Macromolecules **1986**, *19*, 2832–2840

Small-Angle X-ray Scattering from Semidilute Polymer Solutions.
2. Polystyrene in Cyclohexane

Shinichi Kinugasa, Hisao Hayashi, Fumiyuki Hamada,* and Akio Nakajima

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

Received January 2, 1986

ABSTRACT: Semidilute solutions of polystyrene in cyclohexane have been studied by measuring small-angle X-ray scattering. Two structural parameters, the correlation length ξ and g_m ($\propto \partial c/\partial\Pi$), have been determined as a function of temperature t ($34.8 \le t \le 62.4$ °C) and concentration c ($2 \le cM^{1/2} \le 150$ g/cm^3) for four different molecular weights M_w ($2.33 \times 10^5 \le M_w \le 2.0 \times 10^6$). From the ξ and g_m results, we observed the following: (1) at the Θ-temperature, the concentration dependence of both g_m and ξ is consistent with power laws predicted by scaling theory; (2) at high temperatures, while data of g_m support corresponding scaling laws, those of ξ give power laws different from those predicted by theory; (3) both c^2g_m and $c\xi$ are described by a univeral function of a reduced variable τ/c, where $\tau = 1 - \Theta/T$, in semidilute regions; (4) a reduced quantity $g_m/g_{m\Theta}$ ($=(\partial\Pi/\partial c)_\Theta/(\partial\Pi/\partial c)$) can also be described by a universal function of τ/c, which is expressed in terms of binary and ternary cluster integrals in the semidilute–poor region ($\tau/c < 1$), and gives corresponding power laws correctly in the semidilute–good region ($\tau/c > 1$); (5) a mean-field result, $\xi^2 = (A^2M_u/12)g_m$, has been well confirmed, where A is a characteristic ratio appearing in $\langle S^2\rangle_0 = MA^2/6$ and M_u is the molecular weight of the monomeric unit. On the whole, the temperature and concentration dependences of ξ and g_m are consistently described by mean-field theory for poor solvents rather than the scaling theory.

Introduction

Since French groups succeeded in interpreting power law behavior of semidilute polymer solutions by applying scaling theory,[1-5] many theoretical[6-10] and experimental[11-18] studies have been made on static properties of polymer solutions. In particular, semidilute–good solutions have been widely studied by measuring osmotic pressure,[12] light scattering,[14-15] small-angle neutron scattering (SANS),[2,16] and small-angle X-ray scattering (SAXS).[17] As a result, it is widely accepted that scaling theory can be applied to polymer solutions; the concentration dependences of the osmotic pressure Π and the correlation length ξ obey simple power laws predicted by scaling theory.

A semidilute solution is a polymer–solvent mixture whose polymer concentration c is greater than an overlap concentration c^*, which is usually defined as

$$c^* = M/N_A\langle S^2\rangle^{3/2} \qquad (1)$$

where M is the molecular weight of the polymer, $\langle S^2\rangle$ is the mean square of the radius of gyration at infinite dilution, and N_A is Avogadro's number. Near c^*, polymer chains begin to overlap and then interpenetrate each other as the concentration increases. Thus c/c^* is an important measure for coil overlapping in solutions. In fact, for semidilute–good solutions, it has been confirmed that the concentration dependence of Π and ξ can be described by a universal function of c/c^* only.[12,14,17] Semidilute solutions are usually divided into two kinds of solutions:[6] semidilute–good solution and semidilute–poor solution, according to the strength of the excluded volume effect. These solutions respectively correspond to the semidilute–good region (II) and the semidilute–poor region (III) in Daoud and Jannink's phase diagram (DJ diagram) for polymer solutions.[5]

Table I
Predicted Power Laws for ξ and g_m (DJ Diagram)[a]

region	ξ	g_m
I′, dilute–Θ	constant	N_m
I, dilute–good		N_m
II, semidilute–good	$c^{-3/4}\upsilon^{-1/4}$ $(c^{-0.770}\upsilon^{-0.230})^b$	$c^{-5/4}\upsilon^{-3/4}$ $(c^{-1.31}\upsilon^{-0.69})$
III, semidilute–poor	c^{-1}	c^{-2}

[a] N_m is the number of monomeric units per chain, and υ is the excluded volume or the binary cluster integral. [b] Exponents for $\nu = 0.588$[37] are presented in parentheses.

Compared with semidilute–good solutions, semidilute–poor solutions have not been as widely studied,[11,18] and there remain some problems in interpreting experimental results as pointed out by Schaefer recently.[19] First, a problem arises from what theory has been used to explain experimental results: scaling theory or mean-field theories. As an example, while Cotton et al. interpreted their SANS data for the temperature dependence of ξ as the corresponding scaling behavior for semidilute–good solutions,[3] Okano et al. showed that the same data can be described by Moore's mean-field theory proposed for semidilute–poor solutions.[18] Second, more detailed experiments have given embarrassing results. Chu and Nose revealed that while the osmotic compressibility $\partial c/\partial\Pi$ obeys corresponding power laws predicted by scaling theory, the correlation length ξ shows unexpected power laws.[11] Recently, Schaefer claimed that these embarrassing observations arise from misinterpretation of apparent power laws as scaling laws for good solvents: the agreement between observed power laws and scaling predictions is often fortuitous and arises in measurements performed close to the crossover region between the marginal and Θ regions.[19]

By application of a magnetic tricritical theory, Daoud and Jannink proposed a scaling theory followed by a temperature–concentration diagram for polymer solutions.[5] Such a diagram is shown schematically in Figure 1a, where both the reduced temperature τ ($\tau = 1 - \Theta/T$)[20] and mass concentration c are multiplied by M to remove any dependence of the molecular weight of the polymer. As shown in the figure, the diagram is divided into four different regions of behavior by two crossover concentrations c^* and c^{**}: the dilute–Θ (I′), dilute–good (I), semidilute–good (II), and semidilute–poor regions. It is believed that both c^* and c^{**} do not exhibit a sharp boundary separating different regions but rather indicate gradual changes in behavior from one region to another. For each of these regions, power laws are predicted for the temperature and concentration dependence of the radius of gyration $\langle S^2\rangle^{1/2}$, the correlation length ξ, and the osmotic pressure Π. Table I sets out the predicted power laws for ξ and g_m. Here g_m is a structural parameter that can be related to the osmotic compressibility $\partial c/\partial\Pi$ as will be shown in eq 6 in the following section. We have obtained the power laws for

