agreement with the experimental value, -4.09×10^{-3} deg^{-1}, of Nakajima and Saijyo[9] for isotactic configurations. Hamada,[10a] however, has found a considerably lower temperature coefficient, -1.5×10^{-3} deg^{-1} (unpublished results). Therefore, at the moment a final conclusion about the entropy contributions to F_{ω} and $F_{\omega'}$ cannot be made. For atactic polypropylenes the experimental value[10b] -1.7×10^{-3} deg^{-1} is in good agreement with the lower calculated curve in Figure 11a.

The free energies of the rotational isomeric states are generally dependent on the solvent too.[13] If small changes of one free energy, F_{η}, for example, have essential influence on the unperturbed dimensions, the temperature coefficients derived from measurements in different θ solvents may vary to a great extent. Such an effect has been simulated in Figure 11b. The free energy F_{η} for 130° has been assumed to be only 0.036 kcal lower than the corresponding F_{η} at 100°. The temperature coefficients derived in this way decrease up to the half of their original values.

Conclusion

The unperturbed dimensions of polypropylenes can be described by second-order energies, which are quite the same as the corresponding energy for polymethylene. Then the positions of the bond rotation angles in the three-state model of Flory do not deviate more than a few degrees from planar trans and symetrically staggered gauche. In this way good agreement can be obtained with the experimental data for all tacticities, whereas the parameters of Abe,[11] basing on higher second-order energies than ours, have given much higher values for syndiotactic configurations.

With the comparably low second-order energies, the unperturbed dimensions of "isotactic" polypropylenes are only slightly dependent on the content of syndiotactic dyads. The temperature coefficient is also less sensitive to the fraction of syndiotactic dyads. Consequently, the open question about the exact fraction of syndiotactic dyads in "isotactic" polypropylenes—as derived from nmr[12,14]—is of only minor importance for the comparison of the calculated and measured unperturbed dimensions. This agrees with the conclusion of Boyd and Breitling[15] derived from conformational calculations on polypropylenes.

Acknowledgment. We thank Deutsche Forschungsgemeinschaft for financial support. To Dr. E. Klesper we are greatly indebted for fruitful discussions.

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Stress-Optical Behavior of Polymethylene and Poly(dimethylsiloxane)

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ABSTRACT: The strain birefringence of polymethylene (PM) and for poly(dimethylsiloxane) (PDMS) networks, unswollen and swollen with diluents, has been investigated over the temperature ranges 115–220° and 15–90°, respectively. Temperature coefficients of the optical-configuration parameter, Δa, have been determined with much improved accuracy by cycling the temperature at fixed length rather than, as heretofore, by determining stress-birefringence isotherms at a series of temperatures. Dilution of PM with decalin reduces $-10^3 \mathrm{d} \ln \Delta a/\mathrm{d}T$ from 3.8 (±0.1) to 1.4 (±0.1) deg^{-1}. The latter value is virtually coincident with calculations from rotational isomeric state theory. From $\Delta a = 4.0 \times 10^{-24}$ cm^3 in decalin at 150° theory yields $\Gamma_{\mathrm{PM}} \equiv \Delta\alpha_{\mathrm{CC}} - 1.88\Delta\alpha_{\mathrm{CH}} = 1.0 \times 10^{-24}$ cm^3 (where $\Delta\alpha$'s are bond optical anisotropies) compared with 0.56×10^{-24} cm^3 from depolarized scattering by *n*-alkanes in CCl_4. Residual intermolecular correlations in the PM–decalin system are suggested as responsible for the discrepancy. Swelling of PM with *n*-$C_{12}H_{26}$ and *n*-$C_{22}H_{46}$ effects smaller reductions in Δa and $-\mathrm{d} \ln \Delta a/\mathrm{d}T$. For PDMS, the value of Δa is markedly reduced by swelling with decalin, with cyclohexane, and especially with CCl_4. In CCl_4, $\Delta a = 0.18 \times 10^{-24}$ cm^3 at 70°, giving $\Gamma_{\mathrm{PDMS}} \equiv \Delta\alpha_{\mathrm{SiO}} - \Delta\alpha_{\mathrm{SiC}} + \Delta\alpha_{\mathrm{CH}} = 0.047 \times 10^{-24}$ cm^3. The observed (positive) temperature coefficient considerably exceeds theoretical predictions, and would be at variance with the supposition of order in the amorphous polymer. The vanishingly small optical anisotropy of PDMS casts doubt on the significance of the discrepancy with theory.

This investigation was prompted by evidence indicating the stress-optical behavior of cross-linked networks to be at variance with calculations according to rotational isomeric state schemes successfully used to treat other configuration-dependent properties of polymer chains.[1] In particular, the experimental temperature dependence of the stress-optical coefficients for cross-linked amorphous polymethylene[2,3] (PM) and for poly(dimethylsiloxane)[4,5] (PDMS) have been

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(1) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969.

(2) A. N. Gent and V. V. Vickroy, Jr., *J. Polym. Sci., Part A-2*, **5**, 47 (1967).

(3) D. W. Saunders, D. R. Lightfoot, and D. A. Parsons, *ibid.*, **6**, 1183 (1968).

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reported to be considerably greater in magnitude than the values calculated[6-9] using statistical weight parameters consistent with other experimental evidence including the mean dimensions of the linear polymers,[10] their dipole moments (for PDMS and its oligomers),[11] and the temperature coefficients of these quantities.[10,11] Thus, the experimentally determined coefficient $\mathrm{d} \ln \Delta a/\mathrm{d}T$, where Δa is the optical anisotropy-configuration parameter defined rigorously by eq 14 below and directly obtainable from the stress-optical coefficient B, is three to four times the value calculated for PM[2,3,8] both observed and calculated values being negative. (In the classical treatment of strain birefringence given by Kuhn and Grün,[12,13] Δa enters as the optical anisotropy of a segment of the freely jointed chain, a model which is here replaced by the rotational isomeric state representation of the real chain.) The observed coefficient for PDMS[4,5] is positive, as predicted by theory, but it is about an order of magnitude larger than the calculated value. These differences cannot be resolved by any plausible revision of the statistical weights or of the geometric parameters, *i.e.*, bond angles and locations of rotational states, without destroying the agreement between theory and observations on other configuration-dependent properties. This assertion is supported by extensive computations reported only in part here.

Experimental results from a number of sources[14-19] show Δa generally to be reduced in magnitude when the network is swollen by a diluent. This effect, which may be quite large, has been attributed[14-19] to alleviation of orientational correlations in the undiluted polymer. It appears to depend on the optical anisotropy and geometrical asymmetry of the diluent,[14] being most marked when the diluent consists of molecules of near-spherical shape that are not themselves prone to correlations which would enhance the apparent optical anisotropy of the polymer. It seemed essential, therefore, to examine the effect of dilution by diluents of low optical anisotropy on the temperature coefficient of Δa before seeking an explanation for the temperature coefficient of Δa for unswollen networks.

