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Optical Anisotropy of the Polycarbonate of Diphenylolpropane

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ABSTRACT: The mean-squared optical anisotropy $\langle\gamma^2\rangle = (3/2)\langle\mathrm{tr}\,(\hat{\alpha}\hat{\alpha})\rangle$ and the dipolar contribution $\langle\mu^T\hat{\alpha}\mu\rangle$ to the electric birefringence are calculated for the random-coiled polycarbonate (PC) chain from its molecular geometry, the dipole moment μ_C for the carbonate group, and the anisotropic polarizability tensors $\hat{\alpha}_C$ and $\hat{\alpha}_{ph}$ for the carbonate and phenylene groups, respectively, as determined from experiments on model analogues reported in the preceding paper. Averaging over conformations is performed on the basis of calculated torsional potentials affecting rotations about C^{ph}–O and C^{ph}–C bonds linking phenylene with carbonate and with isopropylidene groups. The averaged invariant $\langle\mathrm{tr}\,(\hat{\alpha}\hat{\chi})\rangle$ that determines the magnetic birefringence is similarly evaluated from $\hat{\alpha}$ and the anisotropy tensors $\hat{\chi}$ for the diamagnetic susceptibilities of constituent groups. Our depolarized Rayleigh scattering and electric birefringence measurements on PC yield results in good agreement with calculations. The calculated Cotton–Mouton constant is about 30% lower than the value deduced from the magnetic birefringence measurements of Champion et al. Apart from this unexplained discrepancy, experiments support the postulated additivity of group polarizabilities and, consequently, recommend optical anisotropy as an index of conformation and structure.

Introduction

The results presented in the preceding paper[1] furnish the anisotropic polarizability tensors for the carbonate group and for phenyl groups subject to substitutions corresponding to those occurring in the polycarbonate (PC) formed from 2,2-bis(4-hydroxyphenyl)propane. In the model compounds investigated,[1] namely, diphenyl carbonate (DPC) and 2,2-diphenylpropane (DPP), the phenyl groups are monosubstituted, whereas PC comprises para-disubstituted phenylene groups joined alternately by carbonate and isopropylidene groups. The tensor for the 4-phenylene group in PC may reasonably be formulated by considering the inductive effects of the two bridging groups to be additive.

The structure of the PC chain may be reliably inferred from data for the model compounds.[1] On the premise that it is legitimate to treat the polarizability of the molecule as a constitutive property, the anisotropic polarizability tensor $\hat{\alpha}$ may be calculated for any given conformation of the PC chain as the tensor sum of contributions of its constituent groups. The invariants $\mathrm{tr}\,(\hat{\alpha}\hat{\alpha})$ and $\mu^T\hat{\alpha}\mu$, where μ is the molecular dipole moment, also may be evaluated for any specified conformation. Information on the character of the torsional potentials in the model compounds[1] should be directly applicable to the polymer chain. Hence, the quantities $\langle\gamma^2\rangle = (3/2)\langle\mathrm{tr}\,(\hat{\alpha}\hat{\alpha})\rangle$ and $\langle\mu^T\hat{\alpha}\mu\rangle$ can be evaluated as the required statistical mechanical averages over all conformations. The results may be compared with corresponding quantities obtained from depolarized Rayleigh scattering (DRS) and electric birefringence experiments. One may also calculate the quantity $\langle\mathrm{tr}\,(\hat{\alpha}\hat{\chi})\rangle$ relevant to magnetic birefringence, $\hat{\chi}$ being the anisotropic part of the diamagnetic susceptibility tensor, which is available from tabulated contributions of constituent groups.[2]

The validity and accuracy of values of the identified quantities calculated in the manner indicated rest essentially on the propriety of treating $\hat{\alpha}$ as a sum of locally invariant contributions of constituent groups, in keeping with the premise cited above. The fact that the groups comprising the PC chain are fairly large and that the distances between them are commensurate with their dimensions encourages the expectation that intergroup inductive effects may be comparatively small and, hence, that a constitutive scheme for formulating $\hat{\alpha}$ may be practicable. Additivity of group contributions to the magnetic tensor $\hat{\chi}$ is well authenticated.

