Macromolecules **1982**, *15*, 927–933

for α,ω-carboxylato-Mg-PTBS. For polybutadiene (85% 1, 4), only one prepolymer (Hycar CTB, $\bar{M}_n = 4600$) was studied. Assuming the same relation as before,

$$C_{\text{gel}} = 136M_n^{-0.5} \qquad (7)$$

This unexpected result is to be compared to the apparent dependence of the gelation on the real chain length $\langle r^2\rangle^{1/2}$ of the prepolymer (Figure 5): the shorter the end-to-end distance, the less favorable the gelation. By analogy with eq 3–7, an equation type $C_{\text{gel}} = A\langle r^2\rangle^{-x/2}$ could be proposed.

In conclusion, there is no doubt that the gel results from dipolar interactions between the ionic end groups of the telechelic polymers, but the characteristics of the polymeric backbone ($\bar{M}_n$, $\langle r^2\rangle^{1/2}$) have a determining influence on the process. The higher the average end-to-end distance of a given polymer, the easier the simultaneous incorporation of both ionic ends in multiplets. This can explain why the η_{rel} vs. concentration plots are sharper when the prepolymer heterodispersity is lower (Figure 1, $\bar{M}_\omega/\bar{M}_n \simeq 1.8$; Figure 10, $\bar{M}_\omega/\bar{M}_n \leq 1.2$). A theoretical interpretation of the experimental results reported herein will be presented in a future paper.

Acknowledgment. We are indebted to UNIBRA (Brussels) and the "Services de la Programmation de la Politique Scientifique" for support and a fellowship (to G.B). We acknowledge the gift of several Hycar samples by BFGoodrich Chemical Co. and appreciate the skilful technical assistance of Miss J. Goffard and Mr. G. Renders.

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Scaling Analysis of Static Properties for Semidilute Solutions

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Received November 18, 1981

ABSTRACT: Low-angle scattered laser light from semidilute solutions of relatively monodisperse polystyrene in toluene is measured as a function of concentration and degree of polymerization. The excess chemical potential is observed to scale asymptotically as the $d\nu/(d\nu - 1)$ power of concentration, where $d = 3$ is the dimensionality of space and ν is measured to be 0.575. This value of ν is 4% smaller than that determined from dilute solution measurements and 2% smaller than the value predicted by renormalization group techniques. The excess chemical potential for polymers of molecular weight M at concentration c approaches this asymptote as a function of $(Mc^{1/(d\nu-1)})^{-1}$, in accordance with scaling theory. The data are more satisfactorily described by this model than a generalization of the Flory–Huggins theory that permits the interaction parameter to be a function of polymer concentration.

Introduction

Scaling theory has given polymer scientists a new perspective on interpreting measurements made in semidilute or moderately concentrated solutions.[1] In this regime there is substantial overlap of individual polymer molecules, but the solvent molecules still constitute a significant volume fraction of the solution. Experimentally this corresponds to a concentration

$$c > c^* = M/N_{\text{Av}}R^3 \qquad (1)$$

where the overlap concentration c^* specifies the condition where the average local concentration inside the polymer coil of molecular weight M and average length R equals the concentration of the solution. Avogadro's number is represented by N_{Av}.

Scaling analyses predict both the static and dynamic properties of molecules. Although dynamic predictions for polymers in good solvents have been investigated by light scattering techniques by several investigators,[2–6] static predictions have not been as widely studied. Elegant neutron scattering measurements have confirmed static scaling behavior,[7] but a relatively small number of samples have been studied by this complex method. Chu and co-workers[3,5] have observed some scaling relations by

0024-9297/82/2215-0927$01.25/0

conventional light scattering measurements on systems that show ideal to marginal behavior as the temperature is raised. Recently, Noda et al.[8] presented osmotic pressure data of poly(methylstyrene) in toluene over a wide range of concentrations and showed that the data scaled. In this paper low-angle light scattering measurements of semidilute solutions of polystyrene in toluene are presented and analyzed in terms of scaling models. We are particularly interested in discovering how the excess chemical potential approaches its asymptotic limit. In the process we measure the critical exponent for asymptotic behavior. We then show that scaling theory better describes the data than generalizations of classical theories.

Theory

Scaling theories have successfully described many phase transitions.[9] Insight into the behavior of polymer systems can be gained by finding parallels to modeling work done on ferromagnets.[1,7,9] As a ferromagnet is cooled below a specific temperature T_c, it becomes magnetized even when no external magnetic field exists. The regions in which the individual atomic magnets align grow in size exponentially as this critical temperature is approached; that is, the size of correlation grows as

$$\xi \propto [(T - T_c)/T_c]^{-\nu} = \tau^{-\nu}$$

where τ is the reduced temperature and ν is a critical exponent. This relation is analogous to the way the size of a long, isolated polymer chain grows as its number of segments N is increased:

$$R \propto N^{\nu} \tag{2}$$

The critical exponent ν in each case is the same since in the appropriate limit both processes reduce to self-avoiding random walks on a lattice. These two equations show that for isolated polymers the reduced temperature τ of the magnetic system is analogous to the reciprocal of the degree of polymerization N^{-1} of the polymer system.

