Table V
Probability of Existence of Each Conformation on Poly(propylene oxide) in Solution

Conformation	In C_6D_6 (%)	In $CDCl_3$
X_x	42	34
X_g	46	49
$X_{g'}$	12	17

be the mean value reflecting the probability of the three kinds of conformation. Thus, the observed coupling constant is expressed by

$$J_{\text{H-H}}(\text{vic}) = X_t J_t + X_g J_g + X_{g'} J_{g'}$$

where X_t, X_g, and X_g are the probability of trans (t), gauche (g), and gauche (g') conformations, respectively. If we adopt the J values for dioxane,[19] the probability of each conformation can be calculated approximately. The values obtained (see Table V) suggest that the polymer assumes very similar conformations around carbon-carbon bonds in chloroform and in benzene solution. Thus, the difference in specific rotation may not be due to a difference in the conformation around the carbon-carbon bond.

Table VI
Corelation of Difference in Chemical Shifts between I and S Dyad with Specific Rotation of Optical Active Polymer

Solvent	Difference in Chemical Shifts between *I* and *S* Dyads (Hz)	Specific Rotation of Poly(D(+)-propylene oxide) ($[\alpha]^{25}$D)
$CDCl_3$	0	+22
CCl_4	+4	−18
C_6D_6	+8	−33

We call your attention to a correlation observed between the specific rotation of the optically active polymer and the difference in chemical shift between isotactic and syndiotactic dyads observed in the nmr spectra of poly(propylene-α-*d* oxide) and poly(propylene-β-*d* oxide) (see Table VI), although its interpretation requires more information.

Acknowledgment. The authors express thanks to Dr. M. Sumi of Takeda Chemical Co. Ltd., for measurement of nmr spectra.

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Notes

Effect of Long-Range Interactions in the Determination of Unperturbed Dimensions

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Recent experimental work has revealed a considerable concentration dependence of the thermodynamic (so-called long-range) interaction. This may be represented by the following expression for the χ parameter

$$\chi = \chi^0 + \chi'\phi_2 \qquad (1)$$

where ϕ_2 is the polymer volume fraction. Benoit and Dondos[2,3] have used the Stockmayer-Fixman plot[4] to obtain values of unperturbed polymer dimensions in single and mixed solvents. They find a dependence of the unperturbed dimensions on the nature of some of the single solvents. Very surprisingly, a general and relatively large effect appears when mixed solvents are used, and this depends on the thermodynamic interactions between the two components. The present note suggests that the value of the unperturbed dimensions found by the extrapolation procedure may be affected by the concentration dependence of the long-range interaction (χ' parameter), and that this may be of particular importance for mixed solvents.

We write the Flory-Fox equation in the Flory-Orofino generalization[5]

$$\alpha^5 - \alpha^3 = \xi_1 M^{1/2} + \xi_2 \qquad (2)$$

where

$$\xi_1 = (9/2\pi)^{3/2}(\bar{v}^2/V_1 N)(\langle r^2\rangle_0/M)^{-3/2}\left(\frac{1}{2} - \chi^0\right) \qquad (3)$$

$$\xi_2 = (3^{3/2}/\pi)^3(\bar{v}^3/V_1 N^2)(\langle r^2\rangle_0/M)^{-3}\left(\frac{1}{3} - \chi'\right) \qquad (4)$$

with the usual meaning of the symbols. (The Flory-Orofino symbols χ_1 and χ_2 are normally used instead of the present χ^0 and χ', but this notation can be confusing in our case of mixed solvents). If we put

$$\alpha^3 = [\eta]/(K_\theta M^{1/2}) \qquad (5)$$

and rearrange eq 4, we see that on plotting, after Flory and Fox,[6] $[\eta]^{2/3}M^{-1/3}$ *vs.* $M/[\eta]$, we get an intercept at $M = 0$ which is equal, not to $K_\theta^{2/3}$, but to $K_\theta^{2/3}(1 + \xi_2)$. Here ξ_2 is given by eq 4 and for typical polymer-solvent systems assumes values of the order of $0.5[(1/3) - \chi']$. The effect would thus be significant if $\chi' = 0$, *i.e.*, the original Flory-Huggins equation were obeyed, but would become unimportant if χ' is close to $1/3$. This argument can be intuitively extended to other equations and extrapolation methods, *e.g.*, the Stockmayer-Fixman equation can be modified to the form
where B_1, B_2 are expressions differing from ξ_1 and ξ_2 by