In the present paper, we compare calculated values of $\langle\gamma^2\rangle$, $\langle\mu^T\hat{\alpha}\mu\rangle$, and the molar Cotton–Mouton constant ${}_mC$, which depends directly on $\langle\mathrm{tr}\,(\hat{\alpha}\hat{\chi})\rangle$, with results of experiments on PC. DRS and electric birefringence measurements that provide experimental values of the first two quantities are reported. The experimental value of the Cotton–Mouton constant is taken from the work of Champion, Dessen, and Meeten.[3] Comparison of calculated and observed values of the various quantities that reflect the optical anisotropy of the PC molecule affords a test of the stated premise and, hence, of the utility of optical anisotropy as a measure of structure and conformation of macromolecules.

Experimental Section

Polycarbonate. Measurements reported below were conducted on a sample having a number-average molecular weight of 2700 as determined by vapor phase osmometry. It was prepared by addition of phosgene to bis(4-hydroxyphenyl)propane dissolved in pyridine at 25–30 °C. The phosgene added was less than required for stoichiometric equivalence. The polymer was precipitated from pyridine by addition of methanol. It was further purified by reprecipitating twice from methylene chloride, using methanol as the precipitant. The constitution of the polymer is represented by

$$\mathrm{A{-}(O{-}CO{-}O{-}C_6H_4{-}C_3H_6{-}C_6H_4)_{\bar{x}-2}{-}O{-}CO{-}O{-}A}$$

with $\bar{x} = 10.7$; the A terminal units are presumed to be $\mathrm{HO{-}C_6H_4{-}C_3H_6{-}C_6H_4{-}}$.

Results

Depolarized Rayleigh scattering and electric birefringence measurements were carried out according to the methods and procedures described in the preceding paper.[1] All measurements were conducted in p-dioxane at ca. 25 °C.

Apparent mean-squared optical anisotropies, expressed as the ratio $\langle\gamma^2\rangle/x$, are plotted against the volume fraction ϕ_2 of polymer in dioxane in Figure 1. Extrapolation to infinite dilution yields the results recorded in Table I.

Results of electric birefringence measurements are presented in Figure 2. Extrapolation to infinite dilution

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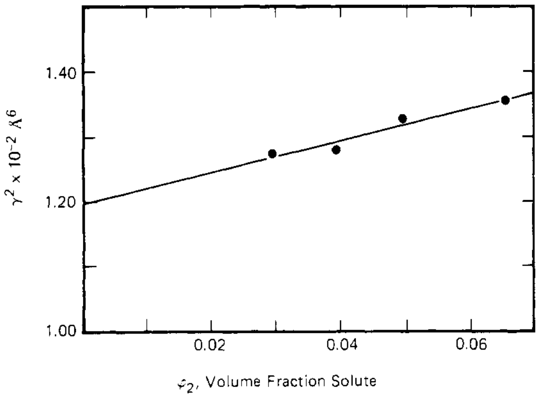

Figure 1. Depolarized Rayleigh scattering data for polycarbonate, $\bar{x} = 10.7$, and extrapolation of $\langle\gamma^2\rangle$ to zero concentration.

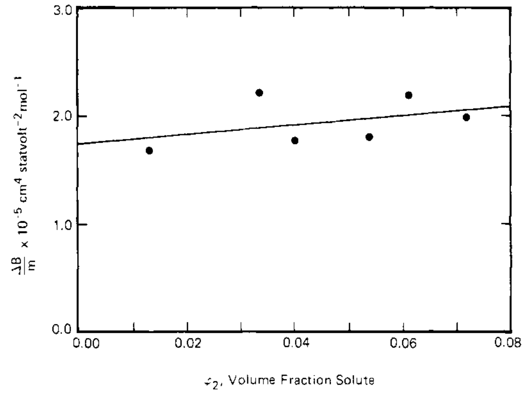

Figure 2. Kerr data for polycarbonate of $\bar{x} = 10.7$ showing the extrapolation of $\Delta B/m$ to zero concentration.