This analogy was extended by des Cloizeaux[10] to represent polymer concentrations at all levels between the infinitesimal range just considered and the semidilute region. The analogy relates the Legendre transform of the excess free energy of the magnetic system to the polymer properties. For

$$\Gamma = F + HM_e$$

where M_e is the magnetization in excess of its appropriate reference state, F is the excess or field-dependent part of the free energy, and H is the applied magnetic field, the polymer properties follow as

$$n \propto \frac{1}{2} M_e \frac{\partial \Gamma}{\partial M_e} \tag{3}$$

$$c \propto \frac{\partial \Gamma}{\partial \tau} \tag{4}$$

and

$$\Delta\mu \propto -\Gamma + M_e \frac{\partial \Gamma}{\partial M_e} \tag{5}$$

where n is the polymer number concentration, c is the polymer weight concentration, and $\Delta\mu$ is the free energy of the polymer system in excess of its standard state. Scaling theory specifies that

$$\Gamma = \tau^{\nu d} g(x) \tag{6}$$

where d is the dimensionality of space and g is a function of only the variable

$$x = M_e/\tau^{\Delta} \tag{7}$$

in which Δ is a second critical exponent. These equations make very definite predictions about the behavior of both dilute and semidilute solutions. The latter are of current interest to us, but we first look briefly at the dilute limit, which is the more familiar experimental situation.

For temperatures above T_c, there is no spontaneous magnetization, so the excess magnetization M_e is identical with the magnetization itself. Near the asymptotic limit, eq 6 becomes

$$\Gamma = \tau^{\nu d}(a_1 x^2 + a_2 x^4 + ...) \tag{8}$$

where the a's are constant coefficients. There is no $a_0 x^0$ term since the excess free energy and its Legendre transform must go to zero as M_e approaches zero above T_c, and there are no odd-order x terms since Γ must be equivalent for positive and negative values of field. When eq 8 is substituted into eq 3 and 4, they become expressions for the experimentally measured quantities n and c in terms of the as-yet unspecified quantities τ and x. Inverting these equations identifies x and τ. Using the fact that $c \propto nN$, through second-order small quantities

$$\tau \propto N^{-1}(1 + \alpha x^2)$$

and

$$x^2 \propto cN^{d\nu - 1}(1 + \beta(cN^{d\nu - 1}))$$

where the α's and β's are constants. The physical significance of the x^2 parameter becomes apparent after eq 2 is used to relate N to R. When $d = 3$, x^2 is a function of cR^3/N or cA_2M in a good solvent, where the second virial coefficient A_2 is proportional to the ratio of the volume to the square of the molecular weight. At low concentrations the reduced temperature is a measure of the reciprocal of the degree of polymerization. Evaluating eq 5 in terms of the measured quantities gives

$$\Delta\mu \propto (c/N)(1 + \gamma c N^{d\nu - 1} + ...) \tag{9}$$

where γ is a constant. When $d = 3$ this expression can be written in terms of the second virial coefficient as

$$\Delta\mu \propto (c/M)(1 + A_2 M c + ...)$$

This equation is the standard expression for the change in the chemical potential of the solvent of a dilute solution.

The limit corresponding to temperatures below the critical temperature was not recognized as a distinct phase in classical polymer physics. In this region the transform of the excess energy (eq 6) is expanded as

$$\Gamma = \tau^{\nu d}(a_0 + a_1 x^i + ...) \tag{10}$$

where the a's are a set of coefficients different from those used for the low-magnetization case. The reference state from which M_e is measured is also different from that in the previous limit: M_e is now the magnetization in excess of the nonzero value on the phase boundary. The a_0 term is included in eq 10 since the free energy on the phase boundary is not zero. It is unclear what power of x is the first to appear in the series, so we designate it by an unspecified power i.[11] Substituting the expression for Γ into eq 3 and 4 permits x and τ to be found in terms of c and n. To first order in small quantities

$$\tau \propto c^{1/(d\nu - 1)}(1 + \alpha' x^i)$$

and

$$x^i \propto (Nc^{1/(d\nu - 1)})^{-1}[1 + \beta'(Nc^{1/(d\nu - 1)})^{-1}]$$

where α' and β' are constants. The expansion parameter

x^i can be given a physical interpretation in terms of the blob model.[1] In a semidilute solution the sequence of p segments in a chain which does not interact with other chains is called a blob. Since interchain effects are missing within the blob, its size is proportional to p^ν. In the semidilute regime, lengths scale as $c^{-\nu/(d\nu-1)}$ ($\sim c^{-3/4}$ for $d = 3$), so $p \propto c^{-1/(d\nu-1)}$. We conclude x^i is a function of p/N, that is, the fraction of each chain making up a blob. When p becomes small compared to N, the reduced temperature becomes a measure of the reciprocal of the number of segments *per blob*, rather than the reciprocal of the number of segments per chain that is measured by the reduced temperature in the dilute regime. Evaluating eq 5 in this limit reveals

$$\begin{aligned}\Delta\mu &\propto c^{d\nu/(d\nu-1)}(1 + \gamma'(Nc^{1/(d\nu-1)})^{-1} + ...)\\ &\propto p^{-1}(1 + \gamma'^*(p/N) + ...) \qquad (11)\end{aligned}$$

where γ' and γ'^* are constants.

