

Remarks on Light Scattering from Polymers in Mixed Solvents: Effects of Polymer Molecular Weight, Molecular Weight Distribution, and Solvent Composition

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ABSTRACT: It is known that light-scattering data for a polymer in a mixed solvent together with the refractive-index increment of the polymer evaluated at osmotic equilibrium (*i.e.*, at fixed chemical potentials of solvent components) permit unambiguous determination of the molecular weight of the polymer—irrespective of preferential interactions between polymer and solvent. However, the analysis presumes *either* of two conditions; the polymer is homogeneous in molecular weight or the “osmotic” refractive increment does not depend on molecular weight. When *both* conditions are violated, the apparent molecular weight obtained may differ from the true weight average. This problem is examined with the aid of parameters derived from light-scattering data of Dondos and Benoît. The error in typical cases is shown to be less than uncertainty in scattering measurements if polymer heterogeneity is not extreme (say $M_w/M_n \leq 2$); but the behavior of each scattering system must be assessed individually. The data also afford material for some observations on the dependence of preferential interactions on composition of a binary solvent.

KEY WORDS Light Scattering / Refractive-Index Increment / Mixed Solvent / Preferential Interaction / Apparent Molecular Weight / Molecular Distribution /

In a number of studies concerning macromolecular solutes in mixed solvents, it has been shown that knowledge of the refractive-index increment for the solute evaluated at osmotic equilibrium between solution and solvent affords a notable simplification of the analysis of light-scattering data and permits molecular weights to be obtained unambiguously, without regard to preferential thermodynamic interactions between polymer and a solvent component (or components).¹⁻⁴ If, however, the polymer is heterogeneous in molecular weight *and* if the amount of solvent preferentially “bound” per unit mass of polymer depends on molecular weight, complications arise. In the following discussion, which elaborates on brief comments given elsewhere,⁵ we consider this problem and offer a quantitative assessment of the effect on molecular weight determinations in some typical cases. The data at hand also prompt some remarks on the dependence of preferential interaction on composition of a binary solvent.

If certain physical approximations are valid,

Rayleigh scattering of radiation from a solution of a single macromolecular species (component 2) in a pure solvent (component 1) is expressed by the familiar relation⁶

$$K'(\partial n/\partial c_2)_P^2 c_2/R_0 = M_2^{-1} + 2A_2 c_2 + O(c_2^2) \quad (1)$$

where K' denotes a combination of optical and numerical constants; c_2 is the concentration (weight/volume) of solute and M its molecular weight; R_0 is the reduced scattered intensity (scattering from solution less that from solvent) extrapolated to zero scattering angle; n is the refractive index of the solution; and A_2 is the second virial coefficient in the expansion of the equation of state in powers of solute concentration.

If component 2 is dissolved in a mixture of two solvents (components 1 and 3) the theory for scattering from multicomponent systems^{1-4,7} leads to a relation of the same form as eq 1;

$$K'(\partial n/\partial c_2)_{P,T,\mu_3}^2 c_2/R_0 = M^{-1} + 2A_2 c_2 + O(c_2^2) \quad (2)$$

with the refractive-index increment $(\partial n/\partial c_2)_{P,T,\mu_3}$

evaluated at fixed pressure, temperature, and chemical potential μ_3 of component 3. Writing the refractive index as a function of c_2 and composition of mixed solvent (*e.g.*, volume fraction ϕ_3 of component 3 in the binary solvent mixture) we obtain

$$\left(\frac{\partial n}{\partial c_2}\right)_{P,T,\mu_3} = \left(\frac{\partial n}{\partial c_2}\right)_{P,T,\phi_3} + \lambda \left(\frac{\partial n}{\partial \phi_3}\right)_{P,T,c_2} \quad (3)$$

where the quantity

$$\lambda = \left(\frac{\partial \phi_3}{\partial c_2}\right)_{P,T,\mu_3} \quad (4)$$

represents the thermodynamic interaction between solute and solvent 3.^{7,8} A positive λ can be thought of as signifying preferential solvation of solute by solvent 3 or, equivalently, rejection of solvent 1 by the solute. For ordinary solutions⁴ it happens that, except for inconsequential error,

$$\left(\frac{\partial n}{\partial c_2}\right)_{P,\mu_3} = \left(\frac{\partial n}{\partial c_2}\right)_{\mu_1,\mu_3} \equiv \left(\frac{\partial n}{\partial c_2}\right)_{\mu} \quad (5)$$

(To simplify notation slightly we suppress the subscript T and use the single subscripts μ to indicate constancy of the potentials of both solvent components and ϕ to indicate a fixed solvent composition.)

