Stress-Induced Birefringence of Swollen Polymer Networks

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ABSTRACT: Stress–optical coefficients have been determined for lightly cross-linked samples of *cis*- and *trans*-polyisoprene, swollen to a high degree in a variety of nonpolar solvents. A strong dependence on the geometrical asymmetry of the solvent molecule has been observed. Solvents with long straight molecules gave large values of the stress–optical coefficient whereas those with compact symmetrical molecules gave minimum values. This effect is attributed to short-range orientational order, due to packing effects in a molecularly anisotropic medium. The large values obtained for unswollen polymers correspond to those in relatively anisotropic solvents, and thus indicate a significant degree of local order in the bulk phase. The minimum values are interpreted using calculated optical anisotropies of chain repeat units as measures of the stiffness of isolated chains.

There is a close parallel between theoretical treatments of the optical and elastic properties of a simple network of Gaussian chains. The difference Δn in the refractive indices in the direction of a deformation and at right angles to it is predicted to be directly proportional to the difference Δt in the corresponding true stresses.[1] For a simple tensile stress t, the ratio $\Delta n/t$, denoted the stress–optical coefficient C, is given by eq 1, where k is Boltzmann's constant, T

$$C = (2\pi/45kT)[(\bar{n}^2 + 2)^2/\bar{n}]\alpha \qquad (1)$$

is the absolute temperature, and $\bar{n}$ is the mean refractive index. If it is assumed that the real molecular chain may be represented both optically and elastically by a statistically equivalent chain of freely jointed rigid links, α is the optical anisotropy, *i.e.*, the difference in polarizability in the chain direction and at right angles to it, for one of the links. The value of α may be determined experimentally by means of eq 1 from the measured stress–optical coefficient C. The ratio of α to the optical anisotropy β of a chain structural unit gives the number q of chain repeat units corresponding to one equivalent freely jointed link. This number provides an indication of chain stiffness.

Saunders[2–4] has carried out a detailed study of the photoelastic properties of networks of *cis*- and *trans*-polyisoprene and polyethylene. He deduced values for q of 2.24, 5.05, and 48.5, respectively, using the procedure given above. Volkenstein[5] has argued that the bond polarizabilities obtained by Bunn and Daubeny,[6] used by Saunders to compute the optical anisotropies β for the three chain repeat units, are not as likely to be correct as those obtained by Denbigh.[7] When Denbigh's values of bond polarizabilities are used to calculate the repeat unit anisotropies β, the values obtained for q from Saunders' photoelastic measurements are appreciably smaller—1.45, 2.8, and 10, respectively. Ranging from 4 to 11 carbon atoms along the molecular chain backbone, these values seem reasonable estimates of the size of an equivalent random link. Moreover, they are in generally satisfactory agreement with values obtained in other ways.

The magnitude of α and its variation with temperature may also be interpreted in terms of the more realistic model of a polymer chain in which a limited number of isomeric rotational states about carbon–carbon single bonds are permitted, with different sequences of bond conformations being assigned specific energy levels.[8–10] These energy levels are assumed to arise from steric effects between successive structural units along the chain and not from environmental effects of a more general nature. Indeed, values of the chain dimensions in dilute solution in Θ solvents are compared with those calculated on the basis of energy levels deduced from thermoelastic measurements on unswollen materials, with fairly good agreement.[11,12]

However, it has recently been found that the stress–optical coefficient C, and hence α, for an amorphous polyethylene network is much smaller in the swollen state than in the unswollen state.[13] The theoretical treatment of photoelasticity in terms of a network of equivalent freely jointed chains predicts no direct effect of swelling (other than that due to a change, if any, in the mean refractive index $\bar{n}$), because both the true stress and the optical anisotropy are predicted to change by the same factor.[1] Thus the observed decrease in α points to a decrease in effective stiffness of the chain on swelling, or, equivalently, to a change in conformational energy levels on swelling.

In order to investigate this effect more thoroughly, measurements have been carried out of the stress–optical coefficient for lightly cross-linked samples of *cis*- and *trans*-polyisoprene, swollen in a large number of nonpolar liquids. The experimental details are given in the following section and the results in a final section of the paper.

