Table II
Ratio of Perpendicular to Parallel Half-Widths $q_{1/2}^{\perp}/q_{1/2}^{\parallel}$ in the Isotropic Scattering Experiment as a Function of Chain Length

N	Trans	Gaussian	Real
5	2.42	1.36	1.73
6	2.74	1.32	1.75
8	3.24	1.20	1.68
10	3.80	1.16	1.50

[a] N is the number of monomers. The column "Trans" gives the ratio $q_{1/2}^{\perp}/q_{1/2}^{\parallel}$ for a chain of which monomers are in a trans configuration with respect to their predecessors. The column "Gaussian" refers to a transfer matrix with identical elements. The matrix elements of the real chain are taken from ref 2.

and $S_{12}(\mathbf{q})$ becomes

$$S_{12}(\mathbf{q}) = 2(a_D - a_H)(a_H - a_C)f(\mathbf{q}) \qquad \text{(A-13)}$$

where using (20), $f(\mathbf{q})$ is

$$f(\mathbf{q}) = S^{HH}(\mathbf{q}) - \frac{[S^{HH}(\mathbf{q}) + S^{HC}(\mathbf{q})]^2}{S_0(\mathbf{q})} = [S^{HH}(\mathbf{q})S^{CC}(\mathbf{q}) - (S^{HC}(\mathbf{q}))^2]\frac{1}{S_0(\mathbf{q})} \qquad \text{(A-14)}$$

$S^B(\mathbf{q})$ is obtained in the same way

$$S^B(\mathbf{q}) = N_p(a_H - a_C)^2 f(\mathbf{q}) \qquad \text{(A-15)}$$

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Light Scattering from Polymers in Mixed Solvents, Polystyrenes

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Received January 21, 1974

ABSTRACT: Light-scattering and viscosity measurements were carried out on anionically prepared polystyrene samples in benzene–cyclohexane mixtures (good or medium solvents) of three different compositions at 30° and in a benzene (64%)–isopropy alcohol (36%) mixture (poor or theta solvent) at temperatures ranging from 23 to 40°. For refractive index increment and scattering-intensity measurements, the test solutions were diluted conventionally, and also under the osmotic condition, following the procedure of Casassa and Eisenberg. This dialysis method gave fairly accurate values of the polymer molecular weight. The relationship, $A_2M_2 = A_{2,\mathrm{ap}}M_{2,\mathrm{ap}}$, derived previously in the distribution-function theory was found to hold in benzene–cyclohexane mixtures with the small preferential adsorption coefficient λ, but not in a benzene–isopropyl alcohol mixture with large λ, where M_2 is the polymer molecular weight, A_2 is its second virial coefficient, and $M_{2,\mathrm{ap}}$ and $A_{2,\mathrm{ap}}$ are the respective apparent quantities. In this connection, a thermodynamic discussion of the difference between A_2M_2 and $A_{2,\mathrm{ap}}M_{2,\mathrm{ap}}$ is given. For the present Θ-solvent system, A_2 vanished at 25.5° (Θ), while $A_{2,\mathrm{ap}}$ vanished at 25.0° (Θ_{ap}). The ratio $[\eta]_\theta/M_2^{1/2}$ first increased with increasing M_2 and then leveled off for $M_2 \gtrsim 7 \times 10^5$ for which λ was nearly independent of M_2, where $[\eta]_\theta$ is the intrinsic viscosity at the Θ temperature. The solvent effect on $[\eta]_\theta/M_2^{1/2}$ and $\langle S^2\rangle_0/M_2$ was also observed, where $\langle S^2\rangle_0$ is the unperturbed mean-square radius of the polymer. The two-parameter theory of the excluded-volume effect was found to work well in the range of M_2 for which $[\eta]_\theta/M_2^{1/2}$ was independent of M_2. This also implies that the method proposed previously for the determination of $\langle S^2\rangle$ is valid.

There have been a number of theoretical and experimental investigations of light scattering from solutions of polymers in mixed solvents, following the pioneering contributions of Ewart *et al.*,[1] Kirkwood and Goldberg,[2] and Stockmayer.[3] Three important aspects may be deduced from these investigations: (1) thermodynamic study of preferential adsorption or interactions between polymer and solvent molecules;[1,4-10] (2) establishment of the light-scattering method of determining molecular weights, second virial coefficients, and mean-square radii of polymers in mixed solvents;[11-16] and (3) study of the validity of the two-parameter scheme in polymer–mixed-solvent systems.[17,18] The present paper is mainly concerned with the second and third topics.

In a previous paper on the distribution-function theory of light scattering in multicomponent systems,[16] it has been shown that the true second virial coefficient and mean-square radius may be determined in mixed solvents by the conventional method of Debye[19] and Zimm[20] under the condition

$$0.8 < M_{2,\mathrm{ap}}^{(Y)}/M_2 < 1.2 \qquad (1)$$

where M_2 is the molecular weight of the polymer and $M_{2,\mathrm{ap}}^{(Y)}$ is its apparent molecular weight defined by Yamakawa.[16] We must note that eq 1 has been derived as a sufficient condition but not as a necessary condition. In fact, this condition is very severe, as will be seen, and the light-scattering procedure we proposed[16] is expected to be applicable over a much wider range of the above molecular weight ratio. Thus, the first purpose of the present paper is to examine experimentally the applicability of our procedure. In particular, the condition on the determination of the second virial coefficient is also discussed from the point of view of thermodynamics. The second purpose is to examine whether the behavior of second virial coefficients and mean-square radii thus determined in mixed solvents satisfies the well-established two-parameter theory of dilute polymer solutions.[21,22] Dondos and Benoit[18] have recently found that in certain mixed-solvent systems, the slope of the Stockmayer–Fixman viscosity plot[23] does not vanish at the Θ temperature at which the second virial coefficient vanishes, suggesting the existence of two Θ temperatures. This problem is also discussed rather in detail in connection with the second purpose.

The polymer samples we used are polystyrenes prepared anionically in tetrahydrofuran. Most of them are the same as those used previously to carry out light-scattering and viscosity measurements in single solvents[24] for the test of the two-parameter theory. The mixed solvents we chose are the following two binary mixtures: (1) benzene–cyclohexane and (2) benzene–isopropyl alcohol. The first mixture was used as a good or medium solvent for polystyrene, and the second was used as a poor or Θ solvent.

Theoretical Section

Definition. For simplicity, we consider three-component systems, *i.e.*, solutions of a homogeneous polymer (species 2) in a binary liquid mixture of a good solvent (species 0) and a nonsolvent, or poor solvent (species 1). Let N_i be the number of molecules of species i contained in the solution of volume V. Then we define three kinds of concentrations of species i: concentration c_i in conventional units (g/cm³), volume fraction ϕ_i, and molarity m_i.

$$\begin{aligned} c_i &= M_iN_i/N_\mathrm{A}V \\ \phi_i &= N_iV_i/\sum_i N_iV_i = \bar{v}_ic_i \\ m_i &= M_iN_i/M_0N_0 = c_i/c_0 \end{aligned} \qquad (2)$$

where N_A is the Avogadro number, and M_i, V_i, and $\bar{v}_i$ are the molecular weight, molecular volume, and partial specific volume of species i, respectively. In particular, if $c_1{}^0$ is the value of c_1 at $c_2 = 0$, *i.e.*, the weight of nonsolvent (or poor solvent) per unit volume of the mixed solvent alone, then we have the relation

$$c_1 = c_1{}^0(1 - \phi_2) = c_1{}^0(1 - \bar{v}_2c_2) \qquad (3)$$

Similarly, the value of ϕ_1 at $c_2 = 0$ is designated by $\phi_1{}^0$, so that $\phi_1{}^0 = \bar{v}_1c_1{}^0$.