Equation 5 shows that the refractive increment needed to permit direct determination of the molecular weight M from scattering data according to eq 2 can be obtained by refraction measurements on solutions equilibrated by dialysis against the mixed solvent of composition ϕ_3 . This possibility is of evident importance if the polymer cannot be dissolved in a single solvent. From another point of view, the coefficient λ is itself of interest and can be determined in various ways; by comparing $(\partial n/\partial c_2)_{\mu}$ and $(\partial n/\partial c_2)_{\phi}$ if $(\partial n/\partial \phi_3)_{c_2}$ is known; from a known M and light-scattering data together with $(\partial n/\partial c_2)_{\phi}$ and $(\partial n/\partial \phi_3)_{c_2}$; or from direct chemical analysis of solution and pure solvent after equilibration by dialysis.

The generalization to a solvent of many components is straightforward and will not be discussed here.

SCATTERING FROM A HETEROGENEOUS POLYMER IN A MIXED SOLVENT

The above relations hold for a homogeneous

solute, but since typical polymer samples exhibit significant dispersion in molecular weight, the effect of this has to be considered. Now we let the solute comprise a number of components J differing in molecular weight M_J , the total concentration being

$$c = \sum_J c_J = c \sum_J w_J \quad (6)$$

where w_J is the weight fraction of polymer J in the solute mixture. If there is but one solvent, and if the refractive increment $\partial n/\partial c_J$ is the same for every solute, the form of eq 1 can still be written, as is well known, in terms of the total solute concentration c and the weight-average molecular weight M_w .⁶

For the heterogeneous solute in a binary solvent mixture, contributions to R_0 due to the presence of each solute species are additive as $c \rightarrow 0$: *i.e.*,

$$R_0 = K' \sum_J M_J (\partial n/\partial c_J)_{\mu}^2 c_J + O(c^2) \quad (7)$$

Then, if the reciprocal scattering function is formulated in terms of the experimental refractive increment

$$\left(\frac{\partial n}{\partial c}\right)_{\mu} = \sum_J \left(\frac{\partial n}{\partial c_J}\right)_{\mu} w_J \quad (8)$$

for the heterogeneous solute, eq 1 is replaced by

$$\lim_{c \rightarrow 0} \left[\frac{K' (\partial n/\partial c)_{\mu}^2 c}{R_0} \right] = \frac{(\partial n/\partial c)_{\mu}^2}{\sum_J (\partial n/\partial c_J)_{\mu}^2 M_J w_J} \equiv \frac{1}{M_w^+} \quad (9)$$

If $(\partial n/\partial c_J)_{\mu}$ is independent of molecular weight M_J , the refractive increments on the right hand side of eq 8 cancel, and a plot of the scattering function *versus* concentration c extrapolates to the reciprocal of M_w . Otherwise, this procedure gives an apparent average molecular weight M_w^+ defined by eq 9. Obviously, dependence of

$$\left(\frac{\partial n}{\partial c_J}\right)_{\mu} = \left(\frac{\partial n}{\partial c_J}\right)_{\phi} + \lambda_J \left(\frac{\partial n}{\partial \phi_3}\right)_{c_J} \quad (10)$$

on molecular weight of solute can arise from variation with molecular weight in $(\partial n/\partial c_J)_{\phi}$ and/or in the interaction coefficient λ_J . Presuming that any variation in $(\partial n/\partial c_J)_{\phi}$ is too small to be important at reasonably high molecular weight, we proceed to consideration of λ .

DEPENDENCE OF PREFERENTIAL INTERACTIONS ON MOLECULAR WEIGHT OF POLYMER

Various assumptions about the behavior of λ with molecular weight of a long-chain homopolymer might be contemplated. Three possibilities are the following:

(I) The interaction expressed by λ can be associated with "sites" on the polymer chain in the sense that a certain average number of molecules of solvent 3 is preferentially bound by each monomer residue in the chain. Hence λ does not depend on the molecular weight of the polymer.⁴