$$\alpha^3 - 1 = B_1 M^{1/2} + B_2 \qquad (6)$$

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small numerical factors only. According to this equation, on plotting $[\eta]M^{-1/2}$ *vs.* $M^{1/2}$ we obtain K_θ enlarged by a factor of $1 + B_2$, where $B_2 \sim \xi_2$. Thus experimental values of K_θ should be too large if $\chi' < 1/3$ and too small if $\chi' > 1/3$. This argument is valid in principle also in case $B_1 = 0$. Hence the same effect on K_θ of the concentration dependence of χ should occur whether K_θ is obtained from viscosity measurements in θ solvents or by extrapolating the results obtained with good solvents to $M = 0$.

Single Solvent Case. It is well known that in not very polar systems with single-component solvents the K_θ value is independent of the solvent[7] and the same statement holds, by virtue of

$$K_\theta = \Phi_0(\langle r^2\rangle_0/M)^{3/2} \qquad (7)$$

for the unperturbed chain dimensions. In fact, for the two best-known θ systems, polystyrene–cyclohexane[8] and poly(isobutylene)–benzene,[9] the χ' value is very close to $1/3$ so that the B_2 term vanishes. There is a range of χ' values for other systems.[10,11] However, there appears to be a rough correlation (see also Morawetz[12]) between solvent quality and small χ' values. This would suggest a difference between K_θ values obtained with θ solvents and with good solvents. Such a difference does not seem to have been noticed experimentally, and it is possible that it is obscured by another systematic error resulting from the approximate character of the theories and equations used for the extrapolation procedure. However, Dondos and Benoit[2,3] report two kinds of regular deviations from the rule of the solvent-independent K_θ. (1) If the polymer is solvated by a hydrogen-bonding solvent, the K_θ value is usually higher (chloroform solutions of poly(vinylpyridine), poly(methyl methacrylate), and poly(vinyl acetate)); Dondos and Benoit explain this by steric hindrances to internal rotation of the chain skeleton, induced by the adsorbed solvent molecules. (2) In self-associating alcohols the K_θ values are lower, the effect being more pronounced the lower the temperature.[13] Here another effect of opposite sense must be assumed to outweigh the rotational hindrances, *e.g.*, ring formation by parts of polymer chains together with associated chains of alcohol.[3]

If, on the other hand, these changes of K_θ were to be attributed to the effect of B_2 on the extrapolation, then the χ' parameter ought to be significantly lower than $1/3$ for the chloroform solutions, and higher for the alcohol systems. (The formalism of eq 2–6 would be expected to hold even for these strongly interacting systems and should be independent of the origin of the semiempirical χ' parameter.) Little experimental evidence[12] seems to be available for these systems. However, it turns out from theoretical calculations based on the theory of equilibrium association[14] that the negative contribution to the χ parameter arising from simple solvation can lose its importance on increasing polymer dilution. This is due to the saturation of most of the polymer solvation sites by the first amounts of solvent added and results in a negative contribution to χ'. This explanation of negative χ' values is also given by Morawetz.[12] However, in the case of self-associating solvents the general trend is an increase of the χ value with polymer concentration, due to the fact that the associated complexes of alcohol are not broken to any considerable extent unless there is a high concentration of the nonassociating component. Thus in strongly interacting systems it seems that the concentration dependences of χ are at least consistent with the above-mentioned anomalies in K_θ.