0024-9297/86/2219-2832$01.50/0

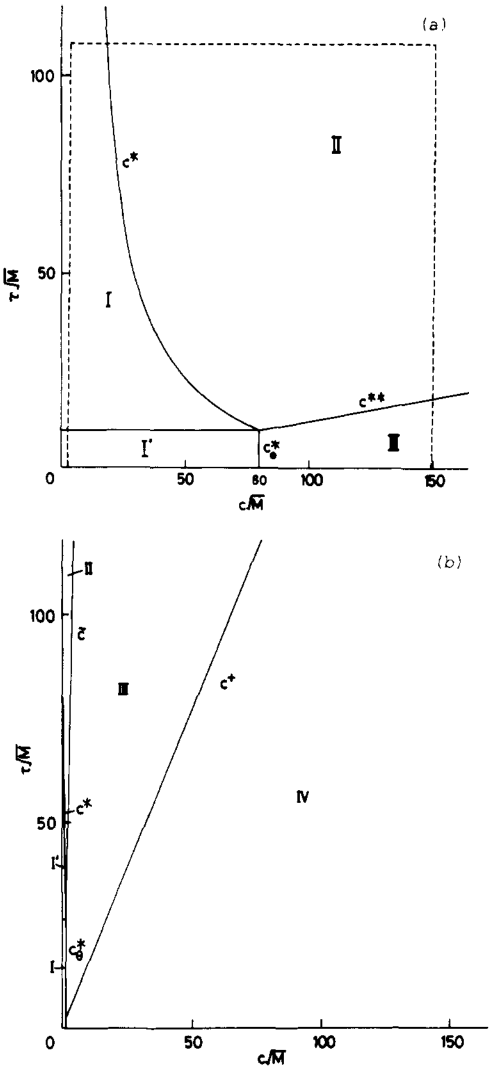

Figure 1. Temperature–concentration diagrams for polystyrene in cyclohexane, where τ is the reduced temperature ($\tau = (T - \Theta)/T$). (a) DJ diagram.[5] The boundaries c^* and c^{**} were determined by Cotton et al.'s SANS experiment applied to polystyrene in deuteriated cyclohexane-d_{12}.[3] The dashed line represents the range of the present experiment. (b) SJP diagram recast from Schaefer's Figure 3 of ref 9. The concentrated region (region V) does not appear because of large values of the crossover $c_bM^{1/2}$ for the present molecular weights.

g_m by differentiating Π with respect to c.

Recently, Schaefer et al. modified the scaling theory of Daoud and Jannink and proposed a new phase diagram (SJP diagram) by considering the local stiffness of polymer chains.[9] Power laws for ξ and g_m predicted by the SJP theory are summarized in Table II, and a schematic SJP diagram for polystyrene in cyclohexane is shown in Figure 1b. In the SJP diagram, compared with the DJ diagram, characteristic is the appearance of a mean-field region, the marginal region (III), which is introduced as an intermediate region between the semidilute-good (II) and the semidilute-Θ (IV) regions. In both the semidilute-marginal and the semidilute-Θ regions, scaling breaks down because of the local stiffness of the polymers, and mean-field types of theory can be applied. In fact, the power laws for these two regions are derived from the results of Moore's theory for semidilute-poor solutions (eq A9 in Appendix A).

Strictly speaking, the ordinate of these diagrams should be scaled in terms of $vM^{1/2}$, where v is the excluded volume or the binary cluster integral per monomeric unit. In the vicinity of the Θ-temperature, however, v is frequently approximated as $v \propto \tau$. For polystyrene in cyclohexane, recent light scattering experiments by Miyaki and Fujita have in fact shown[21]

$$v = 72 \times 10^{-24}\tau \qquad (\mathrm{cm}^3) \tag{2}$$

over the corresponding temperature range we studied. This equation shows that τ is substantially a proper measure for the excluded volume effect. We therefore employ τ in place of v in analyzing and discussing our experimental results.

In the present study we attempt to examine what theory can be applied to semidilute solutions by analyzing results of ξ and g_m gathered by SAXS measurements carried out over a wide range of concentration and temperature for various molecular weights of polystyrene in cyclohexane.

Table II
Predicted Power Laws for ξ and g_m (SJP Diagram)[a]

region	ξ	g_m
I, dilute-Θ		
I', dilute-good		
II, semidilute-good	$c^{-3/4}v^{-1/4}n^{-1/4}$	$c^{-5/4}v^{-3/4}n^{-3/4}$
III, semidilute-marginal	$c^{-1/2}v^{-1/2}n^{3/2}$	$c^{-1}v^{-1}$
IV, semidilute-Θ	$c^{-1}w^{-1/2}n^{2}$	$c^{-2}w^{-1}$

[a] n and w are the rigidity index[9] and the ternary cluster integral per monomeric unit, respectively.

Experimental Section

Scattering Law. We define a pair correlation function $G_m(\mathbf{r})$ for monomer distribution in solution by[1]

$$G_m(\mathbf{r}) = (1/\rho_m)[\langle\rho_m(0)\rho_m(\mathbf{r})\rangle - \rho_m^2] \tag{3}$$

where ρ_m is an average number density of the monomeric unit, $\rho_m(\mathbf{r})$ is an instantaneous number density at point $\mathbf{r}$, and the angular brackets denote statistical mechanical average. The scattering law $S_m(h)$ per monomeric unit is given by the Fourier transform of $G_m(\mathbf{r})$:[22]

$$S_m(h) = \int G_m(\mathbf{r})e^{i\mathbf{h}\cdot\mathbf{r}}\,\mathrm{d}^3r \tag{4}$$

where h is the scattering vector whose magnitude $h = (4\pi/\lambda)\sin\theta$ (λ is the wavelength of the incident X-rays, and θ is half the scattering angle). Several scattering experiments[3,17,18] have demonstrated that $S_m(h)$ has a Lorentzian form in the intermediate h range:

$$S_m(h) = g_m/(1 + \xi^2h^2) \qquad (\langle S^2\rangle^{-1/2} < h < l^{-1}) \tag{5}$$

where l is the step length of a polymer chain. A structural parameter ξ is called the correlation length or screening length and was first introduced by Edwards.[23] Although no proof has been given, another structural parameter g_m may be related to the osmotic compressibility $\partial c/\partial\Pi$ by

$$g_m/N_m = (RT/M)\partial c/\partial\Pi \tag{6}$$

where N_m is the number of monomeric units per polymer chain whose molecular weight is M, R is the gas constant, and T is temperature.