(II) Assumption I is correct as a first approximation, but the picture should be modified by recognizing that intramolecular contacts between chain segments may affect polymer-solvent contacts with something like one-to-one equivalence. Assuming further that the dissolved polymer chain can be represented by a Gaussian distribution of chain segments with its mean-square radius of gyration proportional to the molecular weight and that the probability of occurrence of polymer-polymer contacts in any part of the chain domain is proportional to the square of the local segment density, it can be shown^{9,10} that the average number of intersegmental contacts per chain segment varies inversely with $M^{1/2}$. Hence λ depends linearly on $M^{-1/2}$:

$$\lambda/\lambda_{\infty} = 1 + AM^{-1/2} \quad (11)$$

where λ_{∞} is the limiting value of λ at high molecular weight. However, since the dissolved polymer chain is in effect a rather dilute solution of monomer units (*e.g.*, a mole fraction on the order of 0.01 within the chain domain) intramolecular contacts are rare compared with polymer-solvent contacts; and the second term on the rhs of eq 11 is of little consequence except at low molecular weight.⁹

(III) The preferential solvent "binding" is represented by eq 11, but the second term may be larger than would be expected on the basis of any simple equivalence between intramolecular contacts and polymer-solvent contacts.

From a recent experimental study by Dondos and Benoît,¹⁰ it appears that statement III is reasonable. Using a series of narrow-distribution

polystyrenes prepared anionically, they compared the light-scattering molecular weight measured in a single solvent with the apparent molecular weight M^* obtained by applying eq 1 to data from the same polymer in a binary solvent:

$$\frac{1}{M^*} \equiv \lim_{c_2 \rightarrow 0} \left[\frac{K'(\partial n/\partial c_2)_{\phi}^2}{R_0} \right] = \frac{1}{M} \left[1 + \lambda \frac{(\partial n/\partial \phi_3)_{c_2}}{(\partial n/\partial c_2)_{\phi}} \right]^{-2} \quad (12)$$

Calculating λ from eq 12 (and known values of $(\partial n/\partial \phi_3)_c$ and $(\partial n/\partial c_2)_{\phi}$) they plotted $\lambda M^{1/2}$ vs. $M^{1/2}$

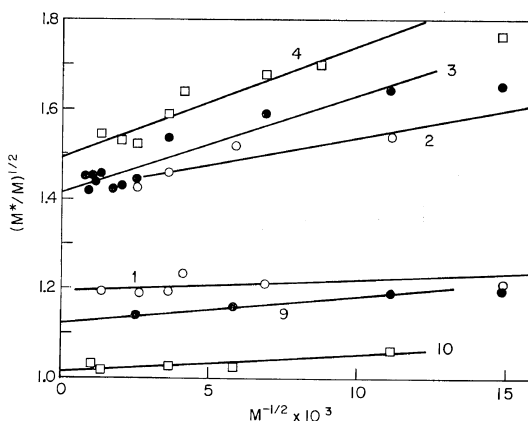


Figure 1. Preferential interactions in three-component solutions: polystyrene-solvent(1)-solvent(3). Plots of $(M^*/M)^{1/2}$ vs. M for solvent mixtures listed in Table I: systems 1, 2, 3, and 4, [benzene(1)+methanol(3)]; system 9, [benzene(1)+heptane(3)]; system 10, [dioxane(1)+methanol(3)].

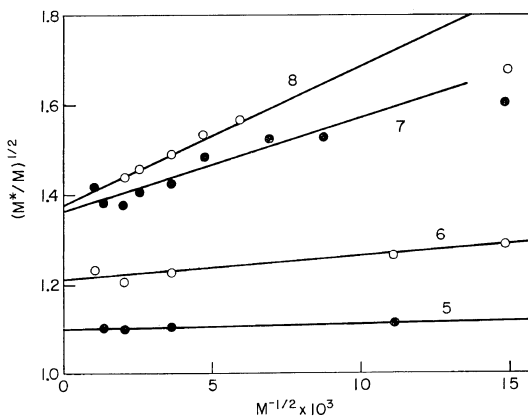


Figure 2. Plots as in Figure 1: systems 5, 6, 7, and 8, [carbon tetrachloride(1)+methanol(3)].