Now, we consider the excess scattering (Rayleigh's ratio) R_θ over that of the mixed solvent as a function of c_1 and c_2. Suppose that the solution is diluted in two ways; in one c_2 and therefore also c_1 are changed at constant temperature T, pressure p, and $c_1{}^0$, and in the other c_2 and also c_1 are changed at constant T, p, and chemical potential μ_1 of species 1. The two processes are indicated by writing

$$\begin{aligned} R_\theta &\equiv R_\theta(c_1,c_2|T,p,c_1{}^0) \\ R_\theta{}^* &\equiv R_\theta{}^*(c_1{}^*,c_2|T,p,\mu_1) \end{aligned} \qquad (4)$$

where the asterisk on c_1 in the second equation indicates the fact that its values in R_θ and $R_\theta{}^*$ are different at the same values of $c_1{}^0$ and c_2. Note that μ_1 in $R_\theta{}^*$ is a function of T, p, and $c_1{}^0$, assuming that the values of $c_1{}^0$ are the same in the two processes. Clearly the first process corresponds to the conventional light-scattering method.

Further we define three scattering constants K.

$$\begin{aligned} K &= \frac{2\pi^2n^2}{N_\mathrm{A}\lambda^4}\left(\frac{\partial n}{\partial c_2}\right)_{p,c_1{}^0}^2 \\ K_0 &= \frac{2\pi^2n_0{}^2}{N_\mathrm{A}\lambda^4}\left(\frac{\partial n}{\partial c_2}\right)_{p,c_1=0}^2 \\ K^* &= \frac{2\pi^2n^2}{N_\mathrm{A}\lambda^4}\left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1}^2 \end{aligned} \qquad (5)$$

where λ is the wavelength of the light under vacuum, n is the refractive index of the solution, which may be regarded as equal to that of the mixed solvent at small c_2, and n_0 is the refractive index of species 0 (good solvent). In eq 5 and the later equations, the subscript T, which should appear on $(\partial n/\partial c_2)$, is omitted, for simplicity. The first of eq 5 corresponds to the usual definition of K in single-solvent systems, K_0 is the constant introduced previously by Yamakawa,[16] and the constant K^* arises from the condition of constant μ_1 corresponding to the second of eq 4. This condition was introduced by Casassa and Eisenberg[11,12] and others.[13,25,26]

An exact experimental determination of $R_\theta{}^*$ and K^* is impossible, since the solution cannot be diluted exactly at constant T, p, and μ_1. In practice, the solution is diluted at osmotic equilibrium, *i.e.*, at constant T, μ_0, and μ_1 instead of constant T, p, and μ_1; this is the so-called dialysis method. In this case, the pressure p of the solution is different from the atmospheric pressure by the osmotic pressure. For polymer solutions of small c_2, this pressure difference is so small that its effect on the scattering intensity may be neglected; that is

$$R_\theta{}^* \simeq R_\theta{}^*(c_1{}^*,c_2|T,\mu_0,\mu_1) \qquad (6)$$

Further, the difference between $(\partial n/\partial c_2)_{p,\mu_1}$ and $(\partial n/\partial c_2)_{\mu_0,\mu_1}$ is of order $M_2{}^{-1}$ and is also negligibly small for polymer molecular weights of ordinary interest.[14] Thus we have

$$K^* \simeq \frac{2\pi^2n^2}{N_\mathrm{A}\lambda^4}\left(\frac{\partial n}{\partial c_2}\right)_{\mu_0,\mu_1}^2 \qquad (7)$$

$R_\theta{}^*$ and K^* are determined on the basis of eq 6 and 7.

Molecular Weights and Second Virial Coefficients. We first consider the osmotic pressure. If the osmotic membrane is permeable to species 0 and 1 but not to species 2, the osmotic pressure π may be expanded in powers of c_2 as follows

$$\pi(c_1{}^*,c_2|T,\mu_0,\mu_1) = RT(c_2/M_2 + A_2c_2{}^2 + \ldots) \qquad (8)$$

with R the gas constant. This is the defining equation for the second virial coefficient A_2. This coefficient is thermodynamically a function of T and $c_1{}^0$ (and also p), and may be expressed formally in terms of the McMillan-Mayer distribution functions.[27]

For light scattering, there are four possible basic equations to be considered for zero scattering angle $\theta = 0$. First, the conventional light-scattering method is based on the equation[2,3,19,20]

$$Kc_2/R_0 = 1/M_{2,\mathrm{ap}} + 2A_{2,\mathrm{ap}}c_2 + \ldots \qquad (9)$$

where R_0 is the value of R_θ at $\theta = 0$, and $M_{2,\mathrm{ap}}$ and $A_{2,\mathrm{ap}}$ are the (conventional) apparent molecular weight and apparent second virial coefficient, respectively. Yamakawa[16] has used the constant K_0 instead of K in the development of his theory. In this case, eq 9 should be replaced by

$$K_0c_2/R_0 = 1/M_{2,\mathrm{ap}}{}^{(\mathrm{Y})} + 2A_{2,\mathrm{ap}}{}^{(\mathrm{Y})}c_2 + \ldots \qquad (10)$$

This is, of course, the defining equation for $M_{2,\mathrm{ap}}^{(\mathrm{Y})}$ and $A_{2,\mathrm{ap}}^{(\mathrm{Y})}$. All apparent quantities in eq 9 and 10 are generally dependent on c_1^0. Third, the basic equation for the dialysis method is[11-14]

$$K^*c_2/R_0^* = 1/M_2 + 2(A_2 + \delta)c_2 + \ldots \qquad (11)$$

where δ is given by

$$\delta = \frac{RT}{2M_2^2}\left[\frac{V_1\phi_1^0}{m_1}\left(\frac{\partial\mu_1}{\partial m_1}\right)_{p,m_2=0}^{-1} + \kappa\right] \qquad (12)$$

with κ the isothermal compressibility of the mixed solvent.

Finally, we consider the ratio K^*c_2/R_0. The quantity R_0 may be expressed in terms of R_0^* as follows

$$R_0(c_1,c_2|T,p,c_1^0) = R_0^*(c_1,c_2|T,p,\mu_1') \qquad (13)$$

where on the right-hand side, the concentration of species 1 should be equal to c_1 (different from c_1^* of eq 4), and therefore its chemical potential differs from μ_1 and has been designated by μ_1'. Since c_1^0 is kept constant in the process indicated by R_0, μ_1' must be a function of c_1^0 and also c_2: μ_1' approaches μ_1 as c_2 becomes zero at constant c_1^0. We then have, from eq 11 and 13

$$K'c_2/R_0 = 1/M_2 + 2(A_2 + \delta)c_2 + \ldots \qquad (14)$$

where

$$K' = \frac{2\pi^2n^2}{N_A\lambda^4}\left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1'}^2 \qquad (15)$$

Strictly, A_2 must be changed slightly in going from eq 11 to 14, but its effect appears in the c_2^2 term of eq 14. Equation 14 may be rewritten in the form

$$K^*c_2/R_0 = (K^*/K')[1/M_2 + 2(A_2 + \delta)c_2 + \ldots] \qquad (16)$$

where

$$K^*/K' = \left[\left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1}\Big/\left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1'}\right]^2 \qquad (17)$$

Now, from thermodynamics, we have

$$\left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1'} = \left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1} + c_2\left(\frac{\partial\mu_1}{\partial c_2}\right)_{p,c_1^0}\left(\frac{\partial\mu_1}{\partial c_1^0}\right)_{p,c_2=0}^{-1} \times \left[\frac{\partial}{\partial c_1^0}\left(\frac{\partial n}{\partial c_2}\right)_{p,\mu_1}\right]_p + \ldots \qquad (18)$$

Substitution of eq 17 and 18 into eq 16 leads to

$$K^*c_2/R_0 = 1/M_2 + 2(A_2 + \delta + \Delta/M_2)c_2 + \ldots \qquad (19)$$

with

$$\Delta = -\left(\frac{\partial\mu_1}{\partial c_2}\right)_{p,c_1^0}\left(\frac{\partial\mu_1}{\partial c_1^0}\right)_{p,c_2=0}^{-1}\left(\frac{\partial n}{\partial c_2}\right)_{\mu_0,\mu_1}^{-1}\left[\frac{\partial}{\partial c_1^0}\left(\frac{\partial n}{\partial c_2}\right)_{\mu_0,\mu_1}\right]_p \qquad (20)$$

This is the fourth basic equation. We note that in eq 20 the subscript pair p, μ_1 has been replaced by μ_0, μ_1 with negligible error as in eq 7.