Tsvetkov and his colleagues have carried out an ex-

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tensive series of investigations into the effect of solvents on the stress–optical coefficient of swollen networks and the flow-induced birefringence of polymer solutions.[14–19] A summary of this work by Tsvetkov and Grishchenko has recently appeared.[20] Their conclusions are rather different from those reached here; they attribute the action of solvents entirely to internal field effects, arising from the difference in refractive indices, and hence polarizabilities, of the solvent and polymer and the anisotropic shape of the polymer molecule and its constituent segments. The reasons for regarding internal field effects (at least, of the kind treated by Tsvetkov, *et al.*) as of minor importance in the present work are given in the discussion which follows the presentation of experimental results.

Frisman and his colleagues have also studied the effect of solvents on the flow-induced birefringence of polymer solutions.[21–25] They concluded that short-range orientational order occurs with anisotropic solvent molecules.[24,25] A similar conclusion was reached by Nagai,[26] from an examination of the effect of solvents upon the optical anisotropies of *n*-alkanes reported by Clément and Bothorel.[27] It thus appears that local ordering exists among geometrically asymmetric molecules in a condensed phase and can give rise to abnormally large optical anisotropies. Further evidence for this in polymeric materials, both in the bulk state and as highly swollen gels, is provided by the work described below.

Experimental Section

A sample of synthetic *trans*-polyisoprene was kindly provided by Dr. E. G. Lovering of Polymer Corp., Sarnia, Canada. It was of high molecular weight, about 3×10^5, and substantially 100% *trans*. The *cis*-polyisoprene was pale crepe plantation rubber. Dicumyl peroxide (1% w/w) was mixed into both materials on a warm mill. The mixtures were then molded into thin sheets and cross-linked by heating them for 60 min at 150°. Test pieces were cut from the cross-linked sheets in the form of parallel-sided strips about 10 cm long, 0.6 cm wide, and 0.1 cm thick. They were suspended vertically in a thermostated bath containing water for measurements in the unswollen state and containing a swelling liquid for measurements in the swollen state. They were allowed to swell to equilibrium in the latter case before the stress–optical measurements were carried out.

The test strips were stretched by weights applied by means of a pulley arrangement. The corresponding extensions were measured by observing the separation of bench marks on the sample. The optical path differences through the sample for light components in the vertical and horizontal planes were determined as described by Treloar,[1] using a Babinet compensator and a beam of light from a sodium lamp, polarized at 45° to the direction of extension. The difference in the refractive indices Δn was found to be proportional to the true stress t in all cases, and the stress–optical coefficient C was obtained as the slope of the experimental relation between them.

The measurements were carried out quite rapidly on the swollen test pieces to minimize any increase in swelling due to extension. A series of eight to ten measurements on a single test piece, using increasing and decreasing tensile loads, was generally completed in about 10 min. As the samples were highly elastic no significant changes in extension or birefringence took place with time under a constant load, at least during times ranging from a few seconds to 2 min.

Owing to the limited extensibility of highly swollen materials, the maximum extension employed was quite small, about 25%, and the measured values of C were therefore somewhat imprecise due mainly to inaccuracies in determining t. Measurements were generally carried out on duplicate test pieces; the results differed by about 4% on the average.

Measurements were made at a temperature of 30°, or at 75° for swelling liquids with melting temperatures above 30°. The results in the latter case were corrected to a temperature of 30° assuming the theoretical dependence on temperature, eq 1, to hold. The refractive index of both polymers at 30° was taken as 1.520 from data given by Saunders.[2] Values of the refractive index for each solvent were taken from the literature. They were adjusted to apply at a temperature T of 30° using the approximate relation

$$(n - 1)_{T_0} = (n - 1)_T[1 + \gamma(T - T_0)]$$

where T_0 represents the temperature of measurement and γ is the coefficient of volume expansion, taken as 6.7×10^{-4} deg^{-1}. Values obtained in this way are listed in Table I. The mean refractive index $\bar{n}$ of the swollen materials was then calculated as a simple volume average of the refractive indices of the swelling liquid and the polymer, using the measured swelling ratio Q, *i.e.*, the ratio of the swollen to the unswollen volume of the polymer.

Results and Discussion

Experimentally determined values of the stress–optical coefficient C and corresponding values of the optical anisotropy α of the equivalent freely jointed link, calculated from them by means of eq 1, are given in Table I. These results are arranged in order of increasing values of α. Substantial differences were found for the different swelling liquids, covering a range of about 2:1 in α for each polymer. The lowest values were lower than those for the unswollen materials, as found previously for polyethylene,[13] but some swelling agents brought about an increase in the optical anisotropy. This was particularly evident for the *cis*-polyisoprene material.

Several possible correlations are now considered between properties of the swelling liquid and its effect on the observed optical anisotropy. It should first be remarked, however, that the swollen gels did differ principally in their optical anisotropy Δn at a given degree of extension and not in the tensile stress t.