For $\nu = {}^3/_5$ in three-dimensional space, eq 11 predicts that for a high degree of polymerization and/or high concentration the excess free energy is proportional to the 2.25 power of concentration. If the value of $\nu = 0.588$ calculated by Le Guillou et al.[12] by renormalization group techniques is used, eq 11 predicts a 2.31 power law limit. The equation also predicts that the deviation for the asymptotic limit is proportional to the first power of $(Nc^{1/(d\nu-1)})^{-1}$. A second-order term in this factor is probably the next correction. The reason for the uncertainty is that the power of the next term in eq 10 is unknown. If that term is proportional to the $j < 2i$ power of x, the next term in eq 11 would be between the first and second powers of $(Nc^{1/d\nu-1)})^{-1}$.

Schaefer et al.[4] argue that eq 11 breaks down for semiflexible chains when the solvent becomes of marginal quality, that is, when the mean distance between interchain contacts decreases to the size over which the local chain is distributed in an essentially Gaussian distribution (thermal blob size[1]). For a marginal solvent the square of the reduced temperature is the order of magnitude of the ratio of the cube of the number of monomers in a Kuhn length to the total number of segments in the chain. Schaefer et al.[4] suggest there are about 1.9 monomers per Kuhn length for polystyrene in a good solvent and Akcasu and Han[13] estimate that the Θ temperature of polystyrene in toluene is about −41 °C. Thus toluene at 23 °C is a marginal solvent for polystyrene of molecular weight on the order of 9 × 10³. To avoid these difficulties we work in this study with samples of substantially higher molecular weight.

The expression for the excess chemical potential given in eq 11 should be seen in contrast to the expression of Flory–Huggins theory[14]

$$\Delta\mu = kN_{\mathrm{Av}}T[\ln(1 - \bar{v}c) + [1 - (V_1/V_2)]\bar{v}c + \chi(\bar{v}c)^2] \qquad (12)$$

where k is the Boltzmann constant, $\bar{v}$ is the partial specific volume of the polymer, V_1 and V_2 are the volumes of solvent and solute molecules, respectively, and χ is an interaction parameter characteristic of the system. We assume that the volumes of the solvent and solute combine to give the total volume, so the volume fraction can be expressed as $\bar{v}c$. Comparing the thermodynamic properties of a family of polymers of different molecular weights that are at the same concentration, we see that eq 12 predicts that the differences result only from the $(V_1/V_2)\bar{v}c$ term. For different values of molecular weight, curves of either $\Delta\mu/c$ or $\mathrm{d}\mu/\mathrm{d}c$ as a function of concentration should have identical shapes and be displaced by an amount proportional to the reciprocal of the number-average molecular weight. This result is in contrast to the predictions made from the scaling expression, eq 11, which indicates that at sufficiently high concentrations different molecular weight curves of either $\Delta\mu/c$ or $\mathrm{d}\mu/\mathrm{d}c$ as a function of c become superimposed. The Flory–Huggins theory is based on a continuous change in thermodynamic properties from the semidilute through concentrated solutions. The scaling model describes the semidilute solution as a separate phase that has a distinct asymptotic behavior.

Table I
Polystyrene Samples Studied

$M_\mathrm{w} \times 10^{-4}$	$M_\mathrm{w}/M_\mathrm{n}$	supplier
3.61	1.05	Pressure Chemical Co.
9.30	1.01	Pressure Chemical Co.
29.3	1.04	Pressure Chemical Co.
92.9	1.03	Pressure Chemical Co.
36.5	1.10	Polysciences
766	1.2	Polysciences

Materials and Methods

Relatively monodisperse polystyrene samples purchased from Pressure Chemical Co. are the major standards used in this study. Data on two monodisperse samples from Polysciences, Inc., are also presented but not used for critical analyses. The weight-average molecular weights we determined from Berry plots[15] of the samples supplied by Pressure Chemical Co. were found to be within the 5% uncertainties specified by the manufacturer. The molecular averages of the Polysciences samples measured were up to 23% below those indicted by the supplier. All samples were used as supplied. Table I identifies the samples by weight-average molecular weight, polydispersity, and supplier. All polydispersity values are supplied by the manufacturer. The weight-average molecular weights provided by Pressure Chemical Co. are listed, but the other values are measured in this laboratory.

The toluene was distilled in glass by Polysciences, Inc. Since the turbidity of this solvent agrees with that of freshly distilled solvent and the value did not change over the course of data collection, the solvent was not redistilled.

Sample concentrations are calculated as

$$c = m_1/(v_0 + m_1\bar{v})$$

where m_1 is the mass of polymer, v_0 is the volume of solvent, and $\bar{v}$ is the partial specific volume of the polystyrene in toluene, 0.917 cm³/g.[16] Concentrated solutions heated in a vacuum oven were found to agree within 4% to this calculation.