Table I
Observed and Calculated Optical Anisotropies, Molar Kerr Constants, and Molar Cotton-Mouton Constants

	$\langle\gamma^2\rangle/x$, Å^6	$10^{12}({}_mK)/x$, statvolt^{-1} cm^5 mol^{-1}	$\langle\mu^T\hat{\alpha}\mu\rangle$, Å^3 D^2	$10^{15}({}_mC)/x$, cm^3 G^{-2} mol^{-1}
exptl, $x = 10.7$	120 ± 5	350 ± 35	−1.38 ± 0.10	4.7[a]
calcd, $x = 11$	111	300	−1.34	
calcd, $x = \infty$	109	279	−1.40	3.4

[a] Deduced from experimental measurements reported by Champion, Dessen, and Meeten.[3]

gives $\Delta B/m = 1.7 \pm 0.17$ cm^4 statvolt^{-2} mol^{-1}. The corresponding Kerr constant per unit calculated from this result in the manner described in the preceding paper is given in Table I.

Theoretical Calculations and Comparisons with Experiments

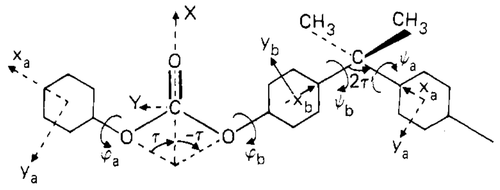

Figure 3. Structure and the coordinate systems for the ith repeating unit of the polycarbonate chain.

Structural Parameters, Group Polarizability Tensors, and Coordinate Transformations. The geometry of the PC chain is shown in Figure 3 together with the coordinate systems embedded in the several groups comprising the repeating unit. The parameters representing these groups as obtained from results for model compounds in the preceding paper[1] may be summarized for present purposes as follows. The carbonate group is planar. The angle τ shown in Figure 3 is 67°. The rotations ϕ_a and ϕ_b are independent and symmetric about the plane of the carbonate group with effective mean values of ±46°. The bond angle at the fully substituted carbon is tetrahedral. Rotations ψ_a and ψ_b about the C$^{\text{Ph}}$–C bonds are interdependent. The optical anisotropy tensor $\hat{\alpha}_C$ for the carbonate group expressed in the coordinate system XYZ in Figure 3 is given by eq 20 of the preceding paper.

Each phenylene group in the chain backbone is subject to the combined effects of substitution by the carbonate group attached through an ether oxygen linkage and by benzylic substitution with $C(CH_3)_2C_6H_4$. We assume that the net increase in $\Delta\alpha_{\phi H}$ due to oxygen substitution can be equated approximately to the difference $(\Delta\alpha_{\phi H})_{DPC} - (\Delta\alpha_{\phi H})_{\text{benzene}}$. Using the values[1] $(\Delta\alpha_{\phi H})_{DPC} = 4.0$ Å^3 and $(\Delta\alpha_{\phi H})_{\text{benzene}} = 1.82$ Å^3,[4] we obtain 2.2 Å^3 for the net effect of oxygen substitution. Combining this increment with[1] $\Delta\alpha_{\phi H} = 5.2$ Å^3 for the phenyl group in DPP, we obtain $(\Delta\alpha_{\phi H})_{PC} = 7.4$ Å^3 for the phenylene group in the PC chain. Inasmuch as the transverse anisotropies $\Delta\alpha^\dagger = \hat{\alpha}_y - \hat{\alpha}_z$ are insensitive to substitution, we adopt the approximate mean value $\Delta\alpha^\dagger = 3.0$ Å^3 found for the phenyl group in various compounds.[1,4] The anisotropy tensor of the phenylene group occurring in PC is thus obtained as

$$(\hat{\alpha}_{\phi H})_{PC} = \text{diag}\ (4.9, -1.0, -3.9) \qquad (1)$$

The anisotropic polarizability tensor $\hat{\alpha}$ for the repeating unit of the PC chain comprises contributions from three subunits: two phenylene groups and the carbonate group. The isopropylidene group is considered to make no contribution to the anisotropy on the grounds[1] that it is the residue obtained by elimination of two molecules of methane from neopentane and two phenyl groups, with $\hat{\alpha} = 0$ for both methane and neopentane. The inductive effects of substitution are included in the tensors assigned to phenylene, however.