Table I. Light scattering from polystyrene in mixed solvents
(Parameters derived from data of Dondos and Benoît¹⁰)

System	Solvent	ϕ_3	$-dn/d\phi_3^{a,b}$	$(\partial n/\partial c)_\phi^b$	$-\lambda_\infty$	A
1	Benzene(1)+methanol(3), 25°C	0.100	0.171	0.123	0.13 ± 0.09	22 ± 15
2		0.190	"	0.140	0.34 ± 0.02	30 ± 7
3		0.220	"	0.145	0.351 ± 0.006	53 ± 4
4		0.255	"	0.150	0.434 ± 0.007	50 ± 1
5	Carbon tetrachloride(1)+methanol(3), 25°C	0.050	0.131	0.150	0.111 ± 0.002	13 ± 3
6		0.100	"	0.154	0.242 ± 0.009	24 ± 6
7		0.185	"	0.162	0.44 ± 0.01	58 ± 3
8		0.210	"	0.164	0.465 ± 0.004	83 ± 2
9	Benzene(1)+heptane(3), 25°C	0.540	0.112	0.160	0.176 ± 0.003	47 ± 2
10	Dioxane(1)+methanol(3), 35°C	0.050	0.0873	0.202	0.03 ± 0.01	250 ± 100

^a Values used by Dondos and Benoît (obtained by approximating n as a linear function of composition of solvent by volume).

^b Refractive increments for 5461 Å.

for ten ternary systems to obtain λ_∞ and the molecular weight dependence of λ , respectively, from slopes and intercepts of the best fitting straight lines.

In Figures 1 and 2 we have plotted the data of Dondos and Benoît as $(M^*/M)^{1/2}$ vs. $M^{-1/2}$, a form that perhaps exhibits more clearly the molecular weight dependence of λ and the experimental uncertainty in the data. From the least-squares straight lines we obtained the values of λ_∞ and A recorded in Table I. The calculation of λ requires knowledge of $(\partial n/\partial c)_\phi$ and of $(\partial n/\partial \phi)_{c_2}$ at $c_2=0$. The first quantity is given by Dondos and Benoît, and the values they used for the second are implied by values of M^* and λ that they list. The probable errors¹¹ in the parameters are included to give some idea of the adequacy of the linear fitting of the data points.

It is clear that eq 11 provides an adequate representation of the experimental data within the experimental uncertainty, although a slight upward convexity in some of the plots—particularly those for systems 3 and 4—suggests a possible dependence of λ on M^{-a} with $a < 1/2$. The points at lowest molecular weight (4500) were omitted in computing the least-squares parameters; thus the values of A reflect, predominantly, molecular weight dependence of λ for molecular weights on the order of 10^4 and above. Although Dondos and Benoît do not tabulate λ_∞ , or a parameter characterizing the molecular weight dependence of λ , it is obvious

that the results obtained here are similar to theirs. Predictably, the different data analysis carried through here cannot alter the character of the results though it does produce some quantitative differences. Our λ 's, unlike those of Dondos and Benoît, are negative: this reflects nothing more than our designation of the poor solvent, the minor component in all but one of the binary mixtures, as component 3.

DEPENDENCE ON SOLVENT COMPOSITION

In Figure 3, the dependence of λ_∞ on solvent composition is exhibited in a plot that would be appropriate if solvent binding could be described in terms of sites on the polymer molecules that compete for the solvent components in such fashion that

$$\frac{\phi_3''}{\phi_1''} = K \frac{\phi_3}{\phi_1} \quad (13)$$

where ϕ_1'' and ϕ_3'' are volume fractions of components 1 and 3 in the "bound" solvent material. Accordingly, preferential interaction with component 3 is positive or negative respectively as K is greater or less than unity. It can be shown (see Appendix A) that the plots of $\phi_1\phi_3/\lambda$ in Figure 3 will be linear if eq 13 is obeyed. The data do in fact fall roughly on straight lines; but it would be unwarranted on this tenuous basis to conclude that the occurrence of site binding has been demonstrated. We can look upon $\phi_1\phi_3/\lambda$ simply as a possibly useful function

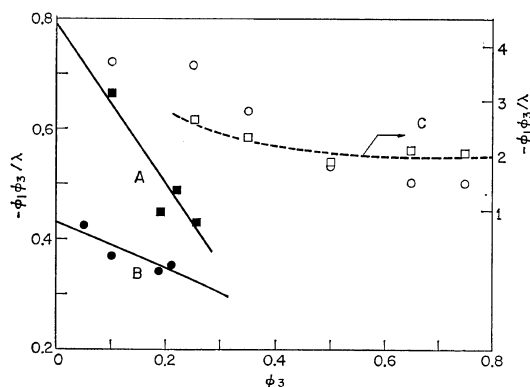


Figure 3. Dependence of λ on solvent composition for polystyrene in mixed solvents at 25°C: plot A, [benzene(1)+methanol(3)]; plot B, [carbon tetrachloride(1)+methanol(3)] from recalculation of data of Dondos and Benoît¹⁰; plot C, ordinate at right, [benzene(1)+cyclohexane(3)] from data of Read⁹ (open squares) and data of Strazielle and Benoît¹¹ (open circles).

that is well behaved at the limits $\phi_3=0$, and $\phi_3=1$ where we expect λ to be zero and $d\lambda/d\phi_3$ to be finite (see Appendix B). Obviously, this form and the model suggesting it cannot be applicable when, as has been reported¹²⁻¹⁴ in a few instances, λ changes sign at some ϕ_3 .