Sample Preparation. Four monodisperse polystyrenes ($M_w \times 10^{-5}$ = 2.33, 6.0, 9.5, and 20; $M_w/M_n < 1.1$) were purchased from Pressure Chemical Co. and were used as samples without further purification. Cyclohexane (Nakarai Chemicals Co.) was dried over calcium hydride and then fractionally distilled. All solutions were prepared under stirring in sealed tubes kept at 45–50 °C for more than a week. To prevent precipitation of the polymer solute, the solutions were kept warm until SAXS measurements.

Sample mass concentrations c in g/cm³ were calculated by

$$c = w\rho \tag{7}$$

where w is the weight fraction of the polymer and ρ is the density of the solution. Values of w were determined by weighing. The density ρ, which depends on both the temperature and concentration, was calculated from Scholte's empirical equation for ρ.[24]

Overlap Concentration c^*. The overlap concentration c^* at a given temperature was calculated by using eq 1, where we used M_w and $\langle S^2\rangle_z$ in place of M and $\langle S^2\rangle$, respectively. We estimated values of $\langle S^2\rangle_z$ by using the relation $\langle S^2\rangle_z = \alpha_S^2\langle S^2\rangle_{0z}$, where α_S is the expansion factor and $\langle S^2\rangle_{0z}^{1/2}$ is the z-average unperturbed chain dimension. The calculation method is as follows: First, we calculated the value of $\langle S^2\rangle_{0z}$ for molecular weight M_w according to the empirical equation obtained by Miyaki et al.;[25]

$$\langle S^2\rangle_{0z} = 8.8 \times 10^{-18} M_w \quad (\mathrm{cm}^2) \tag{8}$$

Second, from the results of light scattering experiments,[26-30] we obtained α_S as a function of the reduced temperature $\tau M_w^{1/2}$ by least squares:

$$\alpha_S^2 = 1 + 7.8 \times 10^{-3}\tau M_w^{1/2} - 2.4 \times 10^{-5}(\tau M_w^{1/2})^2 \qquad (\tau M_w^{1/2} < 200) \tag{9}$$

Then we calculated values of $\langle S^2\rangle_z$ as a function of temperature and molecular weight of the polymer by combining eq 8 and 9.

SAXS Measurements. SAXS measurements were carried out with a Kratky U-slit camera using a Cu-anode tube as an X-ray source. Scattered intensity was measured with a scintillation counter, which was scanned stepwise automatically. Collimation error due to the line-shaped cross section of the primary beam was corrected by Glatter's iterative method.[31] The power of the beam per unit length P was measured by a secondary standard sample, a Lupolen platelet calibrated by Kratky and co-workers.[32] The sample cell was a thin quartz capillary whose diameter d is about 2 mm. The temperature of the sample was controlled within ±0.1 °C by circulating water from an external regulated bath.

The scattering law $S_m(h)$ per monomeric unit was determined by the excess scattered intensity $I(h)$;

$$S_m(h) = (1/KcM_u)(a^2/Pd)I(h) \tag{10}$$

where a is the distance from the sample to the detector. K is a contrast factor given by

$$K = i_e(z - \bar{v}_2\rho_e)^2 N_A \tag{11}$$

where i_e is the Thomson constant (i.e., the scattering cross section of a free electron, 7.94×10^{-26} cm^2), z is the moles of electrons in 1 g of solute, $\bar{v}_2$ is the partial specific volume of the solute, and ρ_e is the moles of electrons per unit volume of solvent. Values of K at different temperatures and concentrations were corrected by estimating $\bar{v}_2$, using Scholte's empirical equations for the solution density.[24]

Results and Discussion

Figure 2 shows typical examples of the reciprocal scattering law $S_m(h)$ plotted vs. h^2 at various temperatures for a semidilute solution. Although a slight downturn appears at smaller angles, especially at high temperatures, the linearity observed at intermediate h range is ensured by eq 5. The intercept and slope of these lines give values of g_m and ξ.

The average slope of the downturn is found to become steeper and steeper with increasing temperature. This "anomalous" scattering was first imputed to ill-removed dust. However, recent light[33-35] and neutron[35] scattering experiments have demonstrated that this phenomenon is genuine and characteristic of conditions of solutions. Unexpectedly, the scattering arises for good solvents such as toluene and tends to vanish for poor solvents such as cyclohexane at the Θ-temperature. In part 1 of this series, concerning polystyrene in toluene,[17] we also found similar scattering behavior, which becomes much more pronounced as concentration increases. Also in the present study, we observe similar scattering behavior; as shown in Figure 2, the scattering effect becomes more pronounced as either temperature or concentration is raised. Although it is interesting to analyze the temperature and concentration dependence of the scattering, we do not attempt to discuss this phenomenon further here.

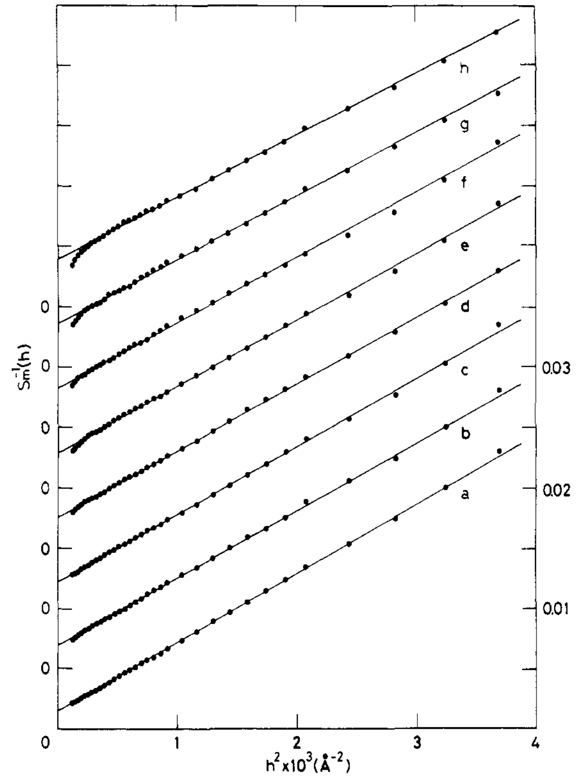

Figure 2. Inverse of the scattering law $S_m(h)$ as a function of h^2 for polystyrene ($M_w = 6.0 \times 10^5$) in cyclohexane at concentration $w = 0.1227$. Measurements were made at temperatures of (a) 34.8, (b) 38.7, (c) 41.0, (d) 44.1, (e) 48.7, (f) 53.3, (g) 57.3, and (h) 62.4 °C from bottom to top.