The three required transformation matrices are

$$\begin{aligned} \mathbf{T}_1 &= \mathbf{R}_x(-\psi_b)\mathbf{R}_Z(2\tau')\mathbf{R}_x(\psi_a) \\ \mathbf{T}_2 &= \mathbf{R}_Z(-\tau)\mathbf{R}_x(\phi_b) \\ \mathbf{T}_3 &= \mathbf{R}_x(-\phi_a)\mathbf{R}_Z(-\tau) \end{aligned} \qquad (2)$$

where the transformations $\mathbf{R}_x$ and $\mathbf{R}_Z$ are given by eq 14 and 15 of the preceding paper.[1]

Mean-Squared Optical Anisotropy $\langle\gamma^2\rangle$. The three generator matrices[5,6] for the calculation of $\langle\gamma^2\rangle$ of the repeat unit, formulated by reference to Figure 3 with indices i = 1, 2, 3 corresponding to those in eq 2, are

$$\mathbf{P}_i = \begin{bmatrix} 1 & 2\hat{\alpha}_i^{R}(\mathrm{T}_i \otimes \mathrm{T}_i) & \hat{\alpha}_i^2 \\ 0 & \mathrm{T}_i \otimes \mathrm{T}_i & \hat{\alpha}_i^{C} \\ 0 & 0 & 1 \end{bmatrix} \qquad (3)$$

where $\hat{\alpha}_1 = \hat{\alpha}_3 = \hat{\alpha}_{\phi H}$ and $\hat{\alpha}_2 = \hat{\alpha}_C$ is the tensor for the carbonate group; $\hat{\alpha}^R$ and $\hat{\alpha}^C$ are the row and column forms of $\hat{\alpha}$, respectively, $\otimes$ indicates the direct product, and $\hat{\alpha}^2 \equiv \text{tr}\,(\hat{\alpha}\hat{\alpha})$. The mean-squared optical anisotropy for the PC chain of x repeat units is given by

$$\langle\gamma^2\rangle \equiv \frac{3}{2}\ \text{tr}\ \langle\hat{\alpha}\hat{\alpha}\rangle = \frac{3}{2}\mathbf{J}^*\langle\mathbf{P}_1\rangle\langle\mathbf{P}\rangle^{x-1}\langle\mathbf{P}_3\rangle\mathbf{J}^\dagger \qquad (4)$$

where

$$\langle \mathbf{P} \rangle = \langle \mathbf{P}_3 \rangle \langle \mathbf{P}_2 \rangle \langle \mathbf{P}_1 \rangle \tag{5}$$

and $\mathbf{J}^* = \text{Row}\ (1, 0, ..., 0)$ and $\mathbf{J}^\dagger = \text{Col}\ (0, ..., 0, 1)$ are the operators that select the first row and last column, respectively. Contributions of the terminal phenylene members of the end groups A are introduced by $\mathbf{J}^*\langle \mathbf{P}_1 \rangle$ and $\langle \mathbf{P}_3 \rangle \mathbf{J}^\dagger$. The very small contributions to the anisotropic polarizability from the hydroxyl terminal groups were ignored (apart from their inductive effects; see below).

The components of $\langle \mathbf{T}_i \rangle$ and $\langle \mathbf{T}_i \otimes \mathbf{T}_i \rangle$ were averaged over the bond rotation angles ϕ_a or ϕ_b and ψ_a or ψ_b shown in Figure 3. The required averages of trigonometric functions were obtained from the torsional energy calculations of the previous paper.[1]

Results of calculations of $\langle \gamma^2 \rangle / x$ are given in Table I, where they are compared with the experimental result. The difference exceeds the experimental error but probably is not greater than uncertainties in the group tensors would allow.

Molar Kerr Constant. The molar Kerr constant ${}_{\mathrm{m}}K$ of PC was calculated according to the relationship given by eq 3 of the preceding paper. The term $\langle \mu^{\mathrm{T}} \hat{\alpha} \mu \rangle$ in the expression for ${}_{\mathrm{m}}K$ was calculated by use of generator matrices and the procedure described previously.[6] Thus

$$\langle \mu^{\mathrm{T}} \hat{\alpha} \mu \rangle = \mathbf{J}^* \langle \mathbf{Q}_1 \rangle \langle \mathbf{Q} \rangle^{x-1} \langle \mathbf{Q}_3 \rangle \mathbf{J}^\dagger \tag{6}$$

where

$$\langle \mathbf{Q} \rangle = \langle \mathbf{Q}_3 \rangle \langle \mathbf{Q}_2 \rangle \langle \mathbf{Q}_1 \rangle \tag{7}$$