Mixed-Solvent Case. In mixed solvents a very considerable dependence of the unperturbed dimensions on the solvent composition has been found by different authors (see, *e.g.*, ref 2, 3, 13, 15–17). For instance, Benoit and Dondos cite many systems where the K_θ values are virtually identical for the polymer in both pure solvents, but where the mixed solvent gives a K_θ value different by some 10–30%. Even when the K_θ values in the pure solvents are different, the mixed solvent K_θ reaches a maximum or minimum value. Furthermore the deviation of the K_θ value obtained with a binary solvent from that calculated, on an assumption of volume-fraction additivity, from values found with pure solvent components is directly proportional to the interaction parameter of the solvent components, χ_{12}. For positive χ_{12} the deviations from additivity are positive, and *vice versa;* the change of these deviations with temperature even parallels the temperature dependence of the χ_{12} parameter.[17]

In the case of pure solvents the interpretation of the solvent dependence of K_θ seems to be plausible in terms of short-range interactions or the effect of B_2. However, in the case of the mixed solvent the influence of χ_{12} clearly rules out the short-range interaction effect. Dondos and Benoit[17] suggest a consideration of "medium-range" interactions; an alternative explanation, however, may be based on eq 6 of the present paper.

As a starting point, we take the experimental fact, that the effect of the χ_{12} parameter on the coil expansion is considerably smaller than predicted by the simple Flory–Huggins theory. Neglecting the effect of the difference in molar volumes of the two solvent components and the influence of the preferential sorption, the classical theory leads to the following expression for the effective χ parameter in a solution of polymer in a mixed solvent

$$\bar{\chi} = u_1\chi_{13} + u_2\chi_{23} - u_1u_2\chi_{12} \qquad (8)$$

where $u_1 = \phi_1/(\phi_1 + \phi_2)$, ϕ_1, ϕ_2, ϕ_3 being the volume fractions of the two liquids and of the polymer, respectively. Thus the mixture is a better solvent than its components if $\chi_{12} > 0$, and *vice versa.*[18] It has been explicitly stated[19,20] and is supported also by other results (intrinsic viscosity,[21] gel swelling;[22] also heats of dilution[23]) that the size of this effect is much smaller than expected on the basis of eq 8. To deal with this fact, the ternary interaction parameter χ_T, defined by the equation

$$\Delta G_M(\text{exptl}) - \Delta G_M(\text{Flory–Huggins}) = RT\chi_T\phi_1\phi_2\phi_3 \qquad (9)$$

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has been used for the theoretical treatment of swelling in binary solvents[24] (the first use of that parameter was made by Read,[25] concerning preferential sorption). The necessity of introducing the ternary χ_T parameter may be due to a deviation of the numbers of molecular contacts from those given by the Flory–Huggins theory. Recently it has been suggested that molecular "surface" fractions[26] (or "site" fractions[27]) should replace the familiar volume fractions, and the formal introduction of the χ_T parameter into the Flory–Huggins theory equation seems to be justifiable by this step. Allowing also for the dependence of χ_{13} and χ_{23} on polymer concentration as given by eq 1, we see after performing the necessary calculation (*cf.* ref 24 and 28), that the eq 8 should be replaced by

$$\bar{\chi} = u_1(\chi_{13}{}^0 + \chi_{13}'\phi_3) + u_2(\chi_{23}{}^0 + \chi_{23}'\phi_3) - u_1u_2[\chi_{12} - 2\chi_T(1 - \phi_3)] \quad (10)$$

The experimental results[19-22] are fitted if the ternary parameter is assumed to be of the same sign as χ_{12} but of numerical value smaller than $\chi_{12}/2$. We can thus write

$$\chi_T = (\gamma/2)\chi_{12} \quad 0 < \gamma < 1 \quad (11)$$

The term with χ_{12} is thus diminished by a factor $1 - \gamma$ for very dilute systems ($\phi_3 \rightarrow 0$), but at the same time its dependence on polymer concentration is apparent. The expression $[(1/3) - \chi']$ in eq 4 for ξ_2 or B_2 is now replaced by

$$\frac{1}{3} - \bar{\chi}' = \frac{1}{3} - (u_1\chi_{13}' + u_2\chi_{23}') + \gamma\chi_{12}u_1u_2 \quad (12)$$