The light scattering measurements were made on a Chromatix KMX-6 low-angle light scattering photometer at 23 °C. The Rayleigh factor is given by

$$R(\theta) = i(\theta)r^2/I_0V$$

where $i(\theta)$ is the intensity scattered at an angle θ from volume V into a detector a distance r away when the incident radiation has intensity I_0. Three different volumes were used at each of three different angles to get an average value for $R(2.3°)$, $R(3.3°)$, and $R(4.3°)$. From each average $R(\theta)$ the scattering of the solvent is removed and the excess $Kc/R(\theta)$ is found, where

$$K = (4\pi^2n^2/\lambda^4N_{\mathrm{Av}})(\mathrm{d}n/\mathrm{d}c)^2 \qquad (13)$$

with n being the index of refraction of toluene (1.492) and λ, the wavelength of the scattered light in a vacuum (6.328 × 10⁻⁵ cm). The differential index of refraction of polystyrene in toluene at this wavelength is 0.110 cm³/g.[17] The value of K is the standard constant of proportionality used for scattering from dilute solutions. It includes the difference between the square of the index of refraction of the solution and the solvent, $n'^2 - n^2$. This is evaluated by expanding n' in a Taylor series in concentration, so

$$n'^2 - n^2 = 2n\frac{\mathrm{d}n}{\mathrm{d}c}c + \left(n\frac{\mathrm{d}^2n}{\mathrm{d}c^2} + \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2\right)c^2 + ...$$

In dilute solution work this expression is used to first order in c. The effect of higher concentrations includes contributions of d^2n/dc^2, which we have not found reported for this system. Typically, d^2n/dc^2 is negative, with the second-order correction giving a change of less than $c(dn/dc)/2n$, i.e., less than 0.3% for $c \sim 0.1$ g/cm^3. Thus our reported values of $Kc/R(\theta)$ for high concentrations may be a few tenths of a percent low. We hope soon to avoid this error by accurately measuring the index of refraction of the solutions.

We note that our eq 13 differs from that given by Chromatix for use with their photometer and that of ref 17 by a factor of $(1 + \cos^2\theta)/2$ since both mistakenly assumed the incident light is unpolarized. The error resulting from the use of their incorrect formula is less than 1% if θ stays below 7°. The three values of excess $Kc/R(\theta)$ are averaged together and used as excess $Kc/R(0)$, which is simply labeled Kc/R_0. No extrapolation to zero angle is necessary since according to Noda et al.,[8] angular dependence of light scattered from semidilute samples of poly(methylstyrene) in toluene is

$$\frac{\Delta(Kc/R)/(Kc/R_0)}{\sin^2(\theta/2)} \approx 1$$

Assuming a similar value for polystyrene, the resulting correction in extrapolating from $Kc/R(4.3°)$ to Kc/R_0 is 0.1%, which is smaller than the precision of the measurements. The correction in the other values is even smaller.

Carbannes corrections for the Rayleigh factor measurements of both the solution and the solvent have been made. These corrections become insignificant on the excess Rayleigh factor. We note that the Carbannes correction given by Chromatix is incorrect because it assumes unpolarized light. The factor should be

$$C_v(\theta) = \left(1 - \frac{7}{3}\frac{\rho_v}{1 + \rho_v}\right)^{-1}$$

where

$$\rho_v = \frac{\bar{\rho}(1 + \cos^2\theta)}{2 - \bar{\rho}(1 - \cos^2\theta)}$$

and $\bar{\rho}$ is the ratio of the horizontally polarized scattered light to the vertically polarized scattered light at angle θ when the incident light is vertically polarized.

Data and Discussion

A. Asymptotic Behavior. The measured values of Kc/R_0 are plotted as a function of polymer concentration for four different molecular weights on a double-logarithmic plot in Figure 1. Actual values may be obtained from the senior author (M.E.McD.). It is observed that at sufficiently high concentrations all molecular weights appear to follow a common power law. We argue in part C of the Discussion that this is not simply the result of plotting the data on a logarithmic scale. This single-power behavior holds to lower concentrations as the molecular weight of the sample is increased. This observation confirms that the asymptotic behavior occurs above a critical concentration that is inversely proportional to molecular weight. In terms of eq 1 and 2

$$c > c^* \propto M/R^3 \propto N^{1-3\nu} \approx N^{0.8}$$

The strength of the scaling concept is that it not only indicates that in certain regions properties acquire simple forms but also that if the appropriate combination of quantities is studied, all samples approach these limits in the same way. In the theory section we describe the excess free energy, which is related to the two directly measurable quantities, the osmotic pressure

$$\Pi = -\Delta\mu/\bar{V}_1 \tag{14}$$

where $\bar{V}_1$ is the partial molar volume of the solvent, and the reciprocal Rayleigh factor

$$Kc/R_0 = \frac{-\partial\mu/\partial c}{\bar{V}_1 N_{Av} kT} = \frac{\partial\pi/\partial c}{N_{Av} kT} \tag{15}$$

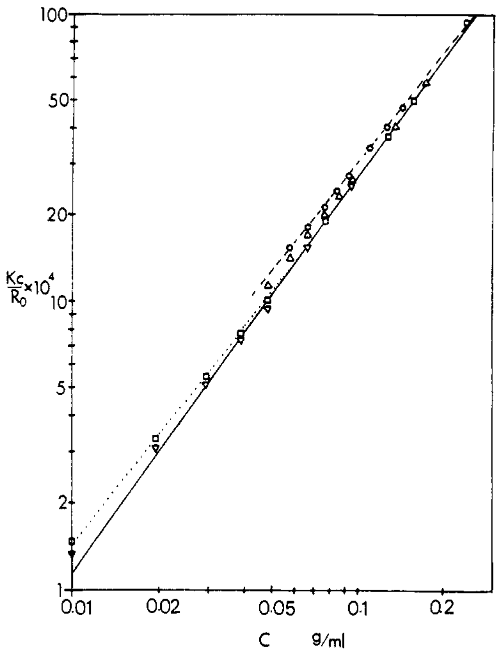

Figure 1. Scattering function Kc/R_0 for polystyrene in toluene as a function of concentration for samples of M_w = 3.61 × 10^4 (○), 9.30 × 10^4 (△), 2.93 × 10^5 (□), and 9.29 × 10^5 (▽). The curves plot eq 21 for M = 3.61 × 10^4 (- - -), 2.93 × 10^5 (···), and ∞ (—).