Scaling theory predicts that g_m/N_m or the reduced osmotic compressibility $(RT/M)\partial c/\partial\Pi$ is a universal function of c/c^* and has the following limiting power law at $c/c^* > 1$,[1,4] irrespective of the molecular weight of the polymer:

$$g_m/N_m = a_\Pi(c/c^*)^{-y} \tag{12}$$

where $y = 1/(3\nu_t - 1)$ in a Θ-solvent and $y = 1/(3\nu - 1)$ in a good solvent. The value of the tricritical exponent ν_t is 0.5, yielding $y = 2$.[5] The exponent ν is the excluded volume exponent appearing in the relation $\langle S^2\rangle \propto M^{2\nu}$ in the limit $M \rightarrow \infty$. The Flory theory gives $\nu = 0.6$ ($y = {}^5/_4$) exactly,[36] while the recent n-vector model with $n = 0$ suggests $\nu = 0.588$,[37] yielding $y = 1.31$. a_Π is a proportionality constant depending only on $vM^{1/2}$. Although somewhat artificial, eq 12 can also be derived from the SJP theory if we notice that the expansion factor α_S is a universal function of the excluded volume parameter or $vM^{1/2}$ and the ternary cluster integral w is expected to be independent of the reduced temperature τ (Appendix B).[39] According to the SJP theory, the same values of y, $y = 1.25$ and $y = 2$, are also predicted for its semidilute–good (II) and semidilute–Θ (IV) regions, respectively, and $y = 1$ is predicted for the semidilute–marginal region (III). As mentioned earlier, since v is proportional to the reduced temperature τ for the present system, g_m/N_m is therefore a function of c/c^* for a given reduced temperature $\tau M^{1/2}$. Many osmotic and light scattering experiments have established the c/c^* universality and the limiting law of eq 12, especially for semidilute–good solutions.[12,14] Moreover, also for semidilute–poor or Θ-solutions, recent light scattering[15] and osmotic pressure[40] experiments have shown the c/c^* universality and the limiting power law.

Figure 3 shows double-logarithmic plots of the reduced g_m/N_m as a function of the reduced concentration c/c^* at

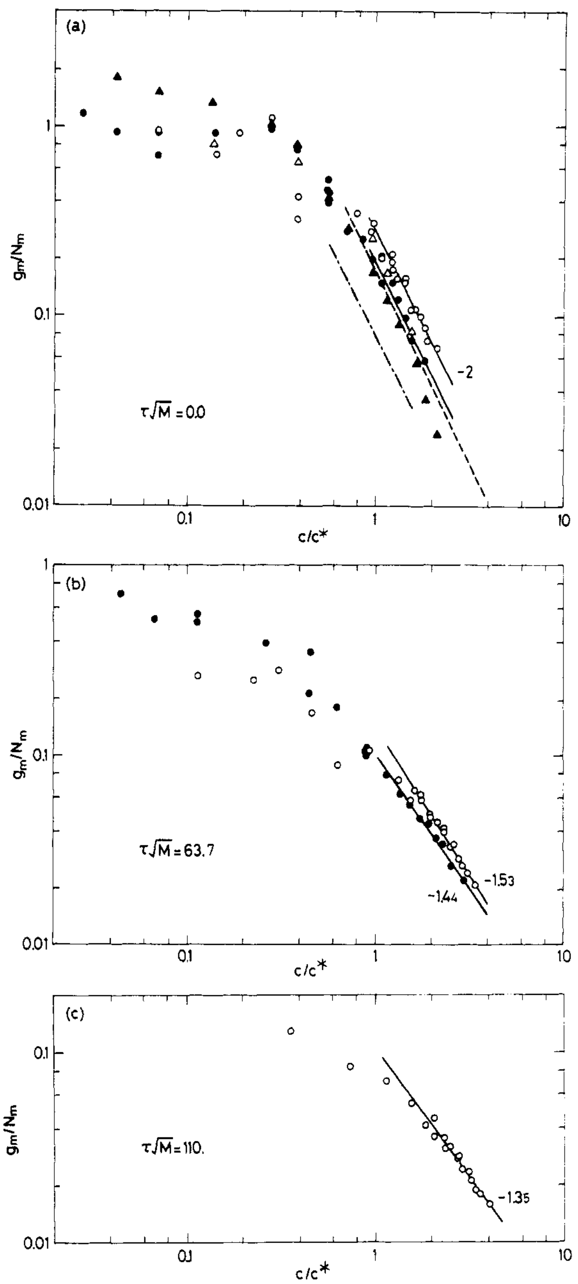

Figure 3. Double-logarithmic plots of g_m/N_m as a function of the reduced concentration c/c^* at various temperatures: (a) $\tau M_w^{1/2} = 0.0$ (Θ-temperature); (b) $\tau M_w^{1/2} = 63.7$; (c) $\tau M_w^{1/2} = 110$. Symbols: (○) $M_w = 2.0 \times 10^6$; (△) $M_w = 9.5 \times 10^5$; (●) $M_w = 6.0 \times 10^5$; (▲) $M_w = 2.33 \times 10^5$. The dashed and dash-dotted lines represent the light scattering result by Stepanek et al.[15] and that of osmotic pressure by Ito et al.,[40] respectively. Solid lines whose slope is -2 are drawn for $M_w = 6.0 \times 10^5$ and 2.0×10^6.

three different reduced temperatures $\tau M_w^{1/2}$ for different molecular weights. At the Θ-temperature ($\tau M_w^{1/2} = 0$), g_m/N_m obeys the limiting law of eq 12; g_m/N_m is proportional to $(c/c^*)^{-2}$ at concentrations $c > c_\Theta^*$. The value of the exponent y observed decreases with increasing temperature. At the highest temperature ($\tau M_w^{1/2} = 110$), the value of y is approximately 1.35, which is in good agreement with that of 1.31 ($\nu = 0.588$) predicted in the semidilute-good region (II).

