of the ideal fiber birefringence is based on the Lorentz–Lorenz equation.[9] This equation connects the average refractive index of the material with electric polarizability of its molecules. However, this method of Δn_{id} assessment arouses reservations because of the fact that the Lorentz–Lorenz equation refers only to the crystalline structure with regular symmetry. Most fiber-forming polymers crystallize in crystallographic systems which differs considerably from the regular one. The birefringence value found by means of this method refers to an fictitious polymer monocrystal in which there do not occur any intermolecular interactions.

In the works[10] it has been tried to assess Δn_{id} analytically for selected synthetic fibers, taking into account intermolecular interactions that were omitted in the Lorentz–Lorenz equation. In this article it is intended to carry out a comparative analysis of the theoretical methods and the obtained values of ideal fibers birefringences.

THEORY

Analitical method used so far for determination of birefringence of the ideal fiber has been based on the Lorentz–Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha \tag{3}$$

where N = number of molecules in a volume unit, α = average polarizability of the molecules, and n = refractive index. Macromolecules of the polymers can be treated approximately as axially symmetric ones. Hence, two polarizability values are prescribed to them: $\alpha_\parallel$ = polarizability in direction of the macromolecule axis and $\alpha_\perp$ = average polarizability in direction perpendicular to the macromolecule axis. $\alpha_\parallel$ and $\alpha_\perp$ values for polymer can be determined based on the structure of the macromolecule chain and polarizability of bonds, from the following equations:

$$\begin{aligned}
\alpha_\parallel &= \left(\sum_{i=1}^{n} a_{zi}\right) = \sum_{i=1}^{n} [(a_{\parallel i} - a_{\perp i}) \cos^2 \varphi_i + a_{\perp i}] \\
\alpha_\perp &= \left(\sum_{i=1}^{n} a_{pi}\right) = \sum_{i=1}^{n} (a_{\parallel i} + 2a_{\perp i} - a_{zi})
\end{aligned} \tag{4}$$

where $a_{\parallel i}$ = polarizability of ith bond in direction of its axis, $a_{\perp i}$ = polarizability of ith bond in direction perpendicular to its axis, a_{zi} = polarizability of ith bond in direction perpendicular to the axis of macromolecule, a_{pi} = polarizability of ith bond in direction perpendicular to the macromolecule axis, and φ_i = angle between axis of the ith bond and that of the macromolecule. Refractive indexes $n_\parallel$ and $n_\perp$ and birefringence $\Delta n = n_\parallel - n_\perp$, calculated in this way are not precise because of the fact that the internal interactions have been omitted. Now the method of birefringence calculation,[10] taking into account these interactions, takes advantage of a modified form of the Lorentz–Lorenz equation. A new form of this equation has been obtained after the calculation of the local electric field $\vec{E}_{loc}$, which acts on a macromolecule of the polymer being in a certain external electric field.

In Refs. 10 the method of $\vec{E}_{loc}$ calculation has been presented, assuming a certain simplified model of the macromolecule chain. The most important was an assumption that the chains of macromolecules are homogeneous with respect to their polarizability on a whole length. This assumption simplifies considerably the calculations of an electric field generated by such a macromolecule and makes it possible to obtain the general expressions that can be used for various types of polymers.

Calculations of the electric field $\vec{E}$ due to a macromolecule may be also carried out by simple summing of the fields originated from all point-dipols contained in it. However, this way would be very complicated, particulary in the case of macromolecules that comprise several types of dipols. Besides, even though it may be possible to obtain by this way the field generated by one macromolecule, determination of the local field $\vec{E}_{loc}$, which is the sum of the fields originated from all macromolecules, would not be possible because of very complicated calculations.

Therefore, it seems that the only way of estimating the local field $\vec{E}_{loc}$ is application of the simplified macromolecule model. However, it should be emphasized that the resulting $\vec{E}_{loc}$ calculated by this method will be only the first approximation of its real value. The consequence of above-mentioned assumption is an introduction of the term "average polarizability per length unit." This value can be determined basing on the polarizabilities of bonds existing in the monomer unit of considered polymer. Using eqs. (4) one can calculate the values of $a_{\parallel}$ and $a_{\perp}$ for the monomer unit, and then the average polarizabilities per length unit, according to equations

$$\alpha'_{\perp} = \alpha_{\perp}/L, \quad \alpha'_{\parallel} = \alpha_{\parallel}/L \tag{5}$$

where L = length of the monomer unit.[10] Based on the above-mentioned assumptions $\vec{E}_{loc}$ has been determined as a function of average macroscopic field $\vec{E}$ existing in the volume of the polymer. This allowed us to link directly the average dipole moment induced in a length unit of the macromolecule with the field $\vec{E}$. The factor linking these two quantities is the so-called tensor of effective polarizability $[a']$,

$$\vec{m} = [a']\vec{E} \tag{6}$$

Based on (6), the polarization vector of the polymer $\vec{P}$ can be determined, which is equal to the dipole moment per volume unit accordingly to its definition. After determination the polarization vector $\vec{P}$ it is possible to calculate refractive indexes and birefringence of the polymer. It is enough to use the relationships:

$$n_i^2 = 1 + 4\pi\frac{P_i}{E_i} \tag{7}$$

and

$$\Delta n_{id} = n_z - \left(\frac{n_x + n_y}{2}\right) \tag{8}$$

Calculations described above can be realized for any type of polymer by means of the computer program in FORTRAN IV. The program is available from the authors on request. The presented method of calculations of ideal fiber birefringence is based on assumptions which simplify the model of fiber fine structure. Particulary it refers to the assumption that the chains of macromolecules are homogenous with respect to their polarizability on a whole length. In this connection, the results obtained by means of this method will be only approximations of the real values of Δn_{id}. It seems, however, that such an approximation will be closer to the correct reality than those determined with the methods used till now.[5,11]