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TABLE I

STRESS–OPTICAL COEFFICIENTS C AND OPTICAL ANISOTROPIES α FOR SWOLLEN MATERIALS

Swelling liquid	n	$\Delta b \times 10^{24}$, cm^3	Q	$C \times 10^4$, cm^2/kg	$\alpha \times 10^{24}$, cm^3
		cis-Polyisoprene Vulcanizate			
Benzene	1.498	1.8	6.0	1.55	3.85
Carbon disulfide	1.624	9.6	6.1	1.75	4.05
Carbon tetrachloride	1.458	0	7.8	1.60	4.15
Toluene	1.494	3.0	6.7	1.75	4.45
None	1.520		1.0	1.90	4.80
n-Decane	1.406		4.6	1.85	4.95
p-Xylene	1.492	1.7	6.1	2.15	5.40
p-Dichlorobenzene	1.538	8.3	7.3	2.45	6.05
Biphenyl	1.604	3.8	4.3	2.75	6.45
		trans-Polyisoprene Vulcanizate			
Decalin	1.476		6.5	2.25	5.75
Cyclopentane	1.404		6.0	2.20	5.85
Carbon tetrachloride	1.458	0	8.1	2.25	5.85
Carbon disulfide	1.624	9.6	7.2	2.55	5.95
Chloroform	1.442	2.3	8.0	2.60	6.85
Benzene	1.498	1.8	6.9	2.85	7.25
Toluene	1.494	3.0	6.0	3.10	7.85
n-Decane	1.406		3.6	3.10	8.20
Hexane	1.372		4.4	3.15	8.55
p-Dichlorobenzene	1.538	8.3	6.1	3.50	8.65
None	1.520		1.0	3.75	9.35
p-Xylene	1.492	1.7	7.5	3.90	9.95
Biphenyl	1.604	3.8	5.7	4.25	10.05

Values of the tensile stress corrected in accordance with the kinetic theory of elasticity[1] for differences in temperature T and degree of swelling Q, $tQ^{1/3}/T$, were determined for each swollen gel at an extension of 20%. They were found to lie within ±10% of the mean value for each polymer and to show no discernible correlation with the magnitude of the stress–optical coefficient. The principal difference between the various swelling agents was thus their effect on the optical, rather than on the elastic, properties of the networks. Possible causes of this solvent effect are (i) an effect of swelling *per se;* (ii) internal field effects, as considered by Tsvetkov, *et al.*,[14–20] due to differences in polarizability of polymer and swelling liquid; (iii) more subtle internal field effects due to differences in anisotropy of polarizability of the various swelling liquids; and (iv) geometrical effects due to anisotropy of *shape* of the liquid molecules, as proposed by Nagai[26] to account for solvent effects on the optical anisotropy of *n*-alkanes observed by Clément and Bothorel,[27] and by Frisman and Dadivanyan[24,25] to account for similar effects in their studies of flow-birefringence in polymer solutions.

The first possibility can be dismissed immediately; there is clearly no correlation between the degree of swelling Q and the optical anisotropy α for the swelling liquids used in the present experiments. The second process has been treated both theoretically and experimentally by Tsvetkov.[14] He related the change in optical anisotropy on swelling to the square of the refractive index difference between polymer and swelling liquid. It is thus always a positive contribution. Indeed, a reduction in stress-optical coefficient was observed by Tsvetkov and Grishchenko[19,20] in one case only—a polydimethylsiloxane material swollen by carbon tetrachloride. They attributed this "anomalous effect" to a specific influence of the solvent upon the optical anisotropy. Internal field effects of the kind treated by Tsvetkov do not seem to be a major factor in the present experiments for two reasons: many of the present swelling agents cause a *reduction* in the optical anisotropy, and there is no correlation between the value obtained for α and the difference in refractive index between polymer and swelling liquid (Table I). The third possibility given above also does not seem to apply to the present experiments. Values of the anisotropy of polarizability Δb ($= b_1 - (b_2 + b_3)/2$, where b_1, b_2, b_3 are the principal polarizabilities) are given in Table I for several of the swelling liquids for which values of the polarizabilities were readily accessible.[28,29] No correlation is discernible between the values of Δb and the optical anisotropies α.