The $\mathbf{Q}_i$ (i = 1, 2, or 3) are defined[6] by

$$\mathbf{Q}_i = \begin{bmatrix} 1 & 2\mu_{\mathrm{u}}{}^{\mathrm{T}}\mathrm{T}_i & \hat{\alpha}_i{}^{\mathrm{R}}(\mathrm{T}_i \otimes \mathrm{T}_i) & (\mu_{\mathrm{u}}{}^{\mathrm{T}} \otimes \mu_{\mathrm{u}}{}^{\mathrm{T}})(\mathrm{T}_i \otimes \mathrm{T}_i) & 2\hat{\alpha}_i{}^{\mathrm{R}}(\mu_{\mathrm{u}} \otimes \mathrm{T}_i) & \hat{\alpha}_i{}^{\mathrm{R}}(\mu_{\mathrm{u}} \otimes \mu_{\mathrm{u}}) \\ 0 & \mathrm{T}_i & 0 & (\mathrm{E}_3 \otimes \mu_{\mathrm{u}}{}^{\mathrm{T}})(\mathrm{T}_i \otimes \mathrm{T}_i) & \hat{\alpha}\mathrm{T}_i & \hat{\alpha}_i \mu_{\mathrm{u}} \\ 0 & 0 & \mathrm{T}_i \otimes \mathrm{T}_i & 0 & 2\mu_{\mathrm{u}} \otimes \mathrm{T}_i & \mu_{\mathrm{u}} \otimes \mu_{\mathrm{u}} \\ 0 & 0 & 0 & \mathrm{T}_i \otimes \mathrm{T}_i & 0 & \hat{\alpha}_i{}^{\mathrm{C}} \\ 0 & 0 & 0 & 0 & \mathrm{T}_i & \mu_{\mathrm{u}} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}_i \tag{8}$$

where $\hat{\alpha}_1 = \hat{\alpha}_3 = \hat{\alpha}_{\phi\mathrm{H}}$, $\hat{\alpha}_2 = \hat{\alpha}_{\mathrm{C}}$, and μ_{u} is the dipole moment of the carbonate group. Dipole moments of the hydroxyl end groups were included in the terminal $\mathbf{Q}$ matrices. The value for phenol, 1.7 D,[7] was used. Elements of the $\mathbf{Q}_i$ were averaged over the bond rotation angles as above. Calculated values of $\langle \mu^{\mathrm{T}} \hat{\alpha} \mu \rangle / x$ and of ${}_{\mathrm{m}}K/x$ are compared in Table I with the corresponding experimental results. The agreement is excellent.

The experimental results presented are supported by measurements of lower accuracy on other samples of polycarbonate.

Magnetic Birefringence. The molar Cotton–Mouton constant ${}_{\mathrm{m}}C$, operationally defined analogously to the molar Kerr constant ${}_{\mathrm{m}}K$, is related to the product of the anisotropies of the polarizability $\hat{\alpha}$ and of the diamagnetic susceptibility $\hat{\chi}$ according to

$${}_{\mathrm{m}}C = (2\pi N / 15kT) \langle \mathrm{tr}\ (\hat{\alpha}\hat{\chi}) \rangle$$

As noted above, $\hat{\chi}$ can be evaluated from susceptibility tensors for benzene and for the C=O, C—O and C—H bonds. From the tabulations of Flygare,[2] these are

$$\chi_{\mathrm{benzene}} = \mathrm{diag}\ (-34.9, -34.9, -94.6)$$

with axes 1 and 2 in the plane of the ring,

$$\chi_{\mathrm{C=O}} = \mathrm{diag}\ (-1.3, 2.2, -13.0)$$

with axis 1 along the bond and axis 2 in the plane defined by the pendant bonds,

$$\chi_{\mathrm{C-O}} = \mathrm{diag}\ (-7.2, -6.7, -3.8)$$

with axis 1 along the bond and axis 2 in the plane defined by the bond pair adjoined to O, and