For comparison we have included in Figure 3 some data from two studies of preferential interactions in polystyrene—benzene(1)—cyclohexane(3) mixtures covering a wide range of solvent composition. According to data of Read⁹ $\phi_1\phi_3/\lambda$ varies weakly with ϕ_3 . The results of Strazielle and Benoît¹⁵ indicate a similar, possibly more pronounced, dependence on ϕ_3 .^{*} Read obtained good agreement between his experimental λ and a more complicated dependence on composition derived by extending a Flory—Huggins lattice-theory formulation to include ternary interaction parameters. Other experimental studies of λ and its variation with solvent composition are summarized in a review by Cowie.¹³

^{*} Volume fraction compositions in Table I and Figure 3 are based on volumes of the unmixed components. Use of the theoretically preferable magnitudes computed from *partial* volumes (see Appendix A) would not materially affect our analysis.

EFFECT OF MOLECULAR WEIGHT DISTRIBUTION ON M_w^+

Using numerical parameters derived from the data of Dondos and Benoît,¹⁰ we turn now to a calculation of M_w^+ for a heterogeneous polymer in a binary solvent. Since we have to assume some specific form for the molecular weight distribution, completely general conclusions cannot be inferred from the results, but they will provide some guidance as to whether in typical circumstances M_w^+ can be identified with M_w without important error.

Because it is easy to manipulate mathematically, we employ the Schulz¹⁶ distribution, described for a continuous distribution of molecular weight M , by

$$f(M) = \left(\frac{Z+1}{M_w}\right)^{Z+1} \frac{M^Z}{\Gamma(Z+1)} \exp\left\{-\frac{(Z+1)M}{M_w}\right\} \quad (14)$$

where $F(M)dM$ is the weight fraction of polymer in the differential increment dM , and Γ denotes the gamma function. With $Z=1$, eq 14 reduces to the “most probable” distribution produced by equilibrium condensation processes and certain vinyl polymerizations. Combining eq 3, 5, 8, 11, and 14 we find

$$\begin{aligned} \left(\frac{\partial n}{\partial c}\right)_\mu &= \left(\frac{\partial n}{\partial c}\right)_\phi + \lambda_\infty \left(\frac{\partial n}{\partial \phi_3}\right) \int_0^\infty \left(1 + \frac{A}{M^{1/2}}\right) f(M) dM \\ &= B \left[1 + Y \frac{(Z+1)^{1/2} \Gamma(Z+1/2)}{\Gamma(Z+1)} \right] \end{aligned} \quad (15)$$

where

$$B = \left(\frac{\partial n}{\partial c}\right)_\phi + \lambda_\infty \left(\frac{\partial n}{\partial \phi_3}\right)_c \quad (16)$$

and

$$Y = \frac{A\lambda_\infty}{BM_w^{1/2}} \left(\frac{\partial n}{\partial \phi_3}\right)_c \quad (17)$$

Similarly we obtain

$$\begin{aligned} \frac{1}{M_w} \sum_J \left(\frac{\partial n}{\partial c_J}\right)_\mu^2 M_J w_J &= \frac{1}{M_w} \int_0^\infty \left[B + \lambda_\infty \left(\frac{\partial n}{\partial \phi_3}\right)_c \frac{A}{M^{1/2}} \right]^2 M f(M) dM \\ &= B^2 \left[1 + 2Y \frac{\Gamma(Z+3/2)}{(Z+1)^{1/2} \Gamma(Z+1)} + Y^2 \right] \end{aligned} \quad (18)$$