If eq 11 and 14 are combined, they give

$$\Pi = Ac^{d\nu/(d\nu-1)}[1 + BX + CX^2 + \ldots] \tag{16}$$

where A, B, and C are constants and

$$X = (Mc^{1/(d\nu-1)})^{-1} \tag{17}$$

The second correction of eq 16 is assumed to be of second order. It follows from eq 15 that

$$\frac{Kc}{R_0} = \frac{A}{N_{Av}kT}c^{1/(d\nu-1)}\left(\frac{d\nu}{d\nu-1} + BX - \frac{2-d\nu}{d\nu-1}CX^2 + \ldots\right) \tag{18}$$

To see how well this model describes the data, the measured values of Kc/R_0 are fit to eq 18, with A, B, and C being parameters to optimize for a given ν. Actually, the logarithm of eq 18 is used in the fitting to give the same relative (or percent) accuracy to each measurement. In Figure 2 the effect of the value of ν on the sum of the squares of the difference between calculated and measured values of ln (Kc/R_0) is shown. These data give an optimum ν of 0.575. The value of ν would have a large uncertainty if variations in A, B, and C alter the curve of Figure 1 in a way similar to variations in ν. This, however, is not the case: ν gives the slope of the straight line below which no data appear, A is the intercept of the line, and B and C describe how the data are positioned above the straight line. We estimate the reproducibility of ν to be less than 1%.

The measured value of ν is 2% smaller than the predicted value of 0.588.[12] For each different molecular weight there is a segment of Figure 1 that is well represented by a larger ν. These segments, however, form a family of parallel lines, rather than a universal asymptote. The data scale only with the lower value of ν.

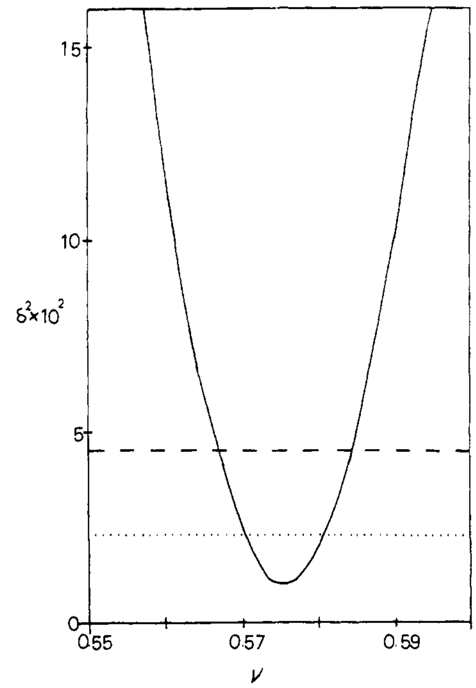

Figure 2. Sum of the squares of the difference between calculated and measured values of Kc/R_0 as a function of critical exponent ν (—). The horizontal lines give the comparable ν-independent sum of the squares for the Flory–Huggins theory generalized to second-order (---) and third-order (···) dependence in $\bar{v}c$.

To verify our assumption that all our data correspond to good, rather than marginal, systems,[4] we omit the data for the 3.61×10^4 molecular weight sample and optimize the remaining values. The result is $\nu = 0.573$, which we judge to be an insignificant change from the value obtained using all the data. We conclude all systems are good.

When Chu and Nose[3] studied a single sample of polystyrene in *trans*-decalin at varying temperatures above the Θ value and concentration, the limiting slope on a plot of $\log (Kc/R_0)$ as a function of $\log c$ corresponded to $\nu = 0.601$. Since the present data are taken at a temperature much higher above its Θ value, we believe that it gives a more reliable determination of ν.

Since we are unaware of any other experimental determinations of ν by examining the semidilute limit of very good systems, we analyze the osmotic pressure data of Noda et al.[8] for comparison. This group published data on five monodisperse samples of poly(methylstyrene) in toluene with number-average molecular weights between 7.1×10^4 and 1.82×10^6. When all their data for $c/c^* > 1$ are used, the deviation of the fit to eq 16 is minimized when $\nu = 0.570$. Their optimum value for ν may be, in fact, closer to 0.559, which results when the 7.1×10^4 data which do not scale as the other four samples are removed.

Determinations of the critical exponent ν in polymer science are more often associated with the power of the degree of polymerization that is proportional to the size of an isolated chain of sufficiently high molecular weight, that is, eq 2. Measuring the radius of gyration by light scattering has led to $\nu = 0.60 \pm 0.01$ for polystyrene of molecular weight above $2. \times 10^5$ in both toluene[18] and benzene.[19] These determinations were both based on measurements from three different laboratories. It is unclear why there is not better agreement between ν determined from extrapolations to infinite dilution and the semidilute asymptote. Interpretation of semidilute data is more straightforward since (1) the value of ν follows from R_0 rather than from the change of R with angle and (2) the effect of polydispersity is smaller.