The fourth possibility, however, appears to have considerable merit. The swelling agents are indeed arranged in Table I approximately in order of their geometrical asymmetry, measured by the ratio of the maximum molecular dimension to the minimum one. When this ratio was determined for all the swelling liquids using Stuart–Briegleb molecular models, it became apparent that for values in excess of about 2 the observed optical anisotropy increased rapidly with increasing molecular asymmetry whereas those swelling liquids with values of the asymmetry ratio of less than about 2 all gave substantially the same (low) value for α. We therefore conclude that it is pronounced anisotropy of shape of the solvent molecules that induces higher optical anisotropy of the swollen polymer. The most probable mode of action of such asymmetric solvent molecules is by a simple packing effect in the neighbor-

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hood of the polymer molecule so that short-range orientational order is present, as proposed by Frisman and Dadivanyan[24,25] and Nagai.[26] The observed optical anisotropy will then be enhanced directly by a contribution from ordered solvent molecules (assuming that they are optically, as well as geometrically, anisotropic) and indirectly by restraints they impose on the polymer molecule, increasing its effective stiffness.

Frisman and Dadivanyan ignored the latter contribution and attributed the increase in α entirely to optical anisotropy Δb of the solvent molecules. The present results show no clear correlation with Δb (Table I) and therefore might be taken to indicate a substantial contribution from changed conformations of the polymer molecule itself. However, possible variations in the degree of orientation of the solvent molecules prevent a definite conclusion from being drawn.[30]

Several important consequences follow from the deduction that local order is present in molecularly asymmetric swelling liquids.

(i) The optical properties of isolated chains are most nearly obtained with samples swollen by liquids having compact symmetrical molecules. The best estimates of α for *cis*- and *trans*-polyisoprene are thus 4.0×10^{-24} cm^3 and 5.9×10^{-24} cm^3, corresponding to values of q of 1.25 and 1.8 isoprene units when Denbigh's values of bond polarizabilities are used to compute anisotropies of the repeat units. These values of q correspond to 3.8 and 5.4 carbon–carbon single bonds in the molecular chain per equivalent freely jointed link. A value of 5.4 bonds was obtained for polyethylene previously.[13] All these polymers can be considered relatively flexible, therefore.

(ii) Values of α for the unswollen materials are substantially higher than for the "isolated chain" system (Table I). This has two implications: the stress–optical coefficient of unswollen materials cannot be interpreted directly in terms of conformational features of isolated molecules, and the polymer molecules themselves constitute an anisotropic medium and are therefore locally ordered.

An estimate of the latter effect can be made by comparing the values of α for the unswollen materials with those obtained with anisotropic solvents. This leads to the conclusion that the effective geometrical anisotropies of *cis*- and *trans*-polyisoprene are similar to those of toluene and *p*-dichlorobenzene, respectively. It is noteworthy that lengths of the equivalent freely jointed link deduced above are comparable to the overall lengths of these molecules also. However, the tensile stress for unswollen materials does not obey the theoretical dependence on strain but contains a large extra term, the C_2 term, of unknown origin. The connection between the C_2 stress component and optical anisotropy is not known and therefore quantitative interpretation of measured stress–optical coefficients in terms of α by means of eq 1 is a somewhat uncertain procedure for unswollen materials.

Conclusions

A solvent effect found by Frisman and Dadivanyan in flow birefringence studies on polymer solutions has been confirmed by measurements of stress–optical coefficients for *cis*- and *trans*-polyisoprene, swollen by a variety of liquids. Enhanced optical anisotropy is found when the swelling liquid has geometrically asymmetric molecules. As deduced by Frisman and Dadivanyan,[24,25] and Nagai,[26] these results are consistent with short-range orientational order developed as a result of simple packing effects. It is not clear, however, to what degree the enhanced optical anisotropy is due to partially ordered solvent molecules or to changed conformational properties of the polymer molecules in a condensed anisotropic medium.

Minimum values of optical anisotropy were obtained with swelling liquids having compact symmetrical molecules. They are assumed to correspond most closely to values appropriate to isolated polymer chains. They yield values for the length of an equivalent freely jointed link of only 1.25 and 1.8 isoprene units, for *cis*- and *trans*-materials, respectively. The larger values of stress–optical coefficient obtained for unswollen samples are similar to those for samples swollen with rather asymmetric molecular liquids. We conclude that local order is present in unswollen materials also.

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(30) The two effects can in principle be distinguished experimentally. Solvent molecules which are optically isotropic but geometrically asymmetric should allow changes in optical anisotropy of polymer molecules on swelling to be studied in isolation. Similarly, optically isotropic polymers should allow orientational effects to be studied with optically anisotropic solvent molecules.