Then, substitution of eq 15 and 18 into eq 9

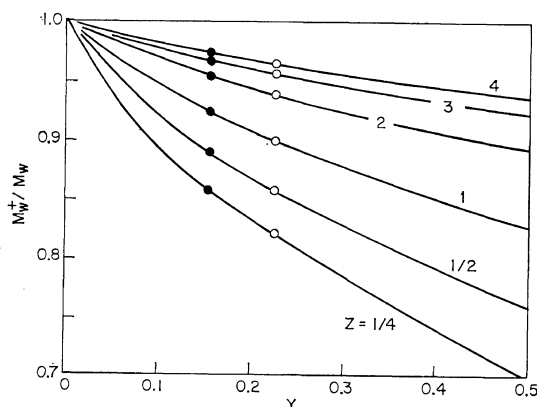


Figure 4. Effect of polymer heterogeneity and molecular weight dependence of λ on apparent molecular weight M_w^+ ; plots of M_w^+/M_w vs. Y for values of the Schulz dispersity parameter Z as indicated. The points mark values of Y for $M_w=10^4$ and the parameters of system 7 (filled circles) and system 8 (open circles).

gives M_w^+ . For example, if $Z=1$, we have

$$\frac{M_w^+}{M_w} = \frac{1 + 1.878Y + Y^2}{1 + 2.506Y + 1.571Y^2} \quad (19)$$

In Figure 4 we exhibit plots of M_w^+/M_w for the Schulz distribution for values of Z between 0.25 and 4 (*i.e.*, for weight-to-number-average molecular weight ratios from 5 to 1.25). The points shown on the graphs are for the parameters of Systems 7 and 8 in Table I and $M_w=10^4$. Analogous points for $M_w > 10^4$ would lie nearer $Y=0$. In all the experimental systems discussed here, it happens that $(\partial n/\partial c)_\phi$ is positive and the solvent component of lower refractive index is selectively rejected by the polymer. Hence Y is positive and $M_w^+ < M_w$, but physically there is no reason to exclude negative Y . Then we would have $M_w^+ > M_w$ at small Y and an interesting consequence in the occurrence of a point at which $M_w^+ = M_w$ for some $Y < 0$ for a given value of Z .

DISCUSSION

The solvent media listed in Table I each contain a good solvent for polystyrene and a precipitant, and were presumably chosen to exhibit marked preferential interactions. The ratios of the slopes to intercepts of the linear plots in

Figures 1 and 2 give $(A\lambda_\infty/B)(\partial n/\partial \phi_3)_c$ as a measure of the effect of the variations in λ on M_w^*/M_w for a homogeneous polymer and thus on M_w^+ for a heterogeneous polymer. By this criterion System 8 shows the largest effect, and systems 3, 4, and 7 fall next at about the same level. The data in Figure 2 suggest that the least-squares line for the points included in the calculation for system 8 may give an overestimate of the slope and that system 7 may be more reliably representative of the extreme effect in the systems studied by Dondos and Benoît. But even for the parameters of system 8, a heterogeneous polymer having a Schulz distribution with $Z > 1$ and $M_w > 10^4$ will show a disparity between M_w^+ and M_w scarcely greater than the absolute uncertainty in molecular weights measured by light scattering (see Figure 4). We conclude that for high polymers with moderate distribution of molecular weight, and particularly for reasonably well-fractionated materials, M_w can often be determined accurately by light scattering without independent knowledge of λ if the refractive increment $(\partial n/\partial c)_\mu$ for the entire solute is determined. However, caution is necessary: M_w^+ is affected by λ —by its magnitude and dependence on molecular weight and on the breadth and form of the molecular weight distribution—and by magnitudes of $(\partial n/\partial c)_\phi$ and $(\partial n/\partial \phi_3)_c$. It is not difficult to imagine situations in which M_w^+ might differ seriously from M_w . For example, a solvent mixture might be found such that $(\partial n/\partial c)_\phi$ vanishes to make $(\partial n/\partial c)_\mu^2$ directly proportional to the molecular weight dependent λ^2 ; and of course an arbitrary molecular weight distribution could be chosen to maximize the effect of the variation of λ . Consequently the reassuring nature of the quantitative results obtained here provides no warrant for indiscriminately assuming that M_w^+ is indistinguishable from M_w .