Assuming γ constant for a given polymer in different solvent mixtures, the proportionality of the last term to χ_{12} is valid. Inspecting eq 12 together with eq 4 and eq 2 or 6, this term offers an explanation of the deviation of the K_θ value, found in mixed solvents, from additivity. For $\chi_{12} = 2$, $\gamma = 0.8$, $u_1 = u_2 = 0.5$, we get a change of B_2, due to χ_{12}, which is at least of order 0.2, with a corresponding change of ~20% in the apparent value of K_θ. The sign of this effect would change with χ_{12} as found experimentally. Thus when mixed solvents are used, there may be an important influence of the thermodynamic interactions on the extrapolation procedure for K_θ.

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Infinite-Dilution Viscoelastic Properties of Poly(dimethylsiloxane)

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Measurements of storage and loss shear moduli have been made recently on several polymers in solution at concentrations sufficiently low to permit extrapolation of the data to infinite dilution for comparison with the predictions of molecular theories.[1] Data for linear polystyrene,[2] poly(α-methylstyrene),[3] and 1,4-polybutadiene[4] agree well with the predictions of the Zimm theory,[5] as evaluated by Lodge and Wu[6] with an arbitrary degree of hydrodynamic interaction, provided the frequency range does not extend far above the reciprocal of the longest relaxation time. Moreover, the degree of hydrodynamic interaction appears to be related to the expansion factor of the random coil as gauged by the intrinsic viscosity relative to that in a Θ solvent.[3]

In the present report, additional measurements on two samples of poly(dimethylsiloxane) (PDMS) are presented and compared with the Lodge–Wu evaluation of the Zimm theory. This polymer is somewhat different from those previously studied in having atoms other than carbon in the backbone; it is generally thought of as having a very high internal flexibility.

Two samples of PDMS with narrow molecular weight distribution were generously provided by Dr. Neal R. Langley of Dow Corning Corp. In order to place the relaxation times in a range appropriate for the frequency scope of our experimental method, it was necessary to use solvents of somewhat higher viscosity than the conventional ones for other dilute-solution measurements such as osmotic pressure and light scattering, and there is a narrow choice of liquids in which PDMS is soluble. We used PDMS oligomer liquids in which there were no components of high enough molecular weight to contribute any viscoelastic effects; these were also kindly furnished by Dr. Langley. Their viscosities (η_s) were determined by the multiple-lumped resonator in the course of the viscoelastic measurements. Intrinsic viscosities of the polymers in their respective oligomer solvents were determined by conventional capillary viscosimetry at 25°. Intrinsic viscosities in toluene were reported by Dr. Langley. Characterization of the polymers and solvents is summarized in Table I, including average molecular weights ($\bar{M}_w$, $\bar{M}_n$) determined at the Dow Corning Corp. No $\bar{M}_n$ is available for the sample of higher molecular weight, but its $\bar{M}_w$:$\bar{M}_n$ ratio was judged to be 1.10 to 1.15 from gel permeation chromatography.

The storage and loss shear moduli, G' and G'', of the solutions were measured by the Birnboim–Schrag multiple-lumped resonator[7] with computerized data acquisition and processing system.[8] The use of two resonators gave 9 working frequencies from 100 to 6060 Hz. The ranges of concentration (c) were 0.003–0.007 g/ml and 0.002–0.007 g/ml for the polymers of lower and higher molecular weights, respectively. All measurements were made at 25.00 ± 0.01°.

The quantities $(G'/c)^{1/2}$ and $(G'' - \omega\eta_s)/c$, where ω is radian frequency, were plotted against c and extrapolated to zero c at each frequency as described in previous studies[2-4] to give the corresponding intrinsic quantities $[G']$ and $[G'']$. The initial concentration dependences, derived from the slopes of these plots, could not be determined as precisely as usual because the concentration range was more limited. However, the ratios $\gamma' = (G'/c)^{-1}\mathrm{d}(G'/c)/\mathrm{d}c$, and γ'' which is the corresponding expression with $G'' - \omega\eta_s$ substituted for G', decreased substantially with in-

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