However, some unexpected results are observed. In contrast to the results of Stepanek et al.,[15] no c/c^* universality is observed over the concentration and temperature range we studied. That is, although the proportionality constant a_Π should be independent of the molecular weight of the polymer, a distinct difference in the values of a_Π can be observed; the value of a_Π for $M_w = 2.0 \times 10^6$ is approximately 0.29, which is somewhat larger than $a_\Pi = 0.20$ for $M_w = 6.0 \times 10^5$. For the purpose of comparison, we also show recent results obtained by Ito et al.[40] and Stepanek et al.,[15] from which we obtain $a_\Pi = 0.08$ and 0.17, respectively. According to a recent mean-field theory of Benoit and Benmouna,[41] the concentration dependence of g_m at the Θ-temperature ($A_2 = 0$) is given up to order c^2 by

$$g_m/N_m \cong (3A_3M)^{-1}c^{-2} \tag{13}$$

from which we obtain $a_\Pi = 6.9 \times 10^{-5}A_3^{-1}$ by substituting both the definition of c^* and the relation of eq 8 into eq 13. It has often been assumed that not only the second virial coefficient A_2 but also the third virial coefficient A_3 vanish at the same time at the Θ-temperature. However, the nonzero values of a_Π suggest that A_3 does not vanish even at the Θ-temperature for this system. Referring to eq 13, we see that the difference in the values of a_Π indicates that A_3 depends on molecular weight of the polymer; the values of A_3 estimated from eq 13 are 2.4×10^{-4} and 3.5×10^{-4} mol cm^6 g^{-1} for $M_w = 2.0 \times 10^6$ and $M_w = 6.0 \times 10^5$, respectively. Some years ago, Vink carried out precise measurements of osmotic pressure,[39] showing that A_3 does not vanish at the Θ-temperature and depends on the molecular weight of the polymer. From his results we obtained $A_3 \simeq 3.6 \times 10^{-4}$ mol cm^6 g^{-1} for $M_w = 4.0 \times 10^5$ at the Θ-temperature, in good agreement with our values.

An unexpected deviation from eq 12 is observed for the data of $M_w = 2.33 \times 10^5$; g_m/N_m decreases more rapidly than c^{-2} with increasing concentration at $c/c_\Theta^* \gtrsim 1.5$. This is probably due to the contribution of the fourth virial coefficient A_4 and higher order virial coefficients.

Similarly, the reduced correlation length $\xi/\langle S^2\rangle^{1/2}$ is often assumed to be a universal function of c/c^* irrespective of the molecular weight of the polymer.[1] In semidilute regions, where $c/c^* > 1$, a limiting law

$$\xi/\langle S^2\rangle^{1/2} = a_\xi(c/c^*)^{-z} \tag{14}$$

is assumed, where a_ξ should be a constant independent of the molecular weight. The value of the exponent z should be 1 in a Θ-solvent and $\nu/(3\nu - 1)$ in a good solvent. As presented in Table I, $z = 0.75$ for $\nu = 0.6$ and 0.77 for $\nu = 0.588$. For a marginal solvent, the SJP theory predicts $z = {}^1/_2$.[9] Equation 14 has been confirmed by light scattering[14] and SAXS[17] experiments for semidilute-good solutions of polystyrene in toluene.

Figure 4 shows the concentration dependence of $\xi/\langle S^2\rangle_z^{1/2}$ observed at the three different reduced temperatures. At the Θ-temperature ($\tau M_w^{1/2} = 0$), the value of the line is approximately -1, in good agreement with $z = 1$ predicted by scaling theory. As the temperature is raised, the value of the slope at $c > c^*$ decreases in magnitude. This seems to indicate the solutions approach the semidilute-good region (II).

Nevertheless, unexpected behavior similar to that of g_m is observed. The value of a_ξ varies with the molecular weight of the polymer; a_ξ decreases with decreasing molecular weight, inconsistent with the assumption of the scaling theory. According to Benoit and Benmouna's theory,[41] a_ξ for the system at the Θ-temperature can be related to A_3 as $a_\xi^2 = 4.2 \times 10^{-5}A_3^{-1}$, where we used the definition of c^* (eq 1) and eq 8. As an example, we obtained the value $a_\xi = 0.43$ for $M_w = 2.0 \times 10^6$, yielding $A_3 = 2.3 \times 10^{-4}$ mol cm^6 g^{-1}, which is in good accord with that estimated from a_Π. This agreement suggests that the variation in the value of a_ξ is due to the molecular weight dependence of A_3.

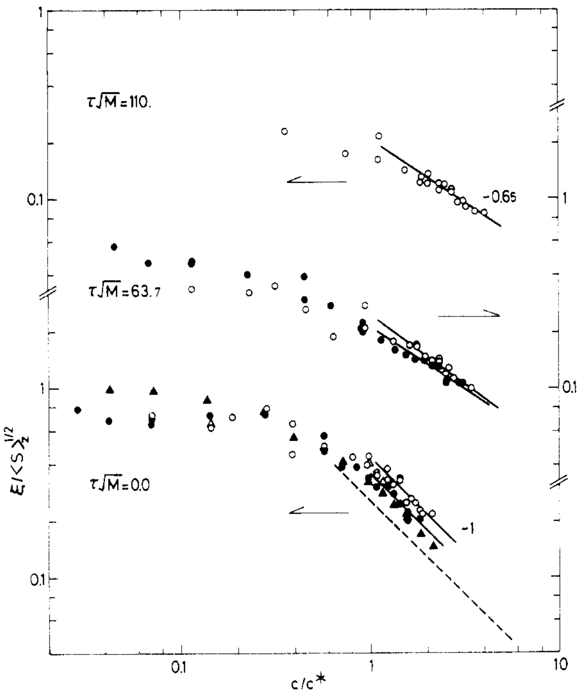

Figure 4. Double-logarithmic plots of the reduced correlation length $\xi/\langle S^2\rangle_z^{1/2}$ as a function of c/c^* at various $\tau M_w^{1/2}$, where $\langle S^2\rangle_z^{1/2}$ is the z-average radius of gyration at infinit dilution. Symbols are the same as in Figure 3.