The numerical coefficient A of eq 16 and 18 can be calculated from both the light scattering data for polystyrene in toluene presented here and the osmotic pressure measurements of Noda et al.[8] for poly(methylstyrene) in toluene. The present data give A equal to 6.76×10^7 in cgs units for $\nu = 0.575$. This compares to an A of 6.48×10^7 for Noda et al.[8] using all data except that of molecular weight 7.1×10^4 when their optimum $\nu = 0.559$ is used. If $\nu = 0.575$ is specified for the data of Noda et al.,[8] the optimal A drops to 4.99×10^7.

The coefficient A, however, is system dependent, and these effects must be noted before the data for polystyrene and poly(methylstyrene) are compared. Kosmas and Freed's[20] scaling analysis indicates

$$A \propto M_0^{-d\nu/(d\nu-1)} l^{2d(2-d\nu)/(d\nu-1)(4-d)} \upsilon^{d(2\nu-1)/(4-d)(d\nu-1)} \tag{19}$$

where l is the Kuhn length of the polymer, M_0 is the atomic weight of the monomer, and υ is the excluded volume of each unit. When $d = 3$ and $\nu = 0.575$

$$A \propto M_0^{-2.379} l^{2.276} \upsilon^{0.621} \tag{20}$$

For poly(methylstyrene) υ, l, and M_0 would all be expected to increase over their polystyrene values. If the change in M_0 from 104 to 118 is the dominant factor, the optimum A value for poly(methylstyrene) should decrease from that of polystyrene. If there was negligible change in υ and l, the M_0 change would lead to a 26% decrease in A for poly(methylstyrene) compared to polystyrene. This, indeed, is the percentage drop found when all data are analyzed with $\nu = 0.575$.

B. Approaching Asymptotic Behavior. The optimized coefficients of eq 16 are $A = 6.76 \times 10^7$, $B = 646$, and $C = 4.67 \times 10^5$ in cgs units so that

$$Kc/R_0 = 2.75 \times 10^{-3} c^{1.379} [2.38 + 646X - 1.746 \times 10^5 X^2 + ...] \tag{21}$$

The resulting curves for the molecular weights of 3.61×10^4, 2.93×10^5, and infinity are plotted on the data in Figure 1. The agreement between the other molecular weight measurements and their curve is comparable.

To convert eq 21 into a universal curve, one can multiply both sides by M to give

$$KcM/R_0 = 2.75 \times 10^{-3} X^{-1} [2.38 + 646X - 1.746 \times 10^5 X^2 + ...]$$

This quantity is plotted as a function of X^{-1} in Figure 3. The reciprocal of X is used on the abscissa to simplify comparison to published plots of $\log (Kc/R_0)$ as a function of $\log (c/c^*) \propto \log X^{-1}$. All data are well described by the single curve.

A more severe visual test of the universality of the scaling relation comes by dividing both sides of eq 21 by $c^{1/(d\nu-1)}$. The resulting function for different molecular weights covers the same range of values rather than consecutive ranges. For convenience, we normalize the constant on the right-hand side to 1 and obtain

$$\frac{Kc/R_0}{6.54 \times 10^{-3} c^{1.379}} = 1.00 + 270X - 7.34 \times 10^4 X^2 + ... \tag{22}$$

This described $(R_0 c^{0.379})^{-1}$ as a polynomial in $(Mc^{1.379})^{-1}$. Since there is little dynamic range in the left-hand side, we plot it on a linear scale. When plotting all the data and the universal curve of eq 22 in Figure 4, we use a logarithmic abscissa to encompass the wide range of values. Two additional sets of data are displayed on this plot.

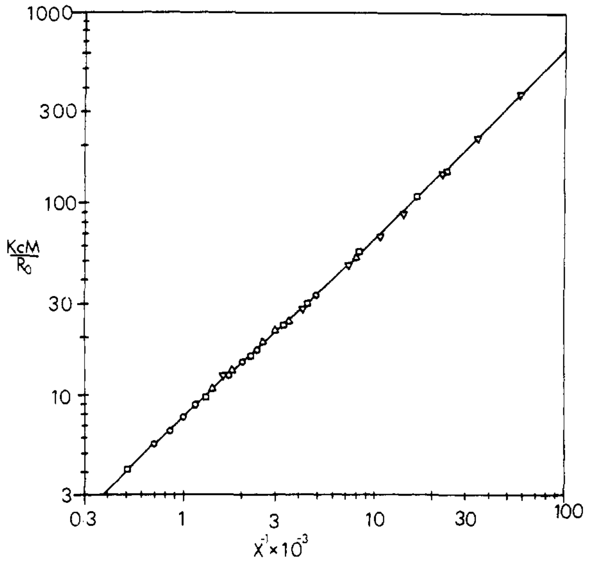

Figure 3. Universal function KcM/R_0 as a function of $X^{-1} = Mc^{1/(\nu d-1)} \propto c/c^*$. Symbols are identified in Figure 1.