$$\chi_{\mathrm{C-H}} = \mathrm{diag}\ (-5.6, -3.1, -3.1)$$

all elements being expressed in 10^6 erg G^{-2} mol^{-1}. Additivity of bond and group susceptibilities holds with good accuracy; inductive effects are quite negligible. It follows that the diamagnetic susceptibility of the carbonate group, confined in this instance to the C=O bond and the two C—O bonds meeting at an angle of 108°, is

$$\chi_{\mathrm{CO_3}} = \mathrm{diag}\ (-15.1, -11.8, -20.6)$$

Hence

$$\hat{\chi}_{\mathrm{CO_3}} = \mathrm{diag}\ (0.7, 4.0, -4.7) \tag{9}$$

Attachment of benzene to the carbonate group involves replacement of a C—H by a C—O bond. We therefore define

$$\begin{aligned} \chi_{\mathrm{phenoxy}} &= \chi_{\mathrm{benzene}} + \chi_{\mathrm{C-O}} - \chi_{\mathrm{C-H}} \\ &= \mathrm{diag}\ (-36.5, -38.5, -95.3) \end{aligned}$$

whence

$$\hat{\chi}_{\mathrm{phenoxy}} = \mathrm{diag}\ (20.3, 18.3, -38.6) \tag{10}$$

As in the formulation of the optical tensor, combination of benzene or phenoxy with the isopropylidene group entails no net change. Hence, the diamagnetic anisotropy tensor for PC can be constructed by assemblage of $\hat{\chi}_{\mathrm{phenoxy}}$ and $\hat{\chi}_{\mathrm{CO_3}}$ tensors, each oriented as required by the conformation of the chain.

Average values of ${}_{\mathrm{m}}C$ can be calculated by resorting to eq 4 revised by replacement of $\hat{\alpha}^2$ by $\mathrm{tr}\ (\hat{\alpha}\hat{\chi})$ and of $\hat{\alpha}^{\mathrm{C}}$ by $\hat{\chi}^{\mathrm{C}}$ in the matrices $\mathbf{P}$ (eq 3). With these changes, eq 4 yields $\langle \mathrm{tr}\ (\hat{\alpha}\hat{\chi}) \rangle$, the factor $^3/_2$ in eq 4 being omitted, of course. The result of calculations of $\lim_{x\to\infty} ({}_{\mathrm{m}}C/x)$ using the above modifications of $\mathbf{P}$ together with eq 8 is given in Table I.

Champion, Dessen, and Meeten[3] have reported magnetic birefringence measurements on samples of PC. The Cotton–Mouton constant is related to the birefringence according to

$${}_{\mathrm{m}}C = 6\lambda n(n^2 + 2)^{-2} V_{\mathrm{s}} \left[\lim_{\phi_2 \to 0} \left(\frac{\Delta C}{\phi_2} \right) + C_0 \right] \tag{11}$$

where ΔC and C_0 are defined analogously to the corresponding quantities ΔB and B_0 for electric birefringence and V_{s} is the molar volume of the solute. Equation 11 is the equivalent of eq 5 of the preceding paper with $\epsilon = 1$. Substitution of the data from Figure 4 of the paper by Champion et al.[3] in this equation yields ${}_{\mathrm{m}}C = 4.7 \times 10^{-15}$ cm^3 G^{-2} mol^{-1}. The value calculated is about 30% lower (see Table I). Thus, the observed and calculated Cotton–Mouton constants are comparable, but, for reasons unknown, the agreement is not as close as for the other quantities listed in Table I.

Conclusion

The overall agreement between observed and calculated quantities reflecting the optical anisotropy $\hat{\alpha}$ of the polycarbonate molecule is confirmatory of the premise according to which this quantity is treated as the tensor sum of contributions of constituent groups. These groups being fairly large, the distances between them are sufficient to lower mutual inductive effects which otherwise might vitiate this premise, as we have noted in the Introduction. The studies here reported demonstrate further the utility of optical anisotropies as sensitive indices of chain conformation and of molecular structure.[1,4]

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Notes

Static and Dynamical Properties of Polystyrene in Carbon Tetrachloride. 3. Effects of Freezing on Solution Properties[†]