The work of Gent and Vickroy[2] on PM suggests that the magnitude of $\mathrm{d} \ln \Delta a/\mathrm{d}T$ is decreased by swelling but their results are inconclusive in this regard. Recently, Mills[20] has shown that Δa and $\mathrm{d}\Delta a/\mathrm{d}T$ for PDMS are decreased drastically by dilution with carbon tetrachloride. However, the values found[20] for Δa scatter to such an extent as to preclude deduction of a reliable value for $\mathrm{d} \ln \Delta a/\mathrm{d}T$. It is this coefficient which is pertinent to the configurational-statistical properties of the chain. The theoretical value of $\mathrm{d} \ln \Delta a/\mathrm{d}T$, unlike that of Δa, is virtually independent of the values assigned to the components of the anisotropic part $\hat{\alpha}_i$ of the group polarizability tensor. The interpretation of the temperature coefficient of $\ln \Delta a$ is therefore free of ambiguities arising from uncertainties in values of the anisotropies of bond polarizabilities.

The investigations reported here were undertaken with the primary objective of accurately determining $\mathrm{d} \ln \Delta a/\mathrm{d}T$ for cross-linked, amorphous PM and PDMS, both in the undiluted condition and when swollen with diluents of comparatively low optical anisotropy. The liquids used with PM were decalin, *n*-dodecane, and *n*-docosane, while decalin, cyclohexane, and carbon tetrachloride were used to swell PDMS. The *n*-alkanes were included as diluents for PM for the express purpose of ascertaining effects of possible intermolecular correlations between the polymer and chain molecules of corresponding structure and conformational tendencies. The temperature coefficients were determined by cycling the temperature at fixed strain, the stress and the birefringence being measured simultaneously as functions of the temperature. Experiments conducted in this manner permit greater accuracy in the determination of $\mathrm{d} \ln \Delta a/\mathrm{d}T$ than can be achieved by comparing values of Δa obtained from several stress-birefringence isotherms, the procedure generally followed heretofore.

A further objective of this investigation has been to compare Δa for PM obtained from strain-birefringence measurements with estimates from values given for the optical anisotropies $\Delta\alpha_{\mathrm{CC}}$ and $\Delta\alpha_{\mathrm{CH}}$ of the C–C and C–H bonds, respectively, *i.e.*, the differences between the parallel and perpendicular components of the bond polarizabilities. Recent studies[21] on the depolarized light scattering by *n*-alkanes in carbon tetrachloride led to lower values for the bond optical anisotropies than those used in most of the recent papers on the subject. Thus, we attempt to reconcile the two methods, depolarized scattering and strain birefringence, for investigating the optical anisotropies of chain molecules.

Experimental Section

Polymethylene. A high molecular weight linear polyethylene Hostalen GUR,[22] was used exclusively. Its molecular weight is reported to be about 10^6 from viscosity measurements and 3.5–4×10^6 from light scattering.[23] It was formed into sheets *ca.* 2 mm thick using a hydraulic press equipped with heated platens.

The samples were cross-linked with ^{60}Co radiation in a Gammacell 650[24] irradiator. Temperatures of 150–160° were maintained during irradiation in order to eliminate possible complications due to crystallinity. This was accomplished using a glass tube wrapped with heating tape. The temperature was controlled through use of a variable transformer and was monitored by a remote-indicating thermometer. The samples were placed in aluminum pans arranged in stacks, which fit into the tube. The apparatus was purged with purified nitrogen to prevent oxidation. The dose rate was about 0.5 Mrad/hr. All samples received a dose of about 8.7 Mrads.

After irradiation, the cross-linked sheets were machined to a thickness of *ca.* 0.07 cm. Dumbbell-shaped test specimens 0.4 cm wide and 4 cm long were die punched from the sheets. The width and thickness were measured at room temperature with a micrometer. Lengths (taken to be the distance between dynamometer clamps) of unstressed, amorphous samples were determined by extrapolation of length–tension plots to zero tension. For unswollen samples, they were converted to temperatures other than that at which the extrapolation was carried out (usually 205–220°)

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(22) Manufactured by American Hoechst Corp.

(23) Product information from American Hoechst Corp.

(24) Manufactured by the Atomic Energy Commission of Canada, Ltd.

using the polyethylene density data of Orwoll and Flory.[25] In the case of swollen samples, the conversion was carried out on the basis of the measured dependence of the equilibrium swelling on temperature.

Equilibrium swelling was measured gravimetrically. Pieces of cross-linked polymer were immersed in diluent for 2–3 hr at each of four different temperatures before weighing. The volume fraction $v_{2;0}$ of polymer in the swollen, unstressed sample was then calculated[26] assuming additivity of specific volumes of the two components.

The diluents *n*-docosane, *n*-dodecane, and decalin (cis:trans = 62:38)[27] were obtained from Humphrey Chemical Co. and Matheson Coleman and Bell and used without further purification.

The apparatus used for the stress-optical measurements is of conventional design.[13] A 4-mW He–Ne (632.8 nm) laser that serves as light source provides a highly polarized and well-defined incident beam. The latter characteristic obviates focusing lenses. The polarizer and analyzer are Glan-Thompson prisms; the birefringence is measured with a Zeiss Ehringhaus compensator viewed through a low-power telescope. These optical components were mounted on a triangular optical bench. The part of the apparatus containing the sample was constructed from Pyrex glass. The sample chamber windows showed negligible birefringence. Dow-Corning DC-550 fluid was used as the heat transfer medium; its temperature was controlled to ±0.4°. Prepurified nitrogen was slowly passed through the sample chamber to minimize oxidative degradation. Ir spectra of samples revealed very little oxidation. Despite the production of highly colored oxidation products, the refractive indices of the diluents were within ±0.0004 unit of their initial values. Such changes have a negligible effect on Δa.

The dynamometer is of similar design to those previously used.[28,29] The strain gauge (Statham, 8- or 24-oz range) was mounted on a water-cooled block to prevent possible thermal effects due to the bath. The conventional strain gauge circuitry[30] was modified by replacing the recorder-zeroing potentiometer with a resistance, box. Thus, the tension on the sample could be obtained from a plot of mass *vs.* the resistance necessary to null the recorder.

The experiments were carried out isometrically by fixing the extension of the sample while measuring the change of the birefringence and tension with temperature. Before beginning a temperature cycle, the sample was held for several hours at the highest temperature in order to assure equilibration[29] of the tension and birefringence. At each temperature of the cycle, 20–30 min was allowed for thermal equilibration. The extension was measured to ±0.003 cm with a cathetometer.

The refractive index $\tilde{n}$ of undiluted, amorphous PM at different temperatures was calculated from its specific refraction[31] and density[25] using the Lorenz–Lorentz equation.[32] This procedure was also used for obtaining $\tilde{n}$ of the swollen samples.[32] All values of $\tilde{n}$ were corrected to λ 632.8 nm.

Poly(dimethylsiloxane). High molecular weight (*ca.* 1. 4 × 10^6) PDMS obtained from General Electric Corp. was pressed between Mylar sheets to obtain slabs about 2 mm thick. The samples were then cross-linked by high-energy electrons from a resonant transformer. They received a nominal dose of 8 Mrads on each side. Sol (<3%) was removed by extraction with carbon tetrachloride.