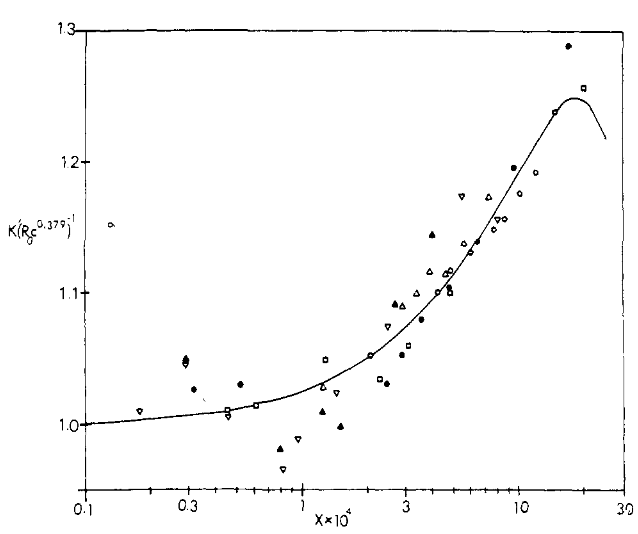

Figure 4. Universal function $K'(R_0c^{(2-d\nu)/(d\nu-1)})^{-1}$ as a function of $X = (Mc^{1/d\nu-1})^{-1}$, where K' is identified in eq 22. Symbols are defined in Figure 1 plus $M = 3.65 \times 10^5$ (●) and 7.76×10^6 (▲).

Note that the data for a polymer of substantially higher molecular weight, 7.76×10^6, are adequately described by eq 22.

The coefficients B and C determined from these data are compared to those found with the data of Noda et al.[8] for poly(methylstyrene). To make meaningful comparisons, it is necessary to use the same value of ν, which we choose as 0.575. Using all the osmotic pressure data except that from the 7.1×10^4 samples, we find $B = 410$ and $C = 91\,000$. Again we use the scaling theory formulation of Kosmas and Freed[20] to find

$$X/[Mc^{1/(d\nu-1)}]^{-1} = [M_0^{-d\nu/(d\nu-1)}l^{2d(2-d\nu)/(d\nu-1)(4-d)}v^{d(2\nu-1)/(4-d)(d\nu-1)}]^{-1} \quad (23)$$

which by comparison to eq 19 is inversely proportional to the system dependence of A. Thus if we wish to maintain the definition of X given by eq 17, there should be one reciprocal factor of eq 23 included in B and two factors in C. For $d = 3$ and $\nu = 0.575$, B should be changed proportionately to A of eq 20 and C proportionately to A^2. We previously noted a 26% decrease in the value of A for the poly(methylstyrene) data of Noda et al.[8] over that of our determination for polystyrene. This implies a 26% reduction in B and a 59% reduction in C. The reductions actually measured are 37% for B and 48% for C. Recalling that the values of A, B, and C for the poly(methylstyrene) system have been calculated for a ν that is not the optimum for these data, it is reasonable that agreement is not closer.

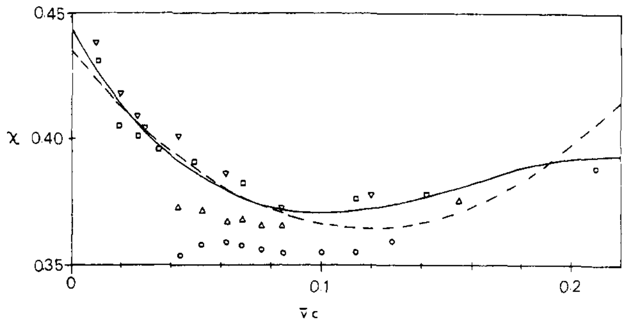

Figure 5. Interaction parameter χ measured as a function of concentration. Symbols are identified in Figure 1. Curves indicate second-order (---) and third-order (—) fits of the data to eq 23.

C. Comparison to Classical Theory. Figures 3 and 4 show that the light scattering data for polystyrene in toluene over a broad range of molecular weights appear to have a universal behavior. To see if this provides a significant improvement in the description of the data from the more classical thermodynamic approach for concentrated solutions, we substitute eq 12 into eq 15 and solve for the interaction parameter χ:

$$\chi = [1/M + (\bar{v}\rho_1/M_1)((1-\bar{v}c)^{-1} - 1) - Kc/R_0]/[2(V_2/V_1)\bar{v}c] \quad (24)$$

Using $\bar{v} = 0.917$ cm^3/g,[16] $\rho_1 = 0.867$ g/cm^3, and $M_1 = 92.1$ for toluene leads to the values of χ plotted in Figure 5. This graph shows that the interaction parameter is both concentration and molecular weight dependent. Both these effects are substantially damped and the latter undoubtedly disappears at sufficiently high concentrations. The point to be made, however, is that at concentrations of several times c^*, solutions of high molecular weight polymers do not have the homogeneity assumed in the Flory–Huggins theory.