Now, in plots of Kc_2/R_0 against c_2, the ratio (slope)/(intercept) is independent of K, assuming that K is independent of c_2. This is also the case for the square-root plots of Berry ($(Kc_2/R_0)^{1/2}$ vs. c_2).[28] We therefore obtain, from eq 9, 10, and 19

$$A_{2,\mathrm{ap}}M_{2,\mathrm{ap}} = A_{2,\mathrm{ap}}^{(\mathrm{Y})}M_{2,\mathrm{ap}}^{(\mathrm{Y})} = A_2M_2 + \delta M_2 + \Delta \qquad (21)$$

In the distribution-function theory,[16] we have already shown that under the condition given by eq 1

$$A_{2,\mathrm{ap}}^{(\mathrm{Y})}M_{2,\mathrm{ap}}^{(\mathrm{Y})} \simeq A_2M_2 \qquad (22)$$

so that under the same condition

$$A_{2,\mathrm{ap}}M_{2,\mathrm{ap}} \simeq A_2M_2 \qquad (23)$$

As mentioned in the introduction, this condition is a sufficient one but not a necessary one; and thus it is not helpful in examining the accuracy of eq 22 or 23. This can be done more explicitly by performing order estimation of the quantities δ and Δ in eq 21.

For this purpose, we need derivatives of μ_1. If we adopt the Flory-Huggins theory[29] for three-component systems, μ_1 may be expressed in the form

$$\mu_1 - \mu_1^0 = kT\{\ln\phi_1 + \phi_2 + \chi_{12}(1 - \phi_1)\phi_2 + [\chi_{01}(1 - \phi_1) - \chi_{02}\phi_2](1 - \phi_1 - \phi_2)\} \qquad (24)$$

where k is the Boltzmann constant, μ_1^0 is the chemical potential of pure species 1, χ_{ij} are the thermodynamic interaction parameters, and we have assumed that $V_0 = V_1 \ll V_2$, for simplicity. The required derivatives of μ_1 may be calculated from eq 24 using eq 2 for the concentrations in various units. Substitution of the results into eq 12 and 20 leads to

$$\delta = \frac{1}{2M_2^2}\left\{\frac{N_AV_1\phi_1^0}{(1 - \phi_1^0)[1 - 2\chi_{01}(1 - \phi_1^0)\phi_1^0]} + RT\kappa\right\} \qquad (25)$$

$$\Delta = \frac{\bar{v}_2\phi_1^0(1 - \phi_1^0)[\chi_{01}(1 - 2\phi_1^0) + \chi_{02} - \chi_{12}]}{\bar{v}_1[1 - 2\chi_{01}(1 - \phi_1^0)\phi_1^0]} \times \left(\frac{\partial n}{\partial c_2}\right)_{\mu_0,\mu_1}^{-1}\left[\frac{\partial}{\partial c_1^0}\left(\frac{\partial n}{\partial c_2}\right)_{\mu_0,\mu_1}\right]_p \qquad (26)$$

Note that $\phi_1^0 \neq 1$ since the hybrid ensemble with $\phi_0^0 \neq 0$ has been used in the derivation of eq 12. Now, the quantity $RT\kappa$ is of order unity, and unless ϕ_1^0 is close to unity, the first term in curly brackets of eq 25 is of order 1–10 since χ_{ij} are of order 10^{-1}–1. Therefore, if $M_2 \gtrsim 10^4$, δ is at most of order 10^{-7}. In general, A_2 is of order 10^{-4} for good-solvent systems, and is measurable down to order 10^{-6} near the Θ temperature at which A_2 vanishes. Thus, δ is always negligibly small compared to A_2 provided M_2 is not small; and in what follows, it is omitted. If $(\partial n/\partial c_2)_{\mu_0,\mu_1} = 0(10^{-1})$, $(\partial/\partial c_1^0)(\partial n/\partial c_2)_{\mu_0,\mu_1} = 0(1)$, and $\chi_{01} > 1$, as is sometimes possible, then Δ is positive and possibly of order unity. Therefore, under certain conditions, Δ is not negligibly small compared to A_2M_2, which is of order 10^{-2}–10^2. Thus, neither $A_{2,\mathrm{ap}}$ nor $A_{2,\mathrm{ap}}^{(\mathrm{Y})}$ vanishes at the Θ temperature; and the Θ temperature can be determined exactly only from the plots based on eq 11. We note that Vrij and Overbeek[13] have derived eq 23 with the exact equility sign, neglecting Δ.

Mean-Square Radius. In the distribution-function theory,[16] we have shown that under the condition given by eq 1

$$(K_0c_2/R_\theta)_0 = (1/M_{2,\mathrm{ap}}^{(\mathrm{Y})})[1 + C\langle S^2\rangle\sin^2(\theta/2) + \ldots] \qquad (27)$$

where $C = 16\pi^2/3(\lambda')^2$ with λ' the wavelength of the light in the solution, $\langle S^2\rangle$ is the mean-square radius of the polymer chain, and $()_0$ indicates infinite dilution with respect to the polymer. In plots of $(Kc_2/R_\theta)_0$ against $\sin^2(\theta/2)$ or its square-root plots, the ratio (slope)/(intercept) is again independent of K. We therefore have

$$(Kc_2/R_\theta)_0 = (1/M_{2,\mathrm{ap}})[1 + C\langle S^2\rangle\sin^2(\theta/2) + \ldots] \qquad (28)$$

Thus, $\langle S^2\rangle$ may be determined from the conventional Zimm plot, or more accurately from the conventional Berry plot. However, the accuracy of this method cannot be examined directly; and we must resort to an indirect examination.

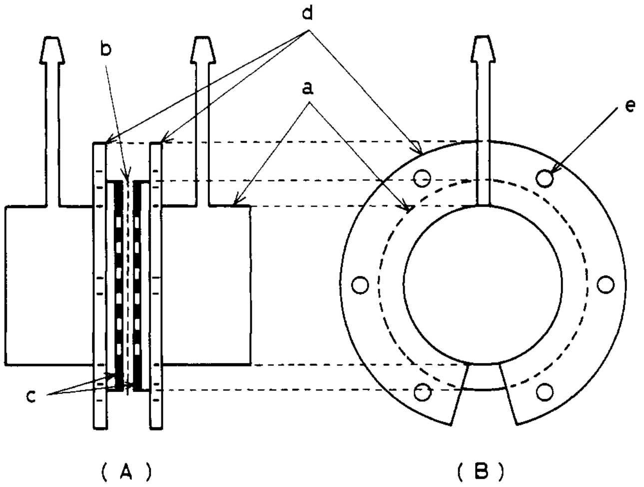

Figure 1. Front view (A) and side view (B) of dialyzer: (a) cell of dialyzer; (b) membrane; (c) perforated Teflon disk supporting membrane; (d) bakelite clamp; (e) bolt hole.

Experimental Section

Materials. All polystyrene samples other than VII-2, VII-3, and X are the same as those previously prepared anionically in tetrahydrofuran and used for the test of the two-parameter theory.[24] Sample X was newly prepared for the present study according to the same procedure. Samples VII-2 and VII-3 are two middle fractions of four fractions of the whole polymer VII previously prepared; and as for sample X, the middle of three fractions of the whole polymer was used. This fractionation was carried out by the addition of methanol to the 0.1–0.3% solution in toluene at 30°. Each of these three new samples was dissolved in toluene, filtered through a 30-μ-sintered glass filter, precipitated into methanol, and dried by evacuation at 50°, as before. Every sample may be considered to have a fairly sharp distribution in molecular weight, and there is no necessity of heterogeneity corrections. The molecular weights M_2 of the three new samples were determined from light-scattering measurements in benzene at 30° for the purpose of characterization.