The procedure and apparatus for performing the experiments were as described except that the sample chamber was surrounded with a water jacket for temperature control. Measurements were then readily carried out below as well as above ambient temperature. Residual birefringence in the windows was small, amounting to *ca.* 2–3 nm in retardation. Correction was necessary only when the relative retardation (*cf.* below) was $\lesssim$20 nm. In the latter range, a λ/20 Zeiss Brace-Kohler compensator was used.

The decalin, carbon tetrachloride, and cyclohexane were Matheson Coleman and Bell Spectrograde and reagent grade.

The value of $\tilde{n}$ for PDMS was found to be 1.4004 at 35°, in agreement with the results of others.[4,5] The dependence of $\tilde{n}$ on temperature and swelling was obtained as described for PM.

Treatment of Data

The relationship between the measured relative retardation R and the stress-induced birefringence is given by

$$R = t\cdot\Delta\tilde{n} \qquad (1)$$

where t is the sample thickness and $\Delta\tilde{n}$ is the difference between refractive indices parallel and perpendicular to the stress. The relationship

$$\Delta\tilde{n} = B\tau \qquad (2)$$

defines the stress-optical coefficient B. Combination of eq 1 and 2 gives

$$B = R/\tau t = wR/f \qquad (3)$$

where f is the tension on the sample and w is its width at a given elongation and temperature. According to theory[18,33]

$$B = (2\pi\Delta a/45kT)(\tilde{n}^2 + 2)^2/\tilde{n} \qquad (4)$$

Hence

$$\Delta a = (wR/f)(45kT/2\pi)\tilde{n}/(\tilde{n}^2 + 2)^2 \qquad (5)$$

For an unswollen sample, assuming the volume to be constant, we have

$$w = w_*(L/L_*)^{-1/2} \qquad (6)$$

where w_* is its unstressed width, and L and L_* are the stressed and unstressed lengths, respectively.

The increase in volume with elongation of a sample in equilibrium with an excess of diluent is taken into account by use of the well-known expression[34,35]

$$\frac{\nu}{V_*}\eta_*^{\,2}\left[\frac{L_*}{L} - \frac{v_2}{2\eta_*^{\,2}}\right] = \frac{1}{V_1}[\ln(1 - v_2) + v_2 + \chi v_2^{\,2}] \qquad (7)$$

where ν is the number of moles of chains in the network, V_* is the volume of the unstressed, unswollen network, v_2 is the volume fraction of polymer in the (stressed) network, V_1 is the molar volume dilutent, and χ is the solvent–polymer interaction parameter; $\eta_* \equiv (\langle r^2\rangle_*/\langle r^2\rangle_0)^{1/2}$, where $\langle r^2\rangle_*$ is the mean-square end-to-end distance of chains in the unstressed, unswollen network and $\langle r^2\rangle_0$ is the value for the unperturbed chains, free of constraints imposed by the network or by long-range interactions. Since the samples were cross-linked in the undistorted state in the absence of diluent, $\eta_* \approx 1$. This quantity may depart from unity only through differences in the temperature coefficients of $\langle r^2\rangle_*$ (due to thermal expansivity of the polymer) and of $\langle r^2\rangle_0$. Because both are small, it is permissible to set η_* equal to unity for treatment of data at a fixed temperature. Recognition of its

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(25) R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89**, 6814 (1967).

(26) The densities of *n*-dodecane, *n*-docosane, and polyethylene are taken from ref 25. Any dependence of polymer density upon molecular weight is assumed to be insignificant.

(27) The composition of the decalin was measured with an Abbé refractometer. Its density was then obtained from the data on the pure isomers of W. F. Seyer and C. H. Davenport, *J. Amer. Chem. Soc.*, **63**, 2425 (1941).

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dependence on temperature is, of course, essential for the analysis of temperature coefficients.

For the unstressed sample at swelling equilibrium, eq 7 becomes

$$\frac{\nu}{V_*}\eta_*^{\,2}\left[\frac{L_*}{L_0} - \frac{v_{2;0}}{2\eta_*^{\,2}}\right] = \frac{1}{V_1}\,[\ln(1 - v_{2;0}) + v_{2;0} + \chi(v_{2;0})^2] \tag{8}$$

where the subscript zero denotes $f = 0$. The quantity $1/v_{2;0}$ is the swelling ratio; *i.e.*, the ratio of the swollen to the unswollen sample volume is given by $1/v_{2;0}$. Dividing eq 7 by eq 8 and expanding the logarithms, we obtain

$$\frac{L_*/L - v_2/2\eta_*^{\,2}}{L_*/L_0 - v_{2;0}/2\eta_*^{\,2}} = \left(\frac{v_2}{v_{2;0}}\right)^2\left[\frac{(1/2 - \chi) + v_2/3 + \ldots}{(1/2 - \chi) + v_{2;0}/3 + \ldots}\right] \approx (v_2/v_{2;0})^2 \tag{9}$$

For isotropic swelling

$$L_0/L_* = w_0/w_* = (v_{2;0})^{-1/3} \tag{10}$$

Substitution of eq 10 into eq 9 with $\eta_* = 1$ (see above) yields

$$v_2 \approx -(v_{2;0})^2/4D + (1/2)[(v_{2;0})^4/4D^2 + 4(L_0/L)(v_{2;0})^{7/3}/D]^{1/2} \tag{11}$$

where $D = (v_{2;0})^{1/3} - v_{2;0}/2$. Equation 11 gives the dependence of v_2 on elongation, as expressed by L/L_0, at swelling equilibrium.[36] The expression for the width of the stressed sample at swelling equilibrium is (*cf.* eq 6)

$$w = w_* v_2^{-1/3}(L/L_i)^{-1/2} \tag{12}$$

where $L_i = L_* v_2^{-1/3}$ is the isotropic length of the sample at the volume prevailing at swelling equilibrium, *i.e.*, the length the swollen sample would have in absence of stress if its volume fraction remained unchanged at v_2. Hence, from eq 10 and 12

$$w = w_0(v_{2;0}L_0/v_2L)^{1/2} \tag{13}$$

Through use of eq 13 in conjunction with eq 5, it is possible to possible to take account of the simultaneous effects of deformation and swelling on Δa.

Experimental Results

Polymethylene. Typical data showing the temperature dependence of Δa, calculated according to eq 5 from the measured retardation and tension, are presented in Figure 1 for both swollen and unswollen PM networks. The direction of the tick attached to each data point distinguishes measurements made during the heating (up) and cooling (down) phases of the temperature cycle. Hysteresis is negligible. The values of L/L_i ($\equiv L/L_*$ for unswollen samples) given in the figure are the extension ratios measured at the highest temperature reached in the experiment on a given sample. The data points for each experiment are well represented by a straight line, with the exception of those for unswollen PM, which indicate positive curvature. Results for both swollen and unswollen samples are approximated by the least-square-straight lines in Figure 1, from which the temperature coefficients d ln Δa/dT were calculated for a mean temperature of 150°. Average values of these coefficients are given in the last column of Table I. Experiments at different elongations (not included here) showed d ln Δa/dT, as well as Δa, to be independent of elongation. Values of Δa at 160° interpolated from experimental data such as are shown in Figure 1 are plotted against L/L_i in Figure 2. They appear to be independent of extension over the range investigated. Only for the undiluted samples is there an indication of dependence on L/L_i; for each of the two samples, Δa appears to increase somewhat with L/L_i. The changes are scarcely greater than the experimental error. Moreover, the close agreement between mean values of Δa from the two sets of data for undiluted samples supports the conclusion that Δa is sensibly independent of L/L_i over the range investigated.