The necessery condition for reliability of the obtained results is knowledge of the real values of bonds polarizabilities existing in polymer macromolecules. Pietralla[12,13] has presented another method of polymer birefringence determination in which, besides the intermolecular interactions, the intramolecular interactions have been taken into account. However, applicability of the proposed routine is limited exclusively to the polymers with the macromolecules, which contain only one type of dipole. In the case of more complicated macromolecules, comprising several types of dipoles, the relationships derived by Pietralla cannot be employed. For this reason, actually, the method of Pietralla can be used only for polyethylene.

RESULTS AND DISCUSSION

The fundamental condition necessery for obtaining the correct birefringence values by means of the method described above is knowledge of the real values of bond polarizabilities existing in macromolecule. In the literature one can find several sets of polarizabilities data, however, the most frequently employed are the data determined by Bunn[14] and Denbigh.[15] The values of bond polarizabilities given by Bunn are inadequate to the method used in this work. They have been calculated basing on the measurements of refractive indexes of polymer crystals ($C_{17}H_{34}$). In this calculation the intermolecular interactions have not been taken into account. Data of Denbigh have been obtained from the measurements of n-paraffins in gaseous state, where the intermolecular interactions can be neglected; for this reason, employment of this data in our calculation is justifiable. The set of Denbigh's data has been used to calculate birefringence of several ideal polymer fibers. For comparison, the birefringence values of this fiber obtained by extrapolation of experimental data are listed too in Table I. The-

TABLE I

No.	Polymer	$\Delta n_{id} \times 10^3$ (theoretical)	$\Delta n_{id} \times 10^3$ (experimental)
1	Polyamide 6	286.4	72,[2] 73,[11] 78[16]
2	Polyamide 6-6	312.9	60,[17] 55[18]
3	Polyamide 6-10	254.0	65,[17]
4	Polyester	236.0	240,[2] 38[19]
5	Polypropylene	63.5	45,[2] 44[18]
6	Polyoxymethylene	34.6	—
7	Polyacrylonitrile	−42.9	—

oretical values of birefringence presented in Table I have been obtained assumming the range of intermolecular interactions (radius of Lorentz sphere) equal to 20 lattice constants. One checkup that the influence of macromolecules lying beyond this range is omittable. From the data presented in Table I it follows good concurence of theoretical and experimental results for polyester and polypropylen.

However, large discrepancies occur in the case of polyamide. The monomer units of PA 6, PA 6-6, and PA 6-10 contains respectively 10, 10, and 14 methyl groups CH_2. It seems that the incorrect values of methyl group polarizabilities: $a_\parallel$ and $a_\perp$ could be one of the reasons of this divergence. Similar doubts in relation to the correctness of Denbigh's data of CH_2-group polarizability has been presented by Keedy et al.[5] Therefore, it will be also impossible to obtain the correct birefringence value for polyethylene using methyl group polarizabilities given by Denbigh.[15]

The values of the anizotropy of polarizability of methylene group were determined by many authors.[20-23] The most important works connected with this problem were presented by Stein with co-authors and by Pietralla.[12] In Ref. 24 the value of the effective anizotropy of the CH_2 group was obtained by using the refractive indexes of n-paraffin crystals given by Bunn and Daubeny.[14] The calculations were carried out taking into account the intermolecular interactions. The internal field that acts on a given macromolecule was determined by summation of the dipolar fields generated by all macromolecular chains contained in the n-paraffin crystal.

However, for the reason of omission of the intramolecular interactions (the interactions between the bonds in the same chain), the obtained value of methylene group polarizability should not be considered as the value for an isolated CH_2-group, but rather those of a CH_2 group subject to the interaction of the rest of the n-paraffin macromolecule. Therefore, the value cannot be used for calculations of birefringence for other polymers. Taking it into account, the recalculations of polyamide birefringences have been carried out, employing data of CH_2-group polarizabilities given by Pietralla.[12] It seems that the data of Pietralla[12] are the most reliable of all others because they have been obtained including as well intermolecular as intramolecular interactions. Pietralla has carried out his calculations using the refractive indexes values of $C_{36}H_{74}$ monocrystal given by Bunn and Daubeny.[14] Results of birefringence recalculations for polyamide-6 and polyamide 6-6 are listed in Table II.