Light-scattering and viscosity measurements were carried out in benzene (species 0)-cyclohexane (species 1) mixtures of $\phi_1{}^0$ = 0.2, 0.5, and 0.8 at 30°, and in a benzene (species 0)-isopropyl alcohol (species 1) mixture of $\phi_1{}^0$ = 0.36 at temperatures ranging from 23 to 40°. The two components of each mixed solvent have nearly the same boiling point, and thereby the change of its composition due to evaporation could be minimized. Benzene and cyclohexane were purified according to standard procedures, and fractionally distilled. Isopropyl alcohol was refluxed over barium monoxide for 1 day, and fractionally distilled. For the densities of single solvents at temperatures of measurement, literature values[30] were used. The densities of mixed solvents were measured pycnometrically. The results for benzene-cyclohexane mixtures at 30° are 0.84492 (0.84836) (g/ml) for $\phi_1{}^0$ = 0.2, 0.81332 (0.81883) for $\phi_1{}^0$ = 0.5, and 0.78514 (0.78929) for $\phi_1{}^0$ = 0.8, and the results for a benzene-isopropyl alcohol mixture of $\phi_1{}^0$ = 0.36 are 0.83211 (0.83523) at 30° and 0.82172 (0.82538) at 40°, the numbers in parentheses being the values calculated assuming the additivity. Refractive indices of single solvents for light of wavelength 436 mμ were calculated using the Lorenz-Lorentz equation as before.[31] The results obtained at 30° are 1.515_5 for benzene, 1.429_6 for cyclohexane, and 1.381_1 for isopropyl alcohol. Refractive indices of mixed solvents were also calculated using the Lorenz-Lorentz equation and assuming the additivity of molar refractions. The results for benzene-cyclohexane mixtures at 30° are 1.495_5 for $\phi_1{}^0$ = 0.2, 1.468_2 for $\phi_1{}^0$ = 0.5, and 1.446_4 for $\phi_1{}^0$ = 0.8, and the results for a benzene-isopropyl alcohol mixture of $\phi_1{}^0$ = 0.36 are 1.463_5 at 30° and 1.456_8 at 40°.

In order to prepare the most concentrated stock solutions of the polymers in mixed solvents, *ca.* 1.2 g of each sample was dissolved in *ca.* 100 ml of a given mixed solvent of composition $\phi_1{}^0$, and the solution obtained was stirred continuously for 1–2 days at room temperature in case of benzene-cyclohexane mixtures, or for 5–7 days at 40° in case of benzene-isopropyl alcohol mixtures. Each stock solution was sequentially diluted with the mixed solvent of the same composition $\phi_1{}^0$ to obtain test solutions of various concentrations c_2. A part of each test solution was used for conventional light-scattering, refractive index increment, and viscosity measurements; and the remaining was dialyzed, followed by light-scattering and refractive index increment measurements. The concentrations c_2 of the most concentrated solutions were determined gravimetrically, and those of all diluted solutions were determined from known dilution factors.

Table I
Refractive Index Increment of Polystyrene in Mixed Solvents at 30° for Wavelength 436 mμ

Sample	$\phi_1{}^0$	$(\partial n/\partial c_2)_{p,\phi_1{}^0}$ (ml/g)	$(\partial n/\partial c_2)_{\mu_0,\mu_1}$ (ml/g)
Benzene (0) + Cyclohexane (1)			
VIII	0.20		0.142
	0.50		0.156
	0.80		0.177
VII-3	0.20	0.138	0.142
	0.50	0.150	0.159
	0.80	0.166	0.175
Benzene (0) + Isopropyl Alcohol (1)			
VIII	0.36		0.216
X	0.36		0.216
VII-2	0.36	0.150	0.216

Dialysis. In order to measure refractive index increments and excess scattering intensities R_θ^* of solutions of various c_2 but with the same μ_0 and μ_1, each test solution was dialyzed. The dialyzer constructed for this purpose is depicted in Figure 1. It is composed of two parts fitted with an adequately conditioned gel-cellophane membrane, each part having a capacity of *ca.* 120 ml and having a capillary tube with scales. The procedure of dialysis is as follows. A solution of concentration ($\phi_1{}^0$, c_2) is poured into the cell through one capillary tube, and a mixed solvent of composition $\phi_1{}^0$ through the other, to fill about one-tenth of each capillary. The two capillary tubes are connected by a silicone tube, and the cell is placed in a bath regulated at temperature T (°C) within ±0.015°. The mixed solvent is replaced by a new one of the same composition $\phi_1{}^0$, and the cell is shaken to make the composition uniform. This is done twice a day. The osmotic pressure gives rise to a difference between heads in the capillaries, but the head of the solution is kept approximately constant so that the volume of the solution and therefore the value of c_2 remains practically unchanged. The attainment of equilibrium requires several days. This may be examined by measuring the change of the refractive index increment of the solution in dialysis with time.

Refractive Index Increment. Refractive index increment measurements were carried out at 30° with 436-mμ light, using a differential refractometer of the Debye type fitted with a cell of the Schulz–Bodmann–Cantow type.[32] The specific increment $(\partial n/\partial c_2)_{p,c_10}$, or $(\partial n/\partial c_2)_{p\phi_10}$, may be considered to be independent of M_2, and its values were obtained only for samples VII-2 and VII-3. For $(\partial n/\partial c_2)_{p,\phi_10}$ in benzene ($\phi_1{}^0$ = 0), we adopted the value of 0.115 (ml/g) obtained previously by Yamamoto *et al.*[24] Now we may write

$$\left(\frac{\partial n}{\partial c_2}\right)_{\mu_0,\mu_1} = \left(\frac{\partial n}{\partial c_2}\right)_{p,\phi_1{}^0} + \lambda\left(\frac{\partial n}{\partial \phi_1}\right)_{p,c_2=0} \tag{29}$$

where λ is the preferential-adsorption coefficient given by

$$\lambda = \left(\frac{\partial \phi_1}{\partial c_2}\right)_{p,\mu_1} \tag{30}$$

The experimental results obtained by Dondos and Benoit[7] show that the λ determined from the ratio $M_{2,\mathrm{ap}}/M_2$ depends on M_2. This means that $(\partial n/\partial c_2)_{\mu_0,\mu_1}$ depends on M_2. Therefore, values of this increment were obtained for all samples on which light-scattering measurements were carried out.

Light Scattering. Light-scattering measurements were carried out in a Shimazu photometer with a cylindrical cell to obtain values of R_θ and R_θ^*. The apparatus was calibrated according to the same procedure as before,[24,31] taking the Rayleigh ratio of pure benzene at 30° as 49.5 × 10^{-6} for light of wavelength 436 mμ.[33] Optical purification of the most concentrated solutions for measurements of R_θ, all solutions for measurements of R_θ^*, and solvents was carried out by centrifugation at 20,000 rpm for 1 hr using a Marusan centrifuge. All measurements were carried out with unpolarized light of wavelength 436 mμ, and data were obtained for four polymer concentrations c_2 for scattering angles θ

Table II
Molecular Weight Data for Polystyrene in Mixed Solvents at 30°

Sample	ϕ_1^0	$M_2 \times 10^{-4}$	$M_{2,ap} \times 10^{-4}$	$M_{2,ap}^{(Y)} \times 10^{-4}$	$M_{2,ap}/M_2$	$M_{2,ap}^{(Y)}/M_2$
		Benzene (0) + Cyclohexane (1)				
VIII	0	287[a]				
	0.20	268	282	406	1.05	1.51
	0.50	303	342	582	1.13	1.92
	0.80	297	335	698	1.13	2.35
VII-3	0	70.5				
	0.20	69.8	73.3	106	1.05	1.52
	0.50	75.6	92.0	157	1.22	2.08
		Benzene (0) + Isopropyl Alcohol (1)				
VIII	0	287[a]				
	0.36	295	630	1072	2.13	3.63
X	0	144				
	0.36	150	303	515	2.02	3.43
VII-2	0	72.1				
	0.36	75.5	175	298	2.31	3.95