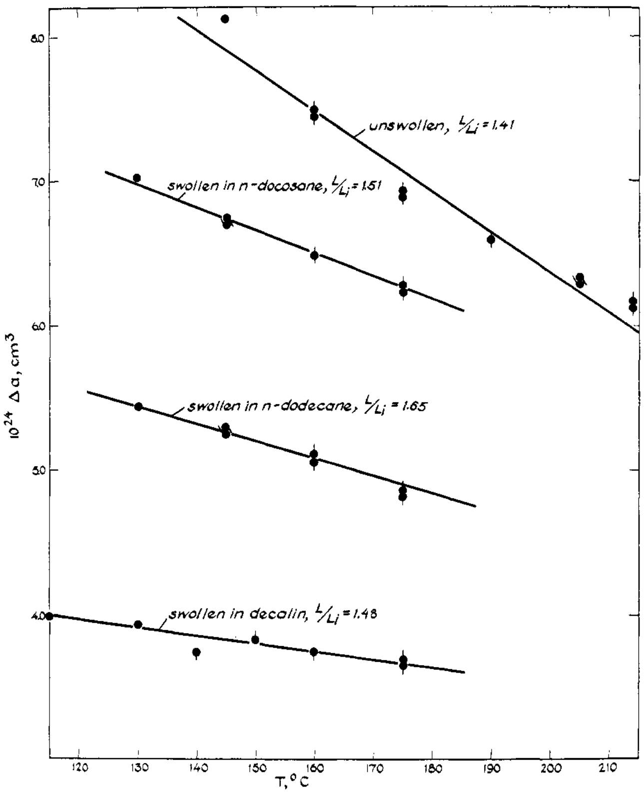

Figure 1. The dependence of Δa for polymethylene on temperature in various diluents. The values of L/L_i refer to the highest temperature of measurement. For purposes of comparison, the examples chosen are for similar values of L/L_i.

Table I
Polymethylene at 150°

Diluent	$v_{2;0}$	$10^{24}\Delta a$, cm³	10^3d ln Δa/dT, deg⁻¹
None	1.0	7.8, 8.4,[a] 8.4[b]	−4.1 (±0.1), 5.0,[a] 3.0[b]
n-$C_{22}H_{46}$	0.41	6.5	−2.6 (±0.1)
n-$C_{12}H_{26}$	0.44	5.1	−2.2 (±0.3)
Decalin	0.33, 0.36[c]	4.0, 3.9,[a] 4.0[c]	−1.4 (±0.1), ≈0 (±1)[a]

[a] Gent and Vickroy.[2] [b] Saunders, Lightfoot, and Parsons.[3] [c] Gent and Kuan.[15]

Mean values of Δa at 150°, determined as above by interpolation from data taken as a function of temperature at fixed length, are presented in the third column of Table I. These results are in good agreement with those previously reported from unswollen[2,3,15] and decalin-swollen[2,15] PM.

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[36] Equation 11 has been derived in a slightly different form by J. Bashaw and K. J. Smith, Jr., *J. Polym. Sci., Part A-2*, 6, 1041 (1968).

TABLE II
POLY(DIMETHYLSILOXANE) AT 70°

Diluent	$v_{2;0}$	$10^{24}\Delta a$, cm^3	10^{27}dΔa/dT, cm^3 deg^{-1}	10^3d ln Δa/dT, deg^{-1}
None	1.0	0.8_1, 0.6_8,[a] 0.3–0.7[b]	6.3	8.5 (±0.1), 7.3,[b] 8.2[a]
Decalin	0.25	0.5_1	3.2	4.9 (±0.5)
Cyclohexane	0.16	0.3_8[d]	4.8	11.7 (±0.7)
CCl_4	0.16, 0.35–0.71[c]	0.1_8,[d] 0.15–0.20[c]	2.0	18 (±3), >0[c]

[a] Tsvetkov and Grishchenko.[4] [b] Mills and Saunders.[5] [c] Mills.[20] [d] By extrapolation of data taken at lower temperatures.

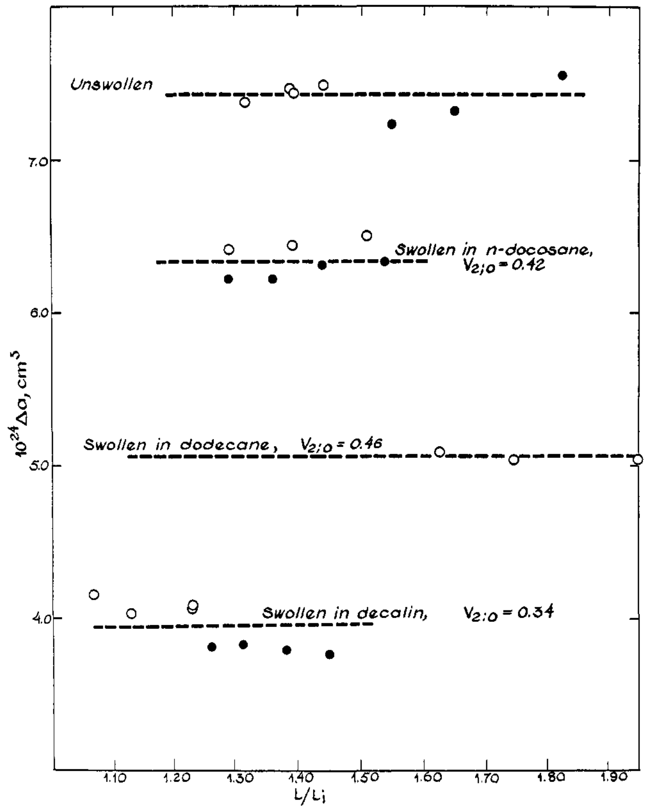

Figure 2. Dependence of Δa on L/L_i for PM at 160°. Open circles and filled circles denote different samples.