As we have seen in the concentration dependence of g_m, the solutions at the highest temperature ($\tau M_w^{1/2} = 110$) show good solvent behavior; i.e., $y = 1.35$. On the other hand, for the same solutions at $\tau M_w^{1/2} = 110$, we have obtained an unexpected value, $z = 0.65$, which is considerably smaller than $z = 0.77$ ($\nu = 0.588$) predicted by scaling theory. This disagreement was also observed in light scattering experiments by Chu and Nose,[11] showing that g_m obeys the scaling laws predicted in the semidilute–good region (II); on the other hand, ξ does not. The value of z reported in their work is approximately 0.61, which is consistent with our value 0.65.

The temperature dependence of g_m is examined in parts a and b of Figure 5, showing typical double-logarithmic plots of g_m as a function of the reduced temperature $\tau M_w^{1/2}$ for molecular weights $M_w = 6.0 \times 10^5$ and 2.0×10^6, respectively. For both molecular weights, g_m decreases with increasing temperature for fixed concentrations. Two distinct regions of behavior are observed. That is, while at low temperatures g_m is almost independent of τ, at higher temperatures ($\tau M_w^{1/2} > 20$) g_m obeys power laws. According to scaling theory, the value of the slope is predicted to be -0.75 for $\nu = 0.6$ and -0.691 for $\nu = 0.588$. Recent light scattering experiments have shown that temperature exponents observed have values of -0.75[11] and -0.68.[15] In our results of $M_w = 2.0 \times 10^6$ shown in Figure 5b, we obtain the corresponding value of the exponent -0.66, in excellent agreement with the prediction and the experimental values mentioned above. The good agreement in the values of the temperature exponent indicates that the solutions at large $\tau M_w^{1/2}$ are in the semidilute–good region (II). This is consistent with the earlier observation in the concentration dependence of g_m, showing good solvent behavior $g_m \propto c^{-1.31}$ at $\tau M_w^{1/2} = 110$. On the other hand, as Figure 5a shows, the results for $M_w = 6.0 \times 10^5$ do not give the expected power law, but a smaller value of the slope, -0.5. Taking into account that $\tau M_w^{1/2}$ is a measure for the strength of the excluded volume effect, the reason for this discrepancy is that the solution does not reach the good solvent limit.

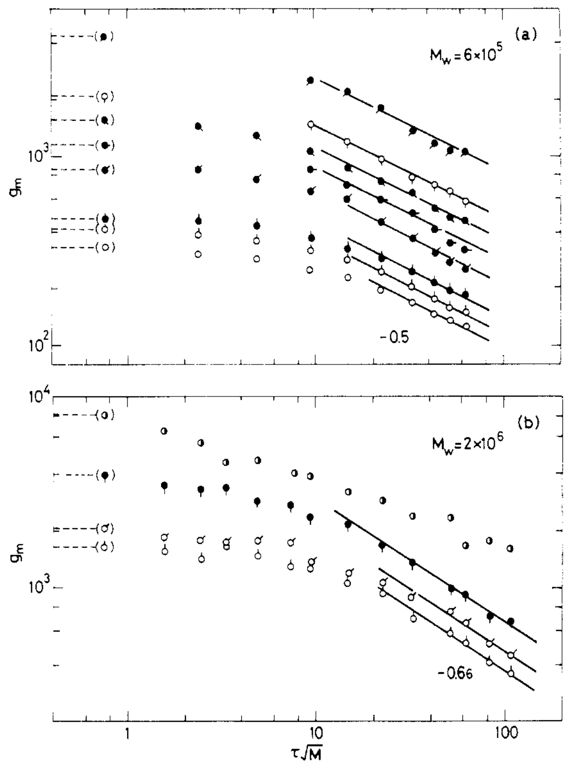

Figure 5. (a) Double-logarithmic plots of g_m as a function of $\tau M_w^{1/2}$ at various concentrations for $M_w = 6.0 \times 10^5$. The slope of the straight lines is -0.5. Symbols: (●) $w = 0.04555$; (ϙ) $w = 0.06676$; (◖) $w = 0.08147$; (●) $w = 0.1110$; (◐) $w = 0.1337$; (●) $w = 0.1616$; (ό) $w = 0.1765$; (○) $w = 0.2070$. (b) Plots for $M_w = 2.0 \times 10^6$. Symbols: (◑) $w = 0.02521$; (●) $w = 0.07668$; (σ́) $w = 0.1034$; (ό) $w = 0.1138$. The slope of the limiting lines is approximately -0.66. Dashed lines represent corresponding values of g_m at the Θ-temperature.

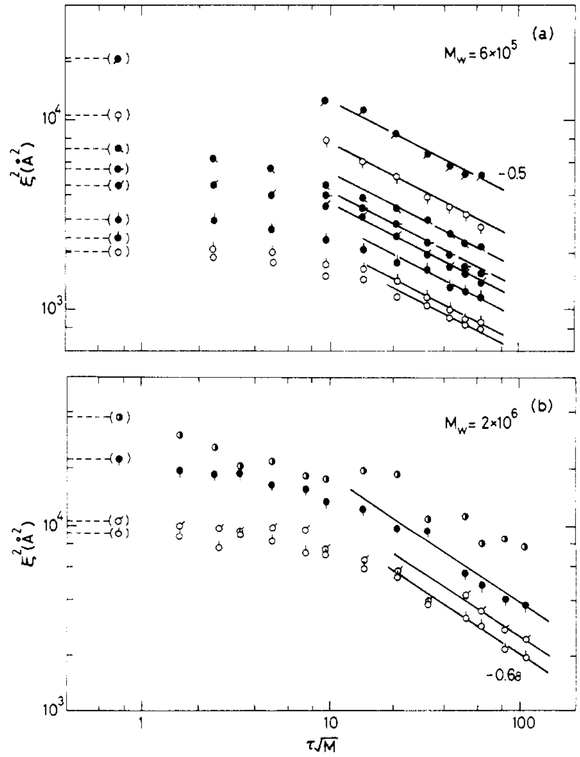

Figure 6. Double-logarithmic plots of ξ^2 as a function of $\tau M_w^{1/2}$ at various concentrations. Symbols are the same as in Figure 5.