Our assumption that the refractive-index increment $(\partial n/\partial c)_\phi$ is independent of molecular weight calls for some comment as this has been a matter of dispute. Since Dondos and Benoît found constant values for this quantity, we have made no provision for a variation with molecular weight. This is the familiar assumption in determination of weight-average molecular weights by light scattering in a single solvent; but it has been questioned recently, especially by measure-

ments of Barrall, *et al.*,¹⁷ who report refraction measurements on polystyrene—toluene and polystyrene—butanone systems covering a very wide molecular weight range. A fairly rapid change in dn/dc_2 at low molecular weights, say less than 10^3 or even 10^4 , is hardly surprising since chain end-groups are of necessity different chemically from the rest of the molecule. The effect has been predicted realistically for polyalkanes¹⁸ on the assumption that molar refractions are constitutive and additive properties. However, the effect on dn/dc_2 that can be accounted for in this way is small for molecular weights above 10^4 . The magnitude of the molecular weight dependence observed at high molecular weights by Barrall, *et al.*, is unexpectedly large and is not in agreement with data reported on other polymers. However, the limited amount of data available and the experimental uncertainty in all of it perhaps leave this matter in the realm of unresolved questions.

Whether or not a contribution from $(\partial n/\partial c_2)_\phi$ should be included in the molecular weight dependence of $(\partial n/\partial c_2)_\mu$, the observed dependence is so large in most of the systems studied by Dondos and Benoît that the effect certainly has to be ascribed primarily to the variation in preferential interaction. From a completely non-committal point of view, however, Figures 1 and 2 can be taken simply as demonstrating empirically a linear relation between $(\partial n/\partial c_2)_\mu$ and $M^{-1/2}$. Then, the calculations for a heterogeneous polymer still give the effect of the variation of $(\partial n/\partial c_2)_\mu$ on M_w^+ : eq 15 and 18 remain applicable with Y interpreted as $A'/M_w^{1/2}$ where A' is the constant in the relation

$$\left(\frac{\partial n}{\partial c_J}\right)_\mu = \left(\frac{\partial n}{\partial c_J}\right)_{\mu,\infty} \left[1 + \frac{A'}{M_J^{1/2}}\right] \quad (20)$$

Equations 10 and 11 constitute a special case of eq 20 with $A' = A\lambda_\infty(\partial n/\partial \phi)_\phi/(\partial n/\partial c_J)_{\mu,\infty}$ if $(\partial n/\partial c_J)_\phi$ is independent of molecular weight.

To conclude, we reiterate that M_w^+ differs from the true weight average only if $(\partial n/\partial c_2)_\mu$ depends on molecular weight and at the same time the polymer is heterogeneous. At the limit of infinite dilution of polymer, eq 2 holds for every component J in the solute. Then if $(\partial n/\partial c_J)_\mu$ is the same for all J , the weight-average molecular weight is obtained in the usual way

according to eq 9. If $(\partial n/\partial c_2)_\mu$ depends on molecular weight of polymer, the correct weight for a homogeneous polymer is obtained from eq 2, but it is necessary to measure $(\partial n/\partial c_2)_\mu$ for the particular polymer under study.

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APPENDIX A

A linear dependence of $\phi_1\phi_3/\lambda$ on ϕ_3 can be derived as follows. We imagine that 1 gram of polymer (component 2) in a solution at osmotic equilibrium with the binary solvent of volume fraction composition ϕ_3' binds ξ_1 grams of component 1 and ξ_3 grams of component 3. One ml of the ternary solution contains c_2 grams of polymer. The partial volume contribution due to the polymer is $c_2\bar{v}_2$ and that of bound material is $c_2(\xi_1\bar{v}_1 + \xi_3\bar{v}_3)$ where $\bar{v}_1, \bar{v}_2, \bar{v}_3$ represent partial specific volumes of the components, assumed to be the same for bound and free solvent components. From the additivity of partial volumes it follows that the total mass of solvent 3 in one ml of the ternary system is

$$c_3 = c_2\xi_3 + c_3'[1 - c_2(\bar{v}_2 + \xi_1\bar{v}_1 + \xi_3\bar{v}_3)] \quad (A.1)$$

where c_3' is the concentration of solvent 3 (g/ml) in the binary solvent mixture equilibrated with the polymer solution (assuming that solution and solvent are incompressible). The volume fraction ϕ_3 of component 3 in all the solvent material in the ternary system is

$$\phi_3 = c_3\bar{v}_3/(1 - c_2\bar{v}_2) \quad (A.2)$$

Combining eq A.1 and A.2, we obtain the difference in solvent composition between the two phases at equilibrium, and then passing to the limit as $c_2 \rightarrow 0$ we find

$$\lim_{c_2 \rightarrow 0} [(\phi_3 - \phi_3')/c_2] = (\partial\phi_3/\partial c_2)_\mu \equiv \lambda \\ = \xi_3\bar{v}_3 - \phi_3(\xi_1\bar{v}_1 + \xi_3\bar{v}_3) \quad (A.3)$$