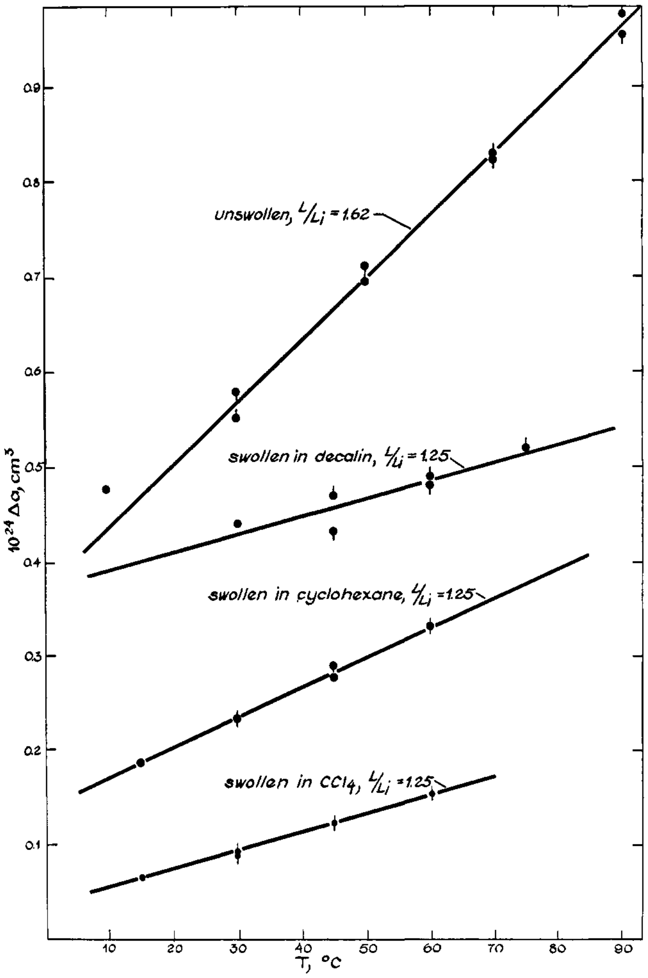

Figure 3. Dependence of Δa for poly(dimethylsiloxane) on temperature in various diluents.

Swelling with decalin decreases Δa to about half its value for the unswollen network. Smaller decreases in Δa are brought about by swelling with the *n*-alkanes.

Our value of d ln Δa/dT for the unswollen polymer falls between the values found by Saunders, *et al.*,[3] and by Gent and Vickroy.[2] We find that swelling with decalin decreases this temperature coefficient to less than half its value for the unswollen network. Smaller decreases are produced by swelling with *n*-docosane and *n*-dodecane. The smaller effects of the long-chain alkanes compared with those of decalin are consistent with the hypothesis that the optical anisotropy is enhanced in the bulk polymer due to correlations between neighboring polymer chains. These may be suppressed by dilution, but in the case of the *n*-alkanes diluent–polymer correlations resembling polymer–polymer correlations may occur and thus increase the apparent Δa over its value in the presence of a less anisotropic diluent such as decalin.

Poly(dimethylsiloxane). Results of typical isometric stress-birefringence–temperature measurements on PDMS, unswollen and swollen with the diluents, are shown in Figure 3. As for PM, Δa varies linearly with temperature within experimental error. There is an intimation of positive curvature for the unswollen polymer, however. Values of Δa interpolated to 70°, of dΔa/dT, and of d ln Δa/dT for the same mean temperature are given in Table II. Results for the unswollen polymer are in good agreement with results reported by previous investigators.[4,5] Our value of Δa for PDMS swollen in carbon tetrachloride is consistent with the approximate value obtained from the recent results of Mills.[20]

The optical anisotropy of PDMS as measured by Δa is much smaller than that for PM. Dilution decreases Δa, the effect being greatest (sixfold) for the isotropic diluent carbon tetrachloride. Smaller decreases are brought about by swelling with decalin or with cyclohexane. Owing to the small optical anisotropy of PDMS, apparent values of Δa appear to be more sensitive to specific effects of diluents than are those for PM. It may be for this reason that decalin produces a relatively small decrease in Δa for PDMS. The effect of carbon tetrachloride, consisting of quasispherical and optically isotropic molecules, is much greater.

Because of the small magnitude of Δa, uncertainties in both Δa and $\mathrm{d}\Delta a/\mathrm{d}T$ are comparatively large. They are magnified in $\mathrm{d}\ln \Delta a/\mathrm{d}T$. The indicated increases in this coefficient upon dilution with cyclohexane and with carbon tetrachloride must be viewed in this light. They are subject to large vitiations due to small effects of spurious origin. The absolute magnitude of the change in Δa with temperature, like Δa itself, is very small.

Analysis of Results

Theoretical Treatmemt. The expression for Δa derived[6–8] under the sole assumption of additivity of group polarizability tensors takes the form[33,37,38]

$$\Delta a = \frac{3}{2}\sum_{i=1}^{n} \langle \mathbf{r}^T\hat{\alpha}_i\mathbf{r}\rangle_0/\langle r^2\rangle_0 \tag{14}$$

where $\mathbf{r}^T$ is the transpose (*i.e.*, the row form) of the end-to-end vector $\mathbf{r}$ and $\hat{\alpha}_i$ is the traceless tensor representing the anisotropy of the polarizability associated with group i of the chain; the sum extends over all groups; the angle brackets with subscript zero denote averages over all configurations of the free, unperturbed chain. With adoption of the rotational isomeric state model, the sum in eq 14 can be evaluated through use of the relation[6–8,33,37]

$$\sum_{i=1}^{n} \langle \mathbf{r}^T\hat{\alpha}_i\mathbf{r}\rangle_0 = 2Z^{-1}\mathbf{J}^*\left(\prod_{i=1}^{n} \mathcal{Q}_i\right)\mathbf{J} \tag{15}$$

where $\mathcal{Q}_i$ is the generator matrix for skeletal bond i and $\mathbf{J}^*$ and $\mathbf{J}$ are the row and column operators defined previously.[33] The matrix $\mathcal{Q}_i$ embodies the tensor $\hat{\alpha}_i$ for group i, geometrical parameters defining the spatial configuration of the chain in various rotational states, and the statistical weights for the various rotational states. Three rotation states, one trans (t) and two gauche (g^+ and g^-), serve to represent the configurational states of the chains investigated here.[39,40] For PM the matrix of statistical weights for states of bond i in relation to those for bond $i - 1$ is[40]

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix}_i \tag{16}$$

the states being indexed on rows and columns in the order t, g^+, g^-. The parameters σ and ω are defined $\sigma = \exp(-E_\sigma/RT)$ and $\omega = \exp(-E_\omega/RT)$, where E_σ is the energy of a gauche state relative to trans; $E_\sigma + E_\omega$ is the energy for bond $i - 1$ in a gauche state followed by bond i in one of the opposite sign.

Two analogous statistical weight matrices are required for each repeat unit in PDMS,[9,11,40,41] as follows

$$\mathbf{U}_a = \mathbf{U}(\mathrm{OSi, SiO}) = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & 0 \\ 1 & 0 & \sigma\psi \end{bmatrix} \tag{17}$$