Parts a and b of Figure 6 show typical double-logarithmic plots of ξ^2 as a function of the reduced temperature

$\tau M_w^{1/2}$ for the same solutions as shown in parts a and b of Figure 5, respectively. A temperature dependence quite similar to that of g_m is observed; ξ is almost temperature independent at small $\tau M_w^{1/2}$ and seems to obey limiting power laws at large $\tau M_w^{1/2}$. As Figure 6a shows, the predicted power law can be observed for semidilute solutions of $M_w = 6.0 \times 10^5$; the value of the slope is approximately -0.5, in good agreement with -0.461 ($\nu = 0.588$) predicted for the semidilute–good region (II). This power law has also been confirmed in an earlier SANS experiment by Cotton et al.[3] However, our data for $M_w = 2.0 \times 10^6$ show an unexpected value for the temperature exponent. The value is approximately -0.68, which is considerably smaller than -0.461. As a matter of fact, a similar value, -0.7, has also been reported in the light scattering experiment by Chu and Nose.[11] Thus, even if the value of the temperature exponent observed in our data for $M_w = 6.0 \times 10^5$ and those obtained by Cotton et al. agree well with the prediction of the scaling theory, this agreement does not give evidence for the scaling theory. Schaefer claims that measured exponents are often misinterpreted as scaling exponents predicted for semidilute–good solutions.[19] Accordingly, it is possible that the unexpected exponents of ξ found at the higher temperatures correspond to the intermediate values expected in the $c^\dagger$ crossover region of the SJP diagram: for example, the observed value -0.65 for the concentration exponent of ξ can be interpreted as an "apparent" or intermediate one between the two values -0.5 and -1, which are expected in the marginal (III) and Θ (IV) regions, respectively. Conversely, this implies that the agreement between the observed power law exponents for g_m ($g_m \propto c^{-1.35}$ and $g_m \propto \tau^{-0.69}$) and the predictions of the scaling theory is fortuitous: according to the SJP diagram,[9] the value -1.35 can be regarded as an intermediate one between the exponent -1 for the marginal region and the exponent -2 for the Θ region.

In light of Stepanek et al.'s findings,[15] we have derived expressions for ξ as a universal function of a reduced variable τ/c from Daoud and Jannink's tricritical theory[5] and Moore's mean-field theory[6] (see Appendix A). That is, in the semidilute regions where $c > c^*$

$$c^2\xi^2 \propto (\tau/c)^{-(4\nu-2)/(3\nu-1)} \qquad (\tau/c \gg 1) \tag{15}$$

$$c^2\xi^2 = A^2[36N_A{}^2B_2 + 12N_AB_{10}(\tau/c)]^{-1} \qquad (\tau/c \ll 1) \tag{16}$$

where $\tau/c \gg 1$ and $\tau/c \ll 1$ correspond to the semidilute–good and semidilute–poor regions, respectively. Here in eq 15 we assume $v \propto \tau$, which is actually valid for the present system.[21] The parameter B_{10} is an initial increment of a parameter B_1, which is related to the binary cluster integral v: i.e., $B_1 = B_{10}\tau$ near the Θ-temperature. B_2 is a parameter that is related to the ternary cluster integral w.[18,42] Since the parameters appearing in eq 16 are assumed to be independent of the molecular weight M of the polymer, $c\xi$ becomes thus a universal function of τ/c only. When $\tau/c \gg 1$, eq 15 gives $\xi \propto c^{-0.77}\tau^{-0.23}$ (for $\nu = 0.588$), which is consistent with the power law predicted for the semidilute–good region (II). More recently, Schäfer has derived a similar formula to eq 15 by applying renormalization group theory and has shown that $c^2\xi^2$ is a universal function of τ/c by examining Cotton et al.'s SANS data of ξ.[8]

In Figure 7 we examine eq 15 and 16 by plotting $c^2\xi^2$ vs. τ/c for $M_w = 2.0 \times 10^6$ and 6.0×10^5. All the data satisfying $c > c_\Theta{}^*$ are included in the plots. Figure 7 clearly shows that $c^2\xi^2$ is a universal function of τ/c over the range we studied. The same behavior as already shown in Figure 6 is observed. Although $c^2\xi^2$ is assumed to be independent of M, careful observation reveals that the value of $c^2\xi^2$ for $M_w = 2.0 \times 10^6$ is slightly larger than that for $M_w = 6.0 \times 10^5$ over the whole range of τ/c. This indicates that parameters B_{10} and B_2 depend on M.

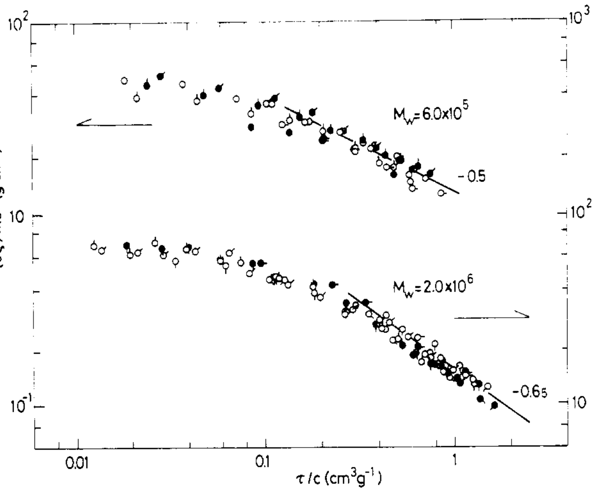

Figure 7. Double-logarithmic plots of $c^2\xi^2$ as a universal function of τ/c for semidilute solutions. All the data satisfying $c > c_\Theta{}^*$ are included. Symbols: (○) $w = 0.1227$, (○) $w = 0.1488$, and (●) $w = 0.1775$ for $M_w = 6.0 \times 10^5$; (●) $w = 0.06817$, (○) $w = 0.06863$, (○) $w = 0.07702$, (●) $w = 0.07740$, (○) $w = 0.08272$, (●) $w = 0.09002$, (○) $w = 0.09006$, (●) $w = 0.09658$, (●) $w = 0.1079$, (●) $w = 0.1187$, and (○) $w = 0.1330$ for $M_w = 2.0 \times 10^6$. Other symbols are the same as in Figure 5.

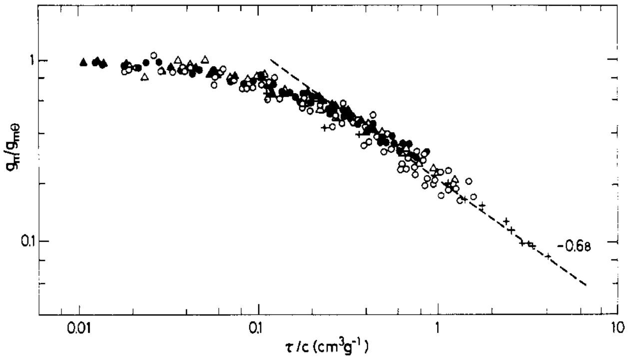

Figure 8. Double-logarithmic plots of $g_m/g_{m\Theta}$ as a universal function of τ/c for semidilute solutions of different molecular weights. Symbols are the same as in Figure 3. The symbol (+) denotes data by Stepanek et al.[15] for very high molecular weight ($M_w = 2.06 \times 10^7$) and the dashed line represents their result: $g_m/g_{m\Theta} = 0.216(\tau/c)^{-0.68}$.