Orofino and Flory[21] generalized the original theory to permit concentration dependence of a molecular weight independent interaction parameter:

$$\chi = \chi_0 + \chi_1(\bar{v}c) + \chi_2(\bar{v}c)^2 + \chi_3(\bar{v}c)^3 + \ldots \quad (25)$$

where the χ_i's are constants. The inclusion of additional concentration dependence does not permit a description of concentrations only slightly above c^*. The calculated values plotted in Figure 5 show that the first-order term plays an important role for $\bar{v}c < 0.06$. The flattening out of χ for $\bar{v}c > 0.06$ indicates that there must be a positive coefficient for a term of higher order, which leads to a positive slope on the graph for sufficiently high $\bar{v}c$. Flory's analysis[14] of the data of Bawn et al.[22] for higher values of $\bar{v}c$ shows the opposite behavior, so we realize there must be even more terms in eq 25. The shortcoming of the interaction parameter approach is that at intermediate concentrations it is unclear how many terms must be included in eq 25 to make it converge.

As a specific test of eq 24 we seek to optimally fit the data with expansions of χ to both the second and third orders in $\bar{v}c$. The square of the deviation of the fit of ln (Kc/R_0) from its measured value is $\delta^2 \times 10^2 = 8.77$ for the second order and $\delta^2 \times 10^2 = 2.40$ for the third order. Adding more $\bar{v}c$ terms to χ has little effect on δ^2 since the deviation at this point is primarily the result of the molecular weight dependence in χ. See Figure 5. These squared deviations should be compared with Figure 2, where ν, A, B, and C are the optimized constants. With χ_0, χ_1, χ_2, and χ_3 used as the constants to fit, δ^2 is more than twice as large as that obtained with a scaling model. More significantly, the analysis in terms of the interaction parameter expanded through the third order still makes predictions for χ that are inconsistent with the reported values in more concentrated solutions.[22] The interaction parameter approach also does not incorporate the observed molecular weight dependence. Rather than considering this concentration range as the edge of the concentrated range, we conclude that the scaling predictions of a separate semidilute phase are verified.

Conclusions

Scaling predictions of a distinct semidilute phase have been confirmed by measuring the amount of light scattered at low angles from polystyrene in toluene. In this phase the chemical potential is proportional to the $d\nu/(d\nu - 1) = 2.38$ power of concentration and independent of molecular weight. The semidilute behavior appears at higher concentrations for polymers of lower molecular weight. The critical exponent $\nu = 0.575$ measured from semidilute measurements is less than the value measured in the dilute limit. This is unexpected.

The approach to the semidilute asymptote is described in terms of the independent variable $(Mc^{1/(d\nu-1)})^{-1}$. Data of different molecular weights fit a universal plot when $(R_0c^{-0.379})^{-1}$ is graphed as a function of $(Mc^{1.379})^{-1}$. This plot should permit generalization to include all good solvent–solute systems.

The scaling approach describes the data in the semidilute region better than the generalization of Flory–Huggins theory to include a concentration-dependent interaction parameter. Calculations of the interaction parameter from the data presented here have concentration dependence with the opposite sign of values reported in more concentrated systems. This observation supports the claim of scaling theory that the semidilute solution is a distinct phase, rather than the extreme portion of the concentrated solution range.

Acknowledgment. This work was supported by National Science Foundation Grant ISP-8011453. Extended discussions with M. V. Ferer, Department of Physics, West Virginia University, and A. M. Jamieson, Department of Macromolecular Science, Case Western Reserve University, have been significant to our understanding of this subject.

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Communications to the Editor

Structural Interpretation of the Origin of the Dipole Moment in Poly(1-olefin sulfones) Which Relaxes at Low Frequencies by Whole-Molecule Motion

We report in a preliminary manner on an experimental investigation by dielectric measurements of the structural origin of the large dielectric dispersion displayed at electric field frequencies below 1 MHz by solutions in benzene of poly(1-hexene sulfone) $[-SO_2CHRCH_2-]_n$ ($R = C_4H_9$). The polymers have been viewed as random coils in which stiffness couples a large component of each sulfone dipole moment perpendicular to the chain contour to a small component that is parallel to the chain contour, in order to account for the magnitude of the dipole moment relaxed at low frequencies and the small dependence of this dipole upon molecular weight.[1,2] Our work was stimulated by the elegant models[3,4] for local chain motions in this polymer which were devised to fit the then known experimental observations of an apparent gross difference between the characteristic time for movement of the sulfone dipoles ($\tau_D \sim 10\ \mu s$ if $\bar{M}_n \sim 3 \times 10^5$) and the characteristic time for the movement of the main chain C–H vectors ($\tau_{CH} \sim 1$ ns[3-5]) obtained by ^{13}C NMR measurements. These local motions reallocated C–H bonds in space but left the sulfone dipoles unchanged in orientation: they required that the main-chain C–C bonds be trans in conformation. Our experiments were designed to test the relationships between this requirement, the stiffness of poly(olefin sulfones), and the magnitude of the dipole moment relaxed by the whole-molecule motion. To do this we modified the structure of the polymer chain, a procedure that was found so useful in earlier studies[3,6] but we maintained the feature responsible for the special dynamic behavior of these polymers—the regular alternation of the sulfone group and 2C-atom hydrocarbon unit along the chain backbone. An earlier consideration of poly(olefin sulfone) conformations had suggested a dependence of a C–C bond conformation upon the presence of hydrocarbon substituents on neighboring units.[7]

According to calculations based upon an assumed tet-

0024-9297/82/2215-0933$01.25/0