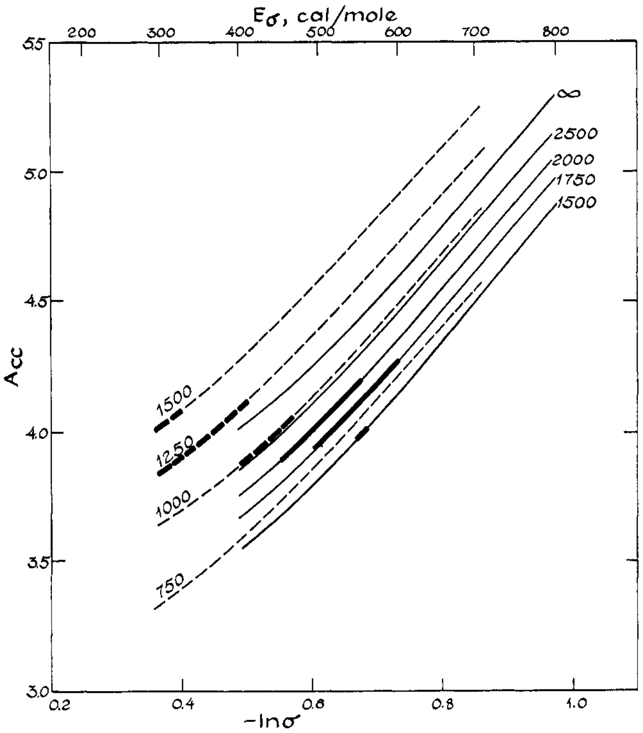

Figure 4. The parameter A_{CC} for PM at 140° plotted against $-\ln \sigma$ for different values of E_ω. Solid lines are for $\varphi_{g\pm} = \pm 120°$, dashed lines for $\varphi_{g\pm} = \pm 110°$. Ranges of $-\ln \sigma$ that reproduce accepted values of $\langle r^2\rangle_0/nl^2$ and $\mathrm{d}\ln \langle r^2\rangle_0/\mathrm{d}T$ are denoted by heavy-line segments.

and

$$\mathbf{U}_b = \mathbf{U}(\mathrm{SiO, OSi}) = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{18}$$

In the former matrix g^+g^- and g^-g^+ pairs are duly suppressed in recognition of the intolerable steric overlaps they entail, and a parameter ψ for g^+g^+ and g^-g^- combinations is appropriately included.[41]

Polymethylene. Numerical calculations were carried out for PM using the following geometric parameters: $\angle$CCC = 112°, $\angle$HCH = 109.5°, and a C–C bond length of 1.53 Å. The statistical weight parameter σ was varied from 0.35 to 0.65; ω was varied from 0 to 0.30. Gauche states were taken at $\varphi_g = \pm 120°$ or at $\pm 110°$. Since the bond optical anisotropies $\Delta\alpha_{CC}$ and $\Delta\alpha_{CH}$ enter separately, and linearly, into $\Delta\alpha$ calculated according to eq 14 and 15, the results of numerical computations may be represented by

$$\Delta a = A_{CC}\Delta\alpha_{CC} - A_{CH}\Delta\alpha_{CH} \tag{19}$$

where A_{CC} and A_{CH} are quantities determined by the geometrical parameters and the statistical weights. Throughout the ranges of the parameters quoted above, the calculations establish that $A_{CH}/A_{CC} = 1.88 \pm 0.02$, in agreement with the result $A_{CH}/A_{CC} = 1.87$ obtained previously by Nagai.[8] Hence, in good approximation we let

$$\Delta a = A_{CC}\Gamma_{PM} \tag{20}$$

where

$$\Gamma_{PM} = \Delta\alpha_{CC} - 1.88\Delta\alpha_{CH} \tag{21}$$

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(37) P. J. Flory, R. L. Jernigan, and A. E. Tonelli, *J. Chem. Phys.*, **48**, 3822 (1968).

(38) Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **3**, 294 (1970).

(39) Reference 1, Chapter III.

(40) Reference 1, Chapter V.

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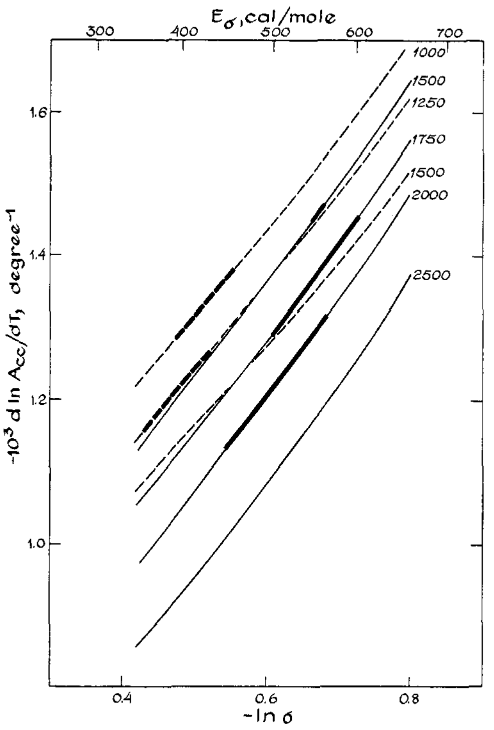

Figure 5. The temperature coefficient d ln A_{CC}/dT for PM at 150° plotted against $-\ln\sigma$. See legend to Figure 4.

If all bonds were tetrahedral,[42,43] this expression for Γ_{PM} would be replaced by $\Delta\alpha_{CC} - 2\Delta\alpha_{CH}$. Through use of eq 20 and 21 we separate the optical anisotropies from the geometrical and statistical factors, the latter being embodied in A_{CC}.

Results of numerical calculations for PM are presented in Figure 4, where A_{CC} is plotted against $-\ln\sigma$ for selected values of ω corresponding to the energies E_ω indicated on each curve and to a temperature of 140°. Heave-line segments represent intervals of σ within which $\langle r^2\rangle_0/nl^2 = 6.8 \pm 0.3$ and d ln $\langle r^2\rangle_0/dT = -1.1\ (\pm 0.1) \times 10^{-3}$ deg^{-1}, these being the ranges found by experiment at 140°.[44] We thus find that consistency with experiments on chain dimensions requires $A_{CC} = 4.0 \pm 0.6$ irrespective of the location of the gauche states over the range φ_g = 110–120°. As is apparent from the figure, moderate variations of a given parameter have comparatively little effect on A_{CC}, provided that the combination of parameters fulfills the foregoing conditions.

According to eq 20 and the premise that the bond anisotropies do not depend on temperature, we may identify d ln $\Delta a/dT$ with d ln A_{CC}/dT. Numerical calculations of A_{CC} as a function of σ and ω serve to evaluate d ln $A_{CC}/d\sigma$ and d ln $A_{CC}/d\omega$, and these quantities, in conjunction with the Boltzmann expressions for σ and ω, yield d ln A_{CC}/dT = d ln $\Delta a/dT$. Results thus obtained are plotted in Figure 5 against $-\ln\sigma$ for selected values of ω. As in Figure 4, segments of curves in ranges of σ that satisfy experimental results on the characteristic ratios (*i.e.*, dimensions) and their temperature coefficients are heavy lined. Consistency with these experiments requires d ln $A_{CC}/dT = -1.25\ (\pm 0.25) \times 10^{-3}$ deg^{-1}. Again, the particular combination of parameters is of little importance provided that they reproduce the chain dimensions and their temperature coefficient.

It will be observed from Figure 5 that the temperature coefficient increases significantly with ω (*i.e.*, as E_ω is reduced). Our calculated values of d ln A_{CC}/dT therefore are greater than those found by Nagai[8] who let $\omega = 0$ and, less importantly, adopted tetrahedral bond angles.

The experimental value for the temperature coefficient (Table I) of samples swollen with decalin is well within the range indicated by the calculations. The inconsistency[2,3,8] between stress-optical behavior exhibited by unswollen samples and predictions from rotational isomeric state theory may thus be resolved. This tentative conclusion rests, of course, on the assumption that the result obtained upon swelling with decalin is representative of independent chains unaffected by intermolecular correlations or other influences. Specifically, to the extent that such effects may persist in the presence of this diluent, we are obliged to assume that they do not change significantly with temperature.