Recently, Stepanek et al. found that a reduced quantity $g_m/g_{m\Theta}$ ($=(\partial\Pi/\partial c)_\Theta/(\partial\Pi/\partial c)$) can be described by a universal function of τ/c.[15] From eq A7 and A11 in Appendix A, we obtain

$$g_m/g_{m\Theta} \sim (\tau/c)^{-(6\nu-3)/(3\nu-1)} \qquad (\tau/c \gg 1) \tag{17}$$

$$g_m/g_{m\Theta} = [1 + (B_{10}/3N_AB_2)(\tau/c)]^{-1} \qquad (\tau/c \ll 1) \tag{18}$$

To examine eq 17 and 18, we plot $g_m/g_{m\Theta}$ vs. τ/c for semidilute solutions of various molecular weights in Figure 8, where we also plot the result by Stepanek et al. together with the limiting law they reported:

$$g_m/g_{m\Theta} = 0.216(\tau/c)^{-0.68} \tag{19}$$

From Figure 8, where all the data satisfying $c > c_\Theta{}^*$ are included, it is evident that $g_m/g_{m\Theta}$ is a universal function of τ/c only. The agreement between our result and that by Stepanek et al. is surprisingly good. Furthermore, the value of the limiting slope at large τ/c is close to that of -0.69 ($\nu = 0.588$) predicted by the scaling theory (eq 19).

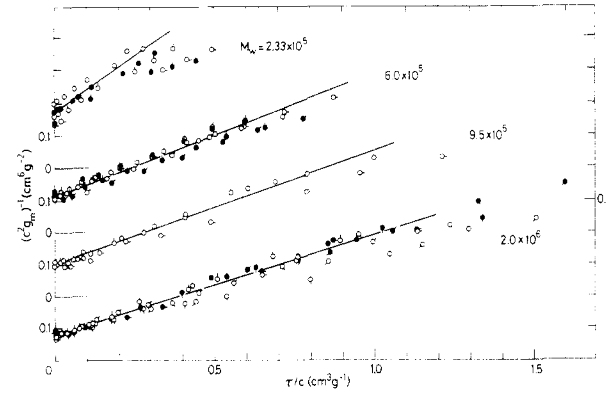

Figure 9. Plots of $(c^2 g_m)^{-1}$ as a function of τ/c for semidilute solutions of different molecular weights. Symbols: (○) $w = 0.2102$, (●) $w = 0.2328$, (○) $w = 0.2748$, (●) $w = 0.3206$, and (○) $w = 0.3647$ for $M_w = 2.33 \times 10^5$; (○) $w = 0.08938$, (○) $w = 0.1075$, and (○) $w = 0.1413$ for $M_w = 9.5 \times 10^5$. Other symbols are the same as in Figures 5 and 7.

Table III
Values of the Parameters B_{10} and B_2 for Polystyrene in Cyclohexane

$M_w \times 10^{-5}$	$B_{10} \times 10^{27}$, cm^3	$B_2 \times 10^{52}$, cm^6	$B_{10}/3N_A B_2$
6.0	6.4	9.4	3.8
9.5	5.8	8.7	3.7
20	5.0	6.8	4.1
other works	6.6[a]	25,[b] 13[c]	3[d]

[a] Reference 21. [b] Estimated from Ito et al.'s data.[40] [c] Estimated by interpolation of A_3 values obtained by Vink.[39] [d] Obtained from eq 15 in ref 15.

Assuming the observed power law as that predicted in the semidilute–good region (II), we can determine the c^{**} crossover. That is, the intersection between the horizontal line $g_m/g_{m\Theta} = 1$ and the observed limiting law of eq 19 gives

$$\tau^{**}/c^{**} \cong 0.1 \tag{20}$$

where τ^{**} is a reduced temperature corresponding to c^{**}. Near $\tau^{**}/c^{**} \cong 0.1$, a gradual change in the behavior of $g_m/g_{m\Theta}$ takes place and it seems to obey the limiting law of eq 19 at $\tau/c \gtrsim 0.5$.

It is believed that mean-field theory is applicable to the poor regions, regions I′ and III, where the excluded volume effect is weak. Since Edwards proposed a mean-field theory[23] for semidilute solutions, several mean-field theories have been proposed. Instead of the recent Benoit–Benmouna theory,[41] we here intend to examine Moore's theory[6] because his theory embodies essential features of mean-field theory. However, instead of the original Moore expressions, we use a modified formula in order to see how the theory is related to the universal properties of g_m. The resultant formula we derived is as follows (see Appendix A):

$$1/c^2 g_m = 3M_u N_A{}^2 B_2 + M_u N_A B_{10}(\tau/c) \qquad (\tau/c \ll 1) \tag{21}$$

from which in fact we obtain eq 18. To verify eq 21, we have plotted the inverse of $c^2 g_m$ vs. τ/c for the respective molecular weights in Figure 9, where all the data plotted in Figure 8 are replotted. The good linearity observed in the figure shows the validity of eq 21. As mentioned earlier, nonzero values of the intercept of these lines indicate that B_2 or A_3 does not vanish even at the Θ-temperature. A departure from linearity at $\tau/c \gtrsim 1$ is due to the scaling behavior in the semidilute–good region. According to eq 21, the intercept and slope of the lines give values of B_{10} and B_2. The values thus determined are summarized in Table III together with those estimated by other experimental methods. Although these parameters should be independent of the molecular weight of the polymer, both B_{10} and B_2 tend to decrease with increasing molecular weight. This may correspond to the observation that both A_2 and A_3 are decreasing functions of the molecular weight of the polymer.[39] Notwithstanding this, the agreement between our values and those estimated by other methods is rather good when we consider the approximations applied to eq 21. Further, it should be noted that the coefficient $B_{10}/3N_A B_2$ appearing in eq 18 is