As can be seen, the results differ from reality much more than in the case of employing the Denbing's data. This shows that the polarizability values given by Pietralla cannot be used in the methods, which does not include the intramolecular interactions. The most reliable birefringence values of ideal fibers could be obtained after elaborating the method that, as the routine of Pietralla used for polyethylene, should include both in-

TABLE II

No.	Polymer	$n_\parallel$	$n_\perp$	Δn_{id}
1	Polyamide 6	1.64955	1.51717	+ 0.13238
2	Polyamide 6-6	1.60697	1.57160	+ 0.03537

termolecular and intramolecular interactions, but also in the case of polymere with macromolecules composed of several types of dipoles. The method presented above, for its universality could be the initial basis for construction of such a theory.

In this method, the intramolecular interactions should be taken into account—without changing the undertaken assumption about the structure of macromolecular chains.[10] Furthermore, the bonds polarizabilities values used in calculations should be determined in the same way that Pietralla have adopted for methylen group CH_2.[12]

References

1. N. Barakat and A. Hindeleh, *Text. Res. J.,* **34,** 581 (1964); A. N. J. Heyn, *Fiber Microscopy,* Wiley-Interscience, New York, 1954; T. Żyliński and J. Godek, *Zeszyty Naukowe P. Ł. Włókiennictwo,* **1,** 21 (1954); G. W. Urbańczyk, *Zeszyty Naukowe P. Ł. Włókiennictwo,* **7,** 141 (1961).

2. H. de Vries, *Text. Res. J.,* **22,** 619 (1952); J. H. Mclean, *Text. Res. J.,* **35,** 242 (1965); G. W. Urbańczyk, *Fizyka Włókna, WNT,* Warsaw, 1970, pp. 309–327; H. De Vries, *Coll. Polym. Sci.,* **257,** 226 (1979).

3. P. H. Hermans and P. Platzek, *Kolloid Z.,* **88,** 68 (1939).

4. C. W. Bunn and E. V. Garner, *Proc. R. Soc. London,* **A189,** 39 (1947); K. Fujimo, H. Kawai, T. Horino, and K. Miyamoto, *Text. Res. J.,* **26,** 825 (1956); V. B. Gupta and S. Kumar, *J. Polym. Sci., Polym. Phys. Ed.,* **17,** 1307 (1979); E. Balcerzyk, E. Wesołowska, and W. Lewaszkiewicz, *J. Appl. Polym. Sci.* **26,** 2573 (1981).

5. C. W. Bunn and R. Daubeny, *Trans. Faraday Soc.,* **50,** 1173 (1954); D. A. Keedy, J. Powers, and R. Stein, *J. Appl. Phys.,* **31,** 1911 (1960).

6. R. S. Stein and F. H. Noris, *J. Polym. Sci.,* **21,** 381 (1956).

7. H. M. Morgan, *Text. Res. J.,* **32,** 866 (1962); W. W. Moseley, Jr., *J. Appl. Polym. Sci.,* **3,** 266 (1960).

8. A. Włochowicz and M. Kramer, Polim., *tw. Wielkocząsteczkowe (Poland),* **25,** 65 (1980).

9. G. Kittel, *Introduction to Solid State Physics,* 4th ed., Wiley, New York, 1971.

10. A. Włochowicz, St. Rabiej, and J. Janicki, *Acta Polym.,* **33,** 117 (1982); A. Włochowicz, St. Rabiej, and J. Janicki, *J. Appl. Polym. Sci.* **28,** 1335 (1983).

11. G. W. Urbańczyk, *Zeszyty Naukowe P. Ł. Włókiennictwo,* **8,** 79 (1962); **23,** 31 (1959).

12. M. Pietralla, *J. Polym. Sci., Polym. Phys. Ed.,* **18,** 1117 (1980).

13. M. Pietralla, H. P. Grossmann, and J. K. Krüger, *J. Poly. Sci., Polym. Phys. Ed.,* **20,** 1193 (1982).

14. C. W. Bunn and P. Daubeny, *Trans. Faraday Soc.,* **50,** 1173 (1954); P. Daubeny, C. W. Bunn, and C. J. Brown, *Proc. R. Soc. London* **226A,** 531 (1954).

15. K. Denbigh, *Trans. Faraday Soc.,* **36,** 936 (1940).

16. T. Kunugi, S. Yokokura, and M. Hashimoto, *Nippon Kagaku Kaishi,* **21,** 125 (1976).

17. C. W. Bunn and E. V. Garner, *Proc. R. Soc. London,* **189A,** 39 (1947).

18. F. J. Padden and H. D. Keith, *J. Appl. Phys.,* **30,** 1479 (1959).

19. W. Wiśniewska, private communication.

20. R. I. Volungis and R. S. Stein, *J. Chem. Phys.,* **23,** 1179 (1955).

21. D. W. Sannders, *Trans. Faraday Soc.,* **52,** 1425 (1965).

22. D. W. Sannders, D. R. Lightfoot, and D. A. Parsons, *J. Polym. Sci. A-2,* **6,** 1183 (1968).

23. R. J. Samuels, *J. Polym. Sci.,* **3A,** 1741 (1965); *ibid. A-2,* **6,** 1101 (1968).

24. S. D. Hong, C. Chang, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.,* **13,** 1447 (1975).