From the experimental value of Δa for samples swollen in decalin, in conjunction with the range of A_{CC} calculated above, we obtain $\Gamma_{PM} = 1.0 \pm 0.2 \times 10^{-24}$ cm^3 according to eq 20. The bond polarizabilities given by Denbigh[45] yield $\Gamma_{PM} = 1.47 \times 10^{-24}$ cm^3, and those of Clément and Bothorel[46] give $\Gamma_{PM} = 0.86 \times 10^{-24}$ cm^{-3}. Recent results of Patterson and one of the present authors[21] on the depolarized scattering of *n*-alkanes dissolved in carbon tetrachloride yield, after extrapolation to infinite dilution and correction for intermolecularly induced scattering, $\Gamma_{PM} = 0.56 \times 10^{-24}$ cm^3. Their results lead to lower values for the bond polarizabilities than those cited above. They are more nearly in accord with those of LeFèvre, *et al.*[47] Thus, Γ_{PM} deduced from the measured stress-optical coefficient for samples swollen with decalin exceeds the value to be expected on the basis of depolarized scattering of *n*-alkanes in the isotropic solvent, carbon tetrachloride, by a factor of 1.5–2.0. Experiments on samples swollen with *n*-alkanes (Table I; see above) or with other diluents that are more anisotropic than decalin[15] yield even larger values of Γ_{PM}.

In assessing the apparent discrepancy between the results of strain birefringence measurements with those obtained from depolarized scattering in CCl_4 extrapolated to infinite dilution, it is good to observe, as Nagai[8] has clearly pointed out, that decalin is neither optically isotropic nor symmetric in shape, although it may more closely approach these desired specifications than other eligible diluents for PM at elevated temperatures. Moreover, the dilutions attained at swelling equilibrium may be insufficient to suppress interchain correlations altogether. Thus, diluent–polymer correlations and residual polymer–polymer correlations may account for the discrepancy between the experimental Γ_{PM} and its value inferred from the depolarized scattering by *n*-alkanes. We suggest that Δa obtained from swollen samples and Γ_{PM} derived from it should be regarded as upper limits to their inherent values.

Poly(dimethylsiloxane). Previously adopted[41] structural parameters ∠SiOSi = 143°, ∠OSiO = 110°, ∠CSiC = 112°, ∠OSiC = 108°, and Si–O and Si–C bond lengths of 1.64 and 1.90 Å, respectively,[48] were used for all calculations reported here. Rotational states were taken at 0 and ±120°.

In the approximation that bonding about the silicon and

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[42] R. A. Sack, *J. Chem. Phys.*, **25**, 1087 (1956).

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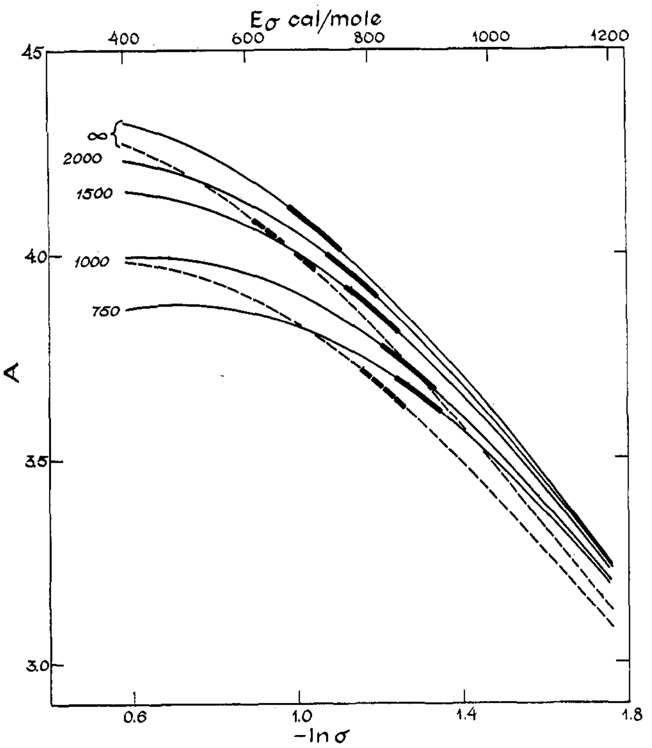

Figure 6. The parameter A for PDMS plotted against $-\ln\sigma$ for different values of E_ω. Solid lines are for $E_\psi = 0$, dashed for $E_\psi = 250$ cal/mol. Heavy-line segments have the same significance as in Figure 4.

carbon atoms is symmetrically tetrahedral, the anisotropic part $\hat{\alpha}$ of the molecular polarizability tensor must be proportional to

$$\Gamma_{\mathrm{PDMS}} = \Delta\alpha_{\mathrm{SiO}} - \Delta\alpha_{\mathrm{SiC}} + \Delta\alpha_{\mathrm{CH}} \qquad (22)$$

for every configuration of the chain. Numerical calculations show that the small departures of the values given above for the angles at Si from the tetrahedral angle, 109.5°, do not vitiate this relationship by more than 1%. Hence, we may let

$$\Delta a = A\Gamma_{\mathrm{PDMS}} \qquad (23)$$

where A is determined by the configurational statistics of the chain.

Proceeding as for PM, calculations were carried out for various values of σ, ω, and ψ bracketing the ranges of σ (0.17–0.55), ψ (0.5–1.0), and ω (0–0.33), which may be inferred from analysis of conformational interactions and which are supported by experimental results on chain dimensions,[10] dipole moments[11] of the polymer and its oligomers, and the temperature coefficients[10,49] of these quantities. Both sets of experiments are consistent with $E_\sigma = 850$ cal mol^{-1}, $E_\omega = 0$, and $E_\omega = 1050$ cal mol^{-1}, corresponding to $\sigma = 0.29$, $\psi = 1.0$, and $\omega = 0.20$ at 70°. Calculated values of A are plotted in Figure 6 against $-\ln\sigma$ at 70° for several values of E_ω and E_ψ. Ranges consistent with observed chain dimensions and their temperature coefficients (and also with dipole moments; see above) are heavy lined. Conformity with these results requires $A = 3.8 \pm 0.3$. From Δa observed in carbon tetrachloride we obtain $\Gamma_{\mathrm{PDMS}} = 0.047 \times 10^{-24}$ cm^3, an extremely small value. At 30° the value of Γ_{PDMS} falls to 0.025×10^{-24} cm^3. Independent information on the bond anisotropies $\Delta\alpha_{\mathrm{SiO}}$ and $\Delta\alpha_{\mathrm{SiC}}$ occurring in eq 22 are not available.