[a] Data obtained by Yamamoto *et al.*[24]

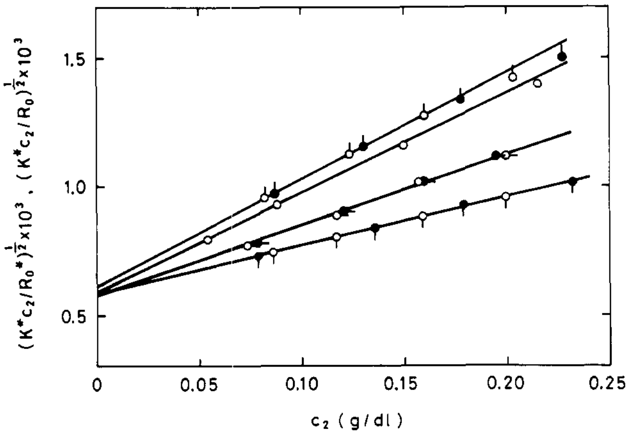

Figure 2. Square-root plots of K^*c_2/R_0^* and K^*c_2/R_0 against c_2 for sample VIII in benzene-cyclohexane mixtures at 30°: open circles with pips, R_0^*; filled circles with pips, R_0; ȯ, ●, ϕ_1^0 = 0.20; ○-, ●-, ϕ_1^0 = 0.50; ọ, ●, ϕ_1^0 = 0.80. The open circles without pips indicate the data in benzene at 30°.

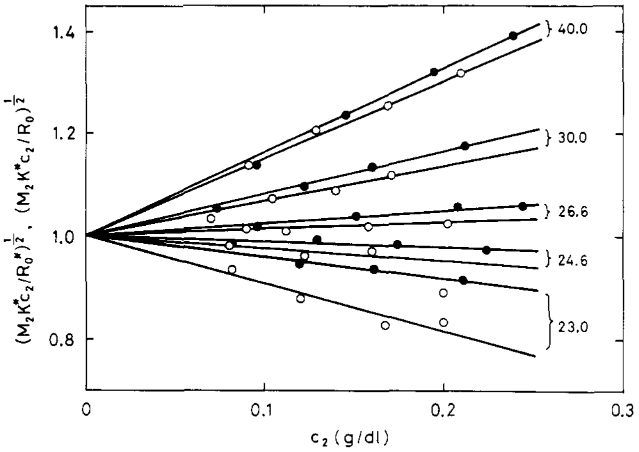

Figure 3. Reduced square-root plots of $M_2K^*c_2/R_0^*$ and $M_2K^*c_2/R_0$ against c_2 for sample VIII in a benzene-isopropyl alcohol mixture of ϕ_1^0 = 0.36: open circles, R_0^*; filled circles, R_0. The numbers attached to the lines indicate the temperatures (°C) of measurement.

from 35 to 145°. The sample temperature was held to ±0.05° over the range of temperature from 23 to 40°.

Treatment of data was made according to the procedure of Berry,[28] *i.e.*, by the square-root plot of Kc_2/R_θ against c_2 and $\sin^2(\theta/2)$. For samples in a benzene-isopropyl alcohol mixture, values of A_2M_2, $A_{2,ap}M_{2,ap}$, A_2, and $\langle S^2\rangle$ were obtained at various temperatures, though values of M_2 and $M_{2,ap}$ were obtained only at 30°, at which the apparatus was calibrated. This is again because of the fact that in the square-root plots, the ratio (slope)/(intercept) is independent of K.

Viscosity. In order to examine the validity of the two-parameter scheme in mixed-solvent systems, viscosity measurements were also carried out using a viscometer of the Ubbelohde type at the same temperatures as those for the light-scattering measurements. The solutions were diluted conventionally with the mixed solvents of the compositions ϕ_1^0. The sample temperature was held to ±0.02°. No kinetic-energy and shear-rate corrections were applied. The data were extrapolated to infinite dilution to determine intrinsic viscosities $[\eta]$, plotting η_{sp}/c_2 against c_2, and also $(\ln \eta_r)/c_2$ against c_2, where η_{sp} and η_r are the specific and relative viscosities of the solutions, respectively.

Results

Table I summarizes values of $(\partial n/\partial c_2)_{p,\phi_1^0}$ and $(\partial n/\partial c_2)_{\mu_0,\mu_1}$ as functions of ϕ_1^0 obtained for polystyrene samples in benzene-cyclohexane and benzene-isopropyl alcohol mixtures at 30° for wavelength 436 mμ. The results show no marked dependence on M_2 of $(\partial n/\partial c_2)_{\mu_0,\mu_1}$ over the range studied.

Table II summarizes molecular weight data obtained from light-scattering measurements on polystyrene samples in benzene and mixed solvents at 30°. The values of M_2 in mixed solvents were obtained by the dialysis method, *i.e.*, from the intercepts of plots of $(K^*c_2/r_0^*)^{1/2}$ against c_2. The table includes also values of the ratios $M_{2,ap}/M_2$ and $M_{2,ap}^{(Y)}/M_2$, where we used the values of M_2 obtained in mixed solvents. Figure 2 shows plots of $(K^*c_2/R_0^*)^{1/2}$ against c_2 (open circles with pips) and $(K^*c_2/R_0)^{1/2}$ against c_2 (filled circles with pips) for sample VIII in benzene-cyclohexane mixtures at 30°, including the conventional (square-root) plots in benzene (open circles). Values of A_2M_2 and $A_{2,ap}M_{2,ap}$ may be obtained from the ratios (slope)/(intercept) of the respective plots in mixed solvents. Figure 3 shows similar plots for sample VIII in a benzene-isopropyl alcohol mixture of ϕ_1^0 = 0.36 at temperatures ranging from 23 to 40°, where the intercepts have been reduced to unity. In this case, values of A_2M_2 and $A_{2,ap}M_{2,ap}$ may be obtained from the slopes of the respective plots. Their values thus determined for all samples in mixed solvents are given in Table III.

Table IV summarizes light-scattering and viscosity data for samples VII-3 and VIII in benzene-cyclohexane mixtures and samples VII-2 and X in benzene at 30°, including also viscosity data for samples III and V of Yamamoto *et al.*[24] Similarly, Table V summarizes light-scattering and viscosity data for samples VII-2, VIII, and X in a benzene-isopropyl alcohol mixture of ϕ_1^0 = 0.36 at various

Table III
Data for the Reduced Second Virial Coefficient of Polystyrene in Mixed Solvents

Sample	Temp (°C)	ϕ_1^0	A_2M_2	$A_{2,\mathrm{ap}}M_{2,\mathrm{ap}}$
	Benzene (0) + Cyclohexane (1)			
VIII	30.0	0.20	668	662
	30.0	0.50	504	517
	30.0	0.80	322	324
VII-3	30.0	0.20	232	232
	30.0	0.50	179	193
	Benzene (0) + Isopropyl Alcohol (1)			
VIII	40.0	0.36	151	163
	30.0	0.36	69.2	82.6
	26.6	0.36	14.3	24.3
	24.6	0.36	−23.3	−10.6
	23.0	0.36	−91.9	−40.5
X	40.0	0.36	96.2	103
	30.0	0.36	38.6	40.7
	26.6	0.36	21.0	31.6
	24.6	0.36	−18.1	−3.67
	23.0	0.36	−45.6	−37.5
VII-2	40.0	0.36	53.8	59.2
	30.0	0.36	21.6	26.4
	26.6	0.36	7.21	11.5
	24.6	0.36		
	23.0	0.36	−19.4	−14.1