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In a recent series of articles,[1-6] we reported our studies of static and dynamical properties of polystyrene in *trans*-decalin from around the Θ temperature to about 20 °C above the Θ temperature. We were interested in the effects of solvent quality on polymer solution properties and did a series of additional measurements using a high molecular weight polystyrene sample (TSK F-1500) and a fairly good solvent, carbon tetrachloride, as our model system.[7-10] In our preliminary investigation of the polystyrene/CCl_4 system, we observed an abnormal behavior in the intermediate concentration range ($C_1^* \sim 3M/N_A\rho_s 4\pi r_g^3$, with ρ_s, M, N_A, and r_g being the density, the molecular weight, Avogadro's number, and the radius of gyration, respectively) and suggested the possible presence of a pseudotransition behavior.[7,8] Subsequent studies[9,10] confirmed the existence of such an anomalous effect in terms of the characteristic frequency Ω (or $1/\tau$), the characteristic length L_{app}, and the osmotic compressibility $(\partial\pi/\partial C)_{P,T}$ in the neighborhood of C_1^*. However, there were difficulties in achieving quantitative results in the neighborhood of this anomaly because of the long equilibration time required to obtain reproducible results. In the intermediate concentration range, where the irregular behavior had occurred, we often encountered unpredictable difficulties. In this Note, we have carried out a range of experiments trying to find out the reasons for the anomaly. The observed strange behavior in both static and dynamical properties of polystyrene in carbon tetrachloride is related to the usually accepted freeze-drying procedures used in biopolymer preparations.

Experimental Methods

Polystyrene, TSK standard F-1500, was purchased from Toyo Soda Manufacturing Co. Ltd., Japan. We used the same sample as that reported previously.[5-10] Reagent grade carbon tetrachloride was dried over CaH_2, distilled under N_2, and filtered through a Teflon filter of 0.22-μm nominal pore diameter. As CCl_4 has an unusually high density, dust-free sample solutions were prepared by substituting the solvent from benzene to CCl_4. The sample cells were then prepared according to the following different procedures.

1. **Flame-Sealed Samples.** After addition of CCl_4, the solution portion of the light scattering cell was dipped in liquid nitrogen, a vacuum was pulled, and the top was sealed by flame. As we were dealing with a high molecular weight polystyrene sample, we permitted mixing of the polymer with the solvent only by mildly shaking the cell several times a day. Solutions at different concentrations were contained in individual sealed cells.

2. **Dilution Method.** Two types of cells were used to study the concentration dependence of polystyrene in CCl_4 by dilution: (i) a cell equipped with a Mininert valve and (ii) a cell with a ground-glass joint. The Mininert valve permits addition of solvent without exposing the solution in the light scattering cell to the atmosphere. We permitted about 7 days for the initial solution of the freeze-dried polystyrene to be dissolved in the dried, distilled, and filtered CCl_4 during each run.

Measurements. We used light scattering spectrometers operating at $\lambda_0 = 488$[11] and 632.8 nm. Temperature was controlled and measured to 0.01 °C in both spectrometers.

Results and Discussion

The TSK F-1500 polystyrene (PS) sample had a reported molecular weight of 1.4×10^7. During our PS/*trans*-decalin studies,[5,6] we determined a molecular weight of 1.2×10^7. A least-squares fit of $1/P(x) - [\lim_{C\to 0} HC/R^{vv}]M_w$ (with $P(x) = 2(e^{-x} - 1 + x)/x_2$, $x = K^2 r_g^2$, and $K = (4\pi/\lambda)\sin(\theta/2)$) yields $r_g = 1.65 \times 10^3$ Å and $M_w = 8.9 \times 10^6$, which agrees with a separate and independent determination of our present polystyrene sample using methyl acetate as the Θ solvent.

The freeze-drying process has obviously broken up the high molecular weight polystyrene sample and decreased its molecular weight from 1.4×10^7 to 1.2×10^7 to finally 9×10^6. In the 0.01-0.02 wt % concentration range, sealed PS/CCl_4 samples showed anomalies of a maximum in $(\partial\pi/\partial C)_{P,T}$ and a minimum in L_{app} near 0.015 wt % polystyrene as shown in Figures 1 and 2, but the samples prepared by the dilution method showed no anomalous behavior over the entire concentration range. Results of the sealed PS/CCl_4 solutions fluctuate more over the entire concentration range when compared with those using the dilution method but are reproducible.

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