Now we assume that binding can be associated with ν sites per gram of polymer, each site capable of binding either g_1 grams of component 1 or g_3

grams of component 3 so that

$$\frac{\xi_1}{g_1} + \frac{\xi_3}{g_3} = \nu \quad (\text{A.4})$$

Further, we assume that competitive binding is governed by an isotherm of the form

$$\frac{\xi_3/g_3}{\xi_1/g_1} = k \left(\frac{\phi_3}{\phi_1} \right) \quad (\text{A.5})$$

Obviously, eq A.5 is symmetrical in the two solvent components, in that at the limits of mixtures dilute in either solvent 1 or 3 it represents the familiar Langmuir isotherm. In effect eq A.5 is a Langmuir expression for distribution of two components among equivalent independent sites, all of which must be occupied.

By combining eq A.4 and A.5 with eq A.3 to eliminate ξ_1 and ξ_3 , we obtain

$$\lambda = \frac{\phi_3(1-\phi_3)I^{-1}}{1+(k-1)\phi_3} \quad (\text{A.6})$$

where

$$I^{-1} = \nu k g_3 \bar{v}_3 - \nu g_1 \bar{v}_1 \quad (\text{A.7})$$

Rearrangement then gives $\phi_1\phi_3/\lambda$ as a linear function of ϕ_3 with an intercept I at $\phi_3=0$ and slope $(k-1)I$. Correspondence with eq 13 is obtained by letting $K = \bar{v}_3 g_3 k / \bar{v}_1 g_1$.

APPENDIX B

The chemical potential μ_J of solute J in a multicomponent solution can be expressed in the form

$$\mu_J = \mu_J^\circ(P, T) + RT \ln m_J + \mu_J^E \quad (\text{B.1})$$

where m_J is the molality of component J (moles per kg of principal solvent, component 1) and μ_J^E is the excess chemical potential. The laws of thermodynamics impose no particular form on the excess potential but experience with non-electrolyte solutions shows that a very large class of mixtures are well behaved in the sense that μ_J^E can be expanded in integral positive powers of concentration:

$$\mu_J^E/RT = \sum_{K=2,3,\dots} \beta_{JK} m_K + \sum_K \sum_L \gamma_{JKL} m_K m_L + \dots \quad (\text{B.2})$$

The reference state is that of unit activity coefficient at infinite dilution of component J .

Considering a ternary mixture (components 1, 2, and 3) at constant temperature and substituting eq B.2 into eq B.1, we differentiate to obtain

$$\frac{1}{RT} \left(\frac{\partial \mu_3}{\partial m_2} \right)_{P, m_3} = \beta_{23} + 2\gamma_{223} m_2 + 2\gamma_{233} m_3 + \dots \quad (\text{B.3})$$

and

$$\frac{1}{RT} \left(\frac{\partial \mu_3}{\partial m_3} \right)_{P, m_2} = \frac{1}{m_3} + \beta_{33} + 2\gamma_{233} m_2 + 2\gamma_{333} m_3 + \dots \quad (\text{B.4})$$

Combining these results we find

$$\frac{(\partial \mu_3 / \partial m_2)_{P, m_2}}{(\partial \mu_3 / \partial m_3)_{P, m_3}} = - \left(\frac{\partial m_3}{\partial m_2} \right)_{P, \mu_3} = \beta_{23} m_3 + O(m_3^2) \quad (\text{B.5})$$

so that

$$\lim_{m_3 \rightarrow 0} \left(\frac{\partial m_3}{\partial m_2} \right)_{P, \mu_3} = 0 \quad (\text{B.6})$$

and

$$\lim_{m_3 \rightarrow 0} \left[\frac{\partial}{\partial m_3} \left(\frac{\partial m_3}{\partial m_2} \right)_{P, \mu_3} \right]_{m_2} = -\beta_{23} \quad (\text{B.7})$$

This establishes the behavior of the interaction parameter λ and its first derivative as $\phi_3 \rightarrow 0$ inasmuch as $\partial \phi_3 / \partial c_2$ is proportional to $\partial m_3 / \partial m_2$ at this limit. Since

$$\partial \phi_3 / \partial c_2 = -\partial \phi_1 / \partial c_2 \quad (\text{B.8})$$

the same argument, with interchange of subscripts 1 and 3, shows that at the other limit, $\phi_3=1$, λ is also zero and its derivative is finite.

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Remarks on Light Scattering from Polymers in Mixed Solvents

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