Table IV
Light-Scattering and Intrinsic Viscosity Data for Polystyrene in Benzene–Cyclohexane Mixtures at 30°

Sample	ϕ_1^0	$A_2 \times 10^4$ (ml mol/g^2)	$\langle S^2\rangle \times 10^{12}$ (cm^2)	$[\eta]$ (dl/g)
VIII	0	2.26[a]	68.7[a]	6.17[a]
	0.20	2.33	64.3	5.71
	0.50	1.76	57.9	4.99
	0.80	1.12	46.3	3.39
VII-3	0	3.46	13.2	2.30
	0.20	3.29	13.3	2.16
	0.50	2.54	12.7	1.92
V[b]	0.20			1.25
	0.50			1.14
	0.80			0.858
III[c]	0.20			0.982
	0.50			0.880
	0.80			0.678
X	0	2.87	29.5	3.70
VII-2	0	3.36	14.0	2.30

[a] Data obtained by Yamamoto *et al.*[24] [b] $M_2 = 34.2 \times 10^4$ (see ref 24). [c] $M_2 = 24.6 \times 10^4$ (see ref 24).

Table V
Light-Scattering and Intrinsic Viscosity Data for Polystyrene in a Benzene–Isopropyl Alcohol Mixture of ϕ_1^0 = 0.36

Sample	Temp (°C)	$A_2 \times 10^4$ (ml mol/g^2)	$\langle S^2\rangle \times 10^{12}$ (cm^2)	$[\eta]$ (dl/g)
VIII	40.0	0.526	35.5	2.55
	30.0	0.241	30.8	2.07
	26.6	0.050	27.7	1.87
	24.6	−0.081	26.0	1.75
	23.0	−0.320	24.7	1.61
X	40.0	0.715	18.5	1.71
	30.0	0.268	16.1	
	26.6	0.219	15.2	1.34
	24.6	−0.026	14.2	1.28
	23.0	−0.260	13.4	1.19
VII-2	40.0	0.746	8.59	1.13
	30.0	0.300	7.90	0.974
	26.6	0.100	7.26	0.930
	24.6			
	23.0	−0.269	6.55	0.870

Table VI
Mean-Square Radii and Intrinsic Viscosities in a Benzene–Isopropyl Alcohol Mixture of ϕ_1^0 = 0.36 at the Θ Temperature (25.5°)

Sample	$\langle S^2\rangle_0 \times 10^{12}$ (cm^2)	$\langle S^2\rangle_0/M_2 \times 10^{18}$	$[\eta]_\theta$ (dl/g)	$[\eta]_\theta/M_2^{1/2} \times 10^4$
VIII	27.1	9.44	1.80	10.6
X	14.5	10.0	1.30	10.8
VII-2	7.1	9.85	0.915	10.8
V[a]			0.591[b]	10.1
III[a]			0.488[b]	9.84

[a] See Table IV. [b] From direct measurements at the Θ temperature.

temperatures. The values of A_2 in these tables were obtained by dividing the values of A_2M_2 by the values of M_2 in benzene.

Discussion

Molecular Weights. The molecular weight data in Table II show that the true molecular weight M_2 may be determined fairly accurately from light-scattering measurements in mixed solvents if the dialyzed solutions are used, as required by the theory. The accuracy depends on the dialysis technique. For the determination of M_2 only, dialysis is necessary only for refractive index increment measurements, and not for scattering-intensity measurements, as seen from eq 19. From Table II, it is seen that the ratio $M_{2,\mathrm{ap}}/M_2$, whose deviation from unity is a simple measure of the preferential adsorption, is larger in benzene–isopropyl alcohol mixtures than in benzene-cyclohexane mixtures. For the systems we studied, $M_{2,\mathrm{ap}}$ is always greater than M_2, and the change of the sign of λ at some ϕ_1^0 does not occur, as already known,[4-6] though it has been observed in several systems.[8,34,35]

Now, comparing the values of the two molecular weight ratios given in the last two columns of Table II, it is seen that under the condition given by eq 1, the ratio $M_{2,\mathrm{ap}}/M_2$ is nearly equal to unity and there is no detectable effect of the preferential adsorption. Therefore, this condition on $M_{2,\mathrm{ap}}{}^{(\mathrm{Y})}/M_2$ derived in the distribution-function theory is not helpful but trivial from the practical point of view.

Second Virial Coefficients. From Figures 2 and 3 and Table III, it is seen that the equality of eq 23 holds in benzene-cyclohexane mixtures within experimental uncertainty, while in benzene-isopropyl alcohol mixtures, it breaks down and the quantity Δ in eq 21 is positive and not negligibly small. This result may rather be expected, since the ratio $M_{2,\mathrm{ap}}/M_2$ does not appreciably deviate from unity in the former and is large in the latter, and moreover, the difference Δ is exaggerated in poor or theta solvent systems with small A_2. Figure 4 shows plots of A_2M_2 (open circles) and $A_{2,\mathrm{ap}}M_{2,\mathrm{ap}}$ (filled circles) against temperature T (°C) for samples VII-2, VIII, and X in a benzene–isopropyl alcohol mixture of $\phi_1^0 = 0.36$. Let Θ be the temperature at which A_2 vanishes, as usual, and let Θ_{ap} be the temperature at which $A_{2,\mathrm{ap}}$ vanishes. Then, Θ and Θ_{ap} are seen to be both independent of M_2 but differ slightly from each other. Our estimates for this system are $\Theta = 25.5°$ and $\Theta_{\mathrm{ap}} = 25.0°$. This value for Θ_{ap} agrees with the corresponding value obtained by Elias and Etter[36] for the same system. We note that the present authors are among the first to measure both K^* and $R_\theta{}^*$ and determine Θ in mixed-solvent systems.

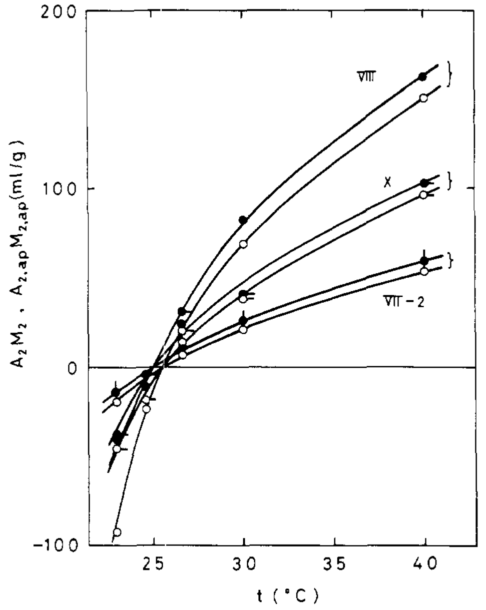

Figure 4. Temperature dependence of A_2M_2 and $A_{2,ap}M_{2,ap}$ for samples VII-2, VIII, and X in a benzene-isopropyl alcohol mixture of $\phi_1^0 = 0.36$: open circles, A_2M_2; filled circles, $A_{2,ap}M_{2,ap}$.

Preferential Adsorption. We first consider the effect of the nonsolvent on the unperturbed molecular dimension of the polymer. Values of the unperturbed mean-square radius $\langle S^2\rangle_0$ and the intrinsic viscosity $[\eta]_\theta$ in a benzene-isopropyl alcohol mixture of $\phi_1^0 = 0.36$ at the Θ temperature (25.5°) are given in Table VI, where the values for samples VII-2, VIII, and X were obtained by interpolation, and the values of M_2 obtained in benzene were used. For these three samples with high molecular weights, the constancies of the ratios $\langle S^2\rangle_0/M_2$ and $[\eta]_\theta/M_2^{1/2}$ are observed within experimental uncertainty, and we assign the following values

$$\langle S^2\rangle_0/M_2 = 9.76 \times 10^{-18} \tag{31}$$

$$[\eta]_\theta/M_2^{1/2} = 10.7 \times 10^{-4} \quad (\text{for } M_2 \gtrsim 7 \times 10^5) \tag{32}$$

Both of these values are definitely greater than the corresponding values of 8.4×10^{-18} and 9.1×10^{-4} obtained previously[24] in cyclohexane at the Θ temperature, 34.6°. However, the value of 2.4×10^{21} for the Flory-Fox viscosity constant Φ_0 (at $T = \Theta$) calculated from eq 31 and 32 is very close to the corresponding value of 2.5×10^{21} in cyclohexane. The results indicate the strong dependence of the unperturbed dimension on solvent. This is rather natural, since our mixed Θ solvent contains the polar nonsolvent.