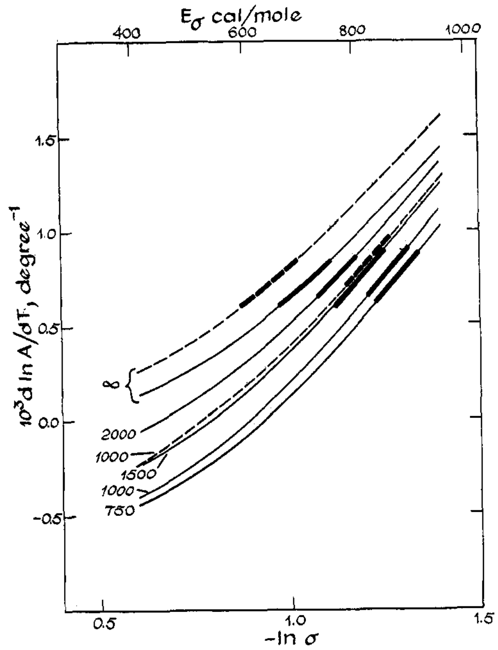

Figure 7. d ln A/dT for PDMS at 70° plotted against $-\ln\sigma$. See legend to Figure 6.

In Figure 7 we show d ln A/dT calculated for the selected values of E_ω and E_ψ as a function of $-\ln\sigma$, again for a temperature of 70°. Compliance with results for chain dimensions (heavy-lined ranges) requires d ln A/dT = 0.7 (±0.2) × 10^{-3} deg^{-1}, arbitrariness in the assignment of the conformational energies, within reasonable limits, having little effect. Experimental values of this coefficient (Table II) are much greater. Because of the very small optical anisotropy of the PDMS chain, the comparison must be made with reservations, as we have already pointed out.

Discussion

The effects of diluents on the optical anisotropy of PM, as manifested in Δa and its temperature dependence, are consistent with the widely held[8,14–20] hypothesis that interchain correlations enhance Δa in the undiluted polymer. Diminution of these correlations by diluents of minimal optical anisotropy decreases the value of Δa; elevation of the temperature may be expected to reduce correlations and thereby depress Δa more rapidly than predicted from the intramolecular configurational behavior of the PM chain.

The marked effect of isotropic diluents on Δa for PDMS invites a similar explanation for the optical anisotropic properties of this polymer. Here, however, dA/dT (and d ln A/dT as well) for the undiluted polymer is much *greater* than predicted. Thus, the disparity between observation and theory *increases* with temperature. This would require the postulated correlations to *increase* with temperature, which is quite implausible. The explanation offered[8,14–20] to account for effects of diluents and temperature on Δa for other polymers is untenable therefore for PDMS.

As we have pointed out, the very small value of Γ_{PDMS} creates a situation in which minor effects normally obscured by a larger inherent anisotropy may assume prominence. According to eq 23

$$\frac{\mathrm{d}\ln\Delta a}{\mathrm{d}T} = \frac{\mathrm{d}\ln A}{\mathrm{d}T} + \frac{\mathrm{d}\ln\Gamma_{\mathrm{PDMS}}}{\mathrm{d}T}$$

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(49) J. E. Mark, *J. Phys. Chem.*, **68**, 1092 (1964).

Ordinarily the second term on the right-hand side may be ignored and the temperature coefficient of Δa may be identified with that of A. But when Γ is near zero, even minute changes in this term are magnified in $\mathrm{d}\ln \Gamma/\mathrm{d}T$ so that it may dominate $\mathrm{d}\ln A/\mathrm{d}T$. These changes may originate, for example, in correlations involving the methyl groups, which are themselves anisotropic. Such correlations may be diatropic (negative) as well as paratropic (positive).[50] The effect of temperature thereon, though normally of no importance, may become significant when $\Gamma \approx 0$.

According to a wealth of evidence,[10] the chain configuration in undiluted polymers, including especially PM and PDMS, differs little from that for the unperturbed chains when well separated from one another as in a dilute solution. The evidence comes largely from investigations of rubber elasticity including, in particular, the temperature coefficient of the stress.[10,51] It is supported also by cyclization equilibrium constants in the case of PDMS.[52] Such correlations as may be responsible for enhancement of the optical anisotropy evidently do not appreciably perturb the configuration.

It may be noteworthy in this connection that the range of intramolecular correlation for group optical anisotropies[33,53] is much shorter (*i.e.*, extends over a lesser number of skeletal bonds) than the correlation range for skeletal bond vectors,[54] the latter being pertinent to the average chain dimensions. Contributions from *intermolecular* effects will therefore be more readily evident in the optical anisotropy than in the chain dimensions. Such intermolecular correlations as exist in the undiluted polymer may suffice to enhance Δa without affecting significantly the mean dimensions measured by $\langle r^2 \rangle_0$. It may be important also to draw a distinction between intermolecular correlations and ordering of chains. Occurrence of the former does not necessarily imply the latter. We shall discuss this matter in greater detail elsewhere.

Acknowledgments. The authors are indebted to Dr. C. S. Munday of Raychem Corp. for irradiating the polymer samples. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Grant No. 71-1960.

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Conformational Characteristics and Flexibility of Poly(2,6-disubstituted-1,4-phenylene oxides) and the Polycarbonate of Diphenylol-2,2′-propane

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ABSTRACT: The conformational energies per independent repeat unit of poly(2,6-dimethyl-1,4-phenylene oxide) and the polycarbonate of diphenylol-2,2′-propane are evaluated through use of a 6–12 potential to account for the van der Waals interactions between nonbonded atoms and groups which accompany rotations about the backbone bonds. Energetically allowed conformations are found to span the entire range of the rotation angle about the virtual bonds connecting neighboring ether oxygen atoms in the phenylene oxide polymer. Rotation about the virtual bonds in the polycarbonate chain is found to be similarly free of significant contraints. Consequently, both classes of polymers exhibit freely rotating chain statistics, as previously deduced by others from experimental chain dimension measurements and chain symmetry arguments. However, rotation about the virtual bonds in the phenylene oxide polymers and in polycarbonate is nearly truly free (each rotational state is appreciably populated) and not just restricted to two symmetrically located rotational states of equal energy at 90 and 270° as has been suggested. The flexibility of both classes of polymers, as manifested in their impact strength and fusion behavior, is discussed in light of the detailed conformational models (nearly true free rotation) developed here. The polysulfone chain is treated by analogy and is found to have a flexibility comparable to the poly(phenylene oxides) and polycarbonate.

The unperturbed chain dimensions have been measured[1–4] for the 2,6-dimethyl-, the 2,6-diphenyl-, and the 2-methyl-6-phenyl-1,4-phenylene oxide polymers and for the polycarbonate of diphenylol-2,2′-propane. Characteristic ratios of the mean-square end-to-end distance $\langle r^2 \rangle_0$ to the number n of backbone virtual bonds (see below) were found to be independent of temperature and equal to 85 Å^2 for the phenylene oxide polymers and 108 Å^2 for polycarbonate. Both ratios and their temperature independence can be predicted by assuming free rotation statistics[5] (N symmetrically located rotational states of equal energy) about the virtual bonds in both classes of polymers.

Barrales-Rienda and Pepper,[1] Akers, Allen, and Bethell,[3] and Shultz[4] proposed the existence of two equally populated chain rotational states at rotation angles of 90 and 270° about the virtual bonds to explain the free rotation statistics exhibited by the phenylene oxide polymers. Williams and

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