Figure 5 shows the Stockmayer-Fixman plots of $[\eta]/M_2^{1/2}$ against $M_2^{1/2}$ for polystyrene samples in benzene-cyclohexane mixtures at 30° and in a benzene-isopropyl alcohol mixture of $\phi_1^0 = 0.36$ at the Θ temperature, including also the previous data[24] obtained in cyclohexane at the Θ temperature. In the case of benzene-cyclohexane mixtures, extrapolations to $M_2 = 0$ were carried out to give the same intercept as that in cyclohexane within experimental uncertainty, as shown in the figure. We note that Dondos and Benoit[37] have reported the disagreement between the intercepts for these two systems. However, the most remarkable result of Figure 5 is that in a benzene-isopropyl alcohol mixture at the Θ temperature, $[\eta]_\theta/M_2^{1/2}$ first increases with increasing M_2 and then becomes constant for $M_2 \gtrsim 7 \times 10^5$. This initial increase is consistent with the results found by Dondos and Benoit[18] for several mixed Θ solvent systems, though they have not obtained data in the range of large M_2 where $[\eta]_\theta/M_2^{1/2}$ might level off. Thus it is clear that the two-parameter scheme breaks down for small M_2. Dondos and Benoit[18] have suggested the existence of two Θ temperatures in the same system; at one A_2 vanishes, and at the other the slope of the Stockmayer-Fixman plot vanishes.

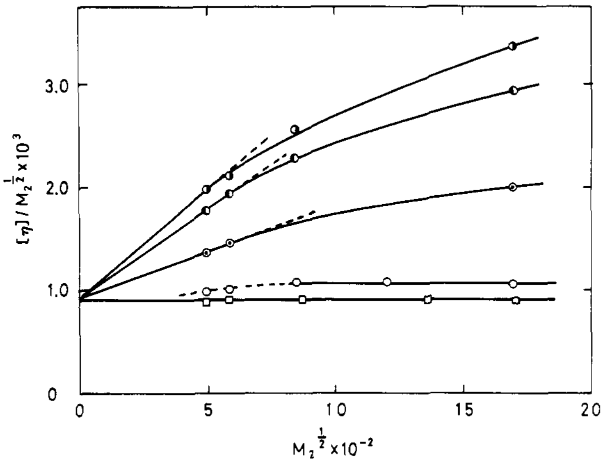

Figure 5. Stockmayer-Fixman plots for polystyrene samples in benzene-cyclohexane mixtures of ϕ_1^0 = 0.20 (◑), 0.50 (◐), and 0.80 (⊙) at 30°, in a benzene-isopropyl alcohol mixture of ϕ_1^0 = 0.36 (○) at 25.5° (Θ), and in cyclohexane (□) at 34.6° (Θ).[24]

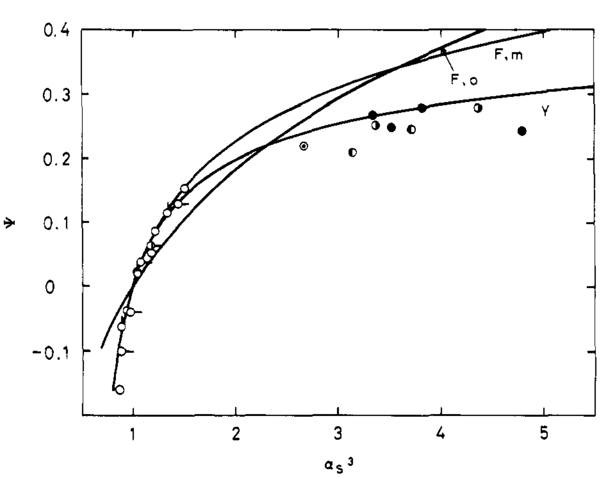

Figure 6. Plots of Ψ against α_S^3 for polystyrene samples in benzene (●) at 30°, in benzene-cyclohexane mixtures of ϕ_1^0 = 0.20 (◑), 0.50 (◐), and 0.80 (⊙) at 30°, and in a benzene-isopropyl alcohol mixture of ϕ_1^0 = 0.36 (○, ○-, ○) at various temperatures. The three curves represent the values predicted by the theories cited in the text.

Now, it appears that the dependence of $[\eta]_\theta/M_2^{1/2}$ on M_2 corresponds to the dependence of λ on M_2; λ decreases with increasing M_2 in the range where $[\eta]_\theta/M_2^{1/2}$ increases, and λ levels off in the range where $[\eta]_\theta/M_2^{1/2}$ levels off. Therefore, the anomalous behavior of $[\eta]_\theta/M_2^{1/2}$ suggests that the intramolecular and intermolecular binary-cluster integrals β differ from each other for small M_2 because of the strong preferential adsorption. This anomaly may also be regarded as arising from the change of the solvent effect on the unperturbed dimension through the dependence on M_2 of the preferential adsorption. In order to draw a definite conclusion, further investigations will be needed.

Test of the Two-Parameter Theory and Mean-Square Radii. As far as the Stockmayer-Fixman plot is concerned, the two-parameter scheme may be regarded as valid for $M_2 \gtrsim 7 \times 10^5$ in the present systems, as seen above. Thus, we proceed to make a more direct examination of the validity of the two-parameter theory of the ex-

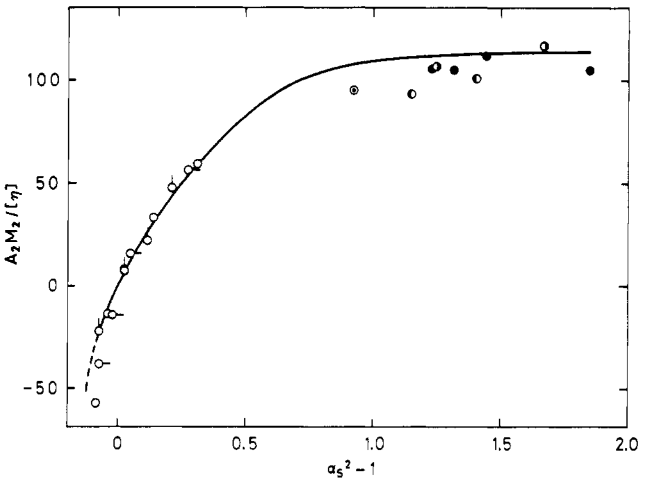

Figure 7. Plots of $A_2M_2/[\eta]$ against $\alpha_S^2 - 1$ for polystyrene. The symbols have the same significance as those in Figure 6. The curve represents the best fit to the data obtained for polystyrene in single solvents.[24]

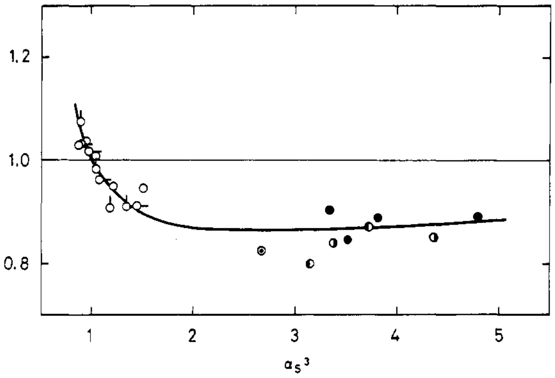

Figure 8. Plots of Φ/Φ_0 against α_S^3 for polystyrene. The symbols have the same significance as those in Figure 6. The curve represents the best fit to the data obtained for polystyrene in single solvents.[24]

cluded-volume effect in mixed-solvent systems over this range of M_2, as in the case of single-solvent systems.[21,22,24,31,38-42] In order to estimate the expansion factors α_S and α_η defined by $\alpha_S^2 = \langle S^2\rangle/\langle S^2\rangle_0$ and $\alpha_\eta^3 = [\eta]/[\eta]_\theta$, we adopted the values of $\langle S^2\rangle_0$ and $[\eta]_\theta$ obtained in cyclohexane[24] in case of benzene-cyclohexane mixtures, and the values given by eq 31 and 32 in case of a benzene-isopropyl alcohol mixture, considering the results displayed in Figure 5. Further, we used the values of M_2 obtained in benzene.

We begin by examining the behavior of the function Ψ defined by

$$\Psi = A_2M_2^2/4\pi^{3/2}N_A\langle S^2\rangle^{3/2} \qquad (33)$$

Values of Ψ calculated from eq 33 with observed values of M_2, A_2, and $\langle S^2\rangle$ given in the tables are plotted against the corresponding values of α_S^3 in Figure 6. Curves F,o, F,m, and Y represent the theoretical values predicted by the original Flory-Krigbaum-Orofino theory[43,44] of Ψ combined with the original Flory theory[45] of α_S, the modified Flory-Krigbaum-Orofino theory[43,44,46] of Ψ combined with the modified Flory theory[45,46] of α_S, and the Kurata-Yamakawa theory[47,48] of Ψ combined with Yamakawa-Tanaka theory[49] of α_S, respectively. This figure should be compared with Figure 4 of ref 24, which shows a similar analysis for the same polystyrene samples in single solvents. Both results are seen to be consistent within experimental uncertainty. Figure 7 shows plots of $A_2M_2/[\eta]$ against $\alpha_S^2 - 1$. The curve represents the best fit to the data for the same samples in single solvents.[24] A similar consistency of the data in single and mixed solvents is also observed for the viscosity-radius expansion factor α_η. Values of the ratio of the viscosity constant Φ to its unperturbed value calculated from the equation, $\Phi/\Phi_0 = \alpha_\eta^3/\alpha_S^3$, are plotted against the corresponding values of α_S^3 in Figure 8. Figure 9 shows plots of α_η^3 against the well-known excluded-volume parameter z defined by

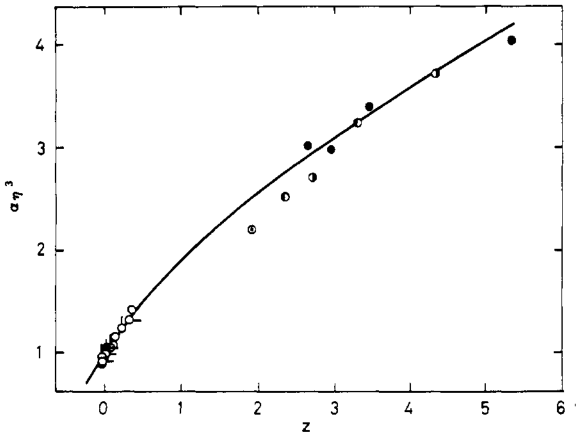

Figure 9. Plots of α_η^3 against z for polystyrene, where the values of z were calculated from the values of α_S using eq 35. The symbols have the same significance as those in Figure 6. The curve represents the best fit to the data obtained for polystyrene in single solvents.[24]

$$z = (4\pi\langle S^2\rangle_0)^{-3/2}\beta N^2 \qquad (34)$$

with N the number of segments in the polymer chain. Here, the values of z for the data points were determined from the values of α_S using the Yamakawa-Tanaka equation[49]

$$\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \qquad (35)$$

The curves in Figures 8 and 9 represent the respective best fits to the data for the same samples in single solvents.[24]

From the analysis displayed in Figures 6-9, we may conclude that the two-parameter theory works well in mixed-solvent systems as well as in single-solvent systems provided M_2 is so large that $[\eta]_\theta/M_2^{1/2}$ is independent of M_2. This also implies that our procedure of determining $\langle S^2\rangle$ is correct, though there are no direct means of examining its validity. In conclusion, we emphasize that our method of determining $\langle S^2\rangle$ is valid in a range wider than that for which the equality of eq 23 holds, and that this equality holds in a range much wider than that given by eq 1.

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Light Scattering from Wormlike Chains. Determination of the Shift Factor

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ABSTRACT: The light-scattering form factor of wormlike chains without excluded volume is evaluated by the use of the Hermite polynomial expansion of the distribution function. The good convergence is obtained in the practically important range by taking account of the moments $\langle R^{2m} \rangle$ with m = 1-11. Evaluation of the latter is carried out by the operational method. The final results are obtained only numerically by the use of a digital computer. A method of determining the shift factor M_L and the Kuhn segment length λ^{-1} from light-scattering data is proposed. It is applied to DNA. The estimates of these parameters are then found to be in good agreement with those obtained previously from a comparison of viscosity and sedimentation.

In a previous paper,[1] a method on the assumption of a continuous wormlike model for stiff-chain macromolecules has been proposed for the determination of the shift factor M_L, as defined as the molecular weight per unit contour length, and of the Kuhn segment length λ^{-1} from a comparison of viscosity and sedimentation. The object of the present paper is to present a similar method of determining the same parameters from light-scattering measurements alone. It requires the light-scattering form factor $P(\theta)$.

For the wormlike chain, only approximate expressions for $P(\theta)$ have been derived by Peterlin,[2] Benoit and Doty,[3] Hearst and Harris,[4] Sharp and Bloomfield,[5] and many others; a complete list of the literature is found elsewhere.[6] Some of them are very poor in the typical stiff-chain region, and cannot be used to obtain correct estimates of the parameters. In particular, there is a controversy about the light-scattering estimate of the Kuhn segment length of DNA,[7-9] and it should be reexamined. Therefore, our first problem is to evaluate $P(\theta)$ exactly.

If all lengths are measured in units of λ^{-1}, the scattering factor for the chain of contour length L and without excluded volume is given by

$$P(\theta) = 2L^{-2} \int_0^L (L - t) I(\mathbf{k};t) \mathrm{d}t \qquad (1)$$

where $I(\mathbf{k};t)$ is the characteristic function, or the Fourier transform of the distribution function of the end-to-end distance $\mathbf{R}$, for the chain of contour length t, and $\mathbf{k}$ is the scattering vector, whose magnitude is

$$k = (4\pi/\lambda') \sin(\theta/2) \qquad (2)$$

with θ the scattering angle and λ' the (reduced) wavelength of light in the solution. Peterlin[2] has adopted the Gaussian approximation to $I(\mathbf{k};t)$. It is equivalent to approximating the distribution function by the leading term of its Hermite polynomial expansion of the Nagai–Jernigan–Flory type[10-13] with the exact moments $\langle R^{2m} \rangle$. Benoit and Doty[3] have used the first two terms of the moment expansion of $I(\mathbf{k};t)$, including only $\langle R^2 \rangle$ and $\langle R^4 \rangle$. In this paper, we extend the first of these two lines to include as many higher moments as possible, since the convergence of the second is poorer. This is done by an application of the operational method developed previously by Yamakawa[13] and simplified further here, the involved operation and calculations being carried out by the use of a digital computer. We note that the other approaches cited above are difficult to improve from the point of view of successive approximations.

The method of calculation and the results are summarized in sections I and II. In section III, we discuss the determination of the mean-square radius $\langle S^2 \rangle$ of the chain and propose a method of determining M_L and λ on the basis of our $P(\theta)$ curves. In section IV, the proposed method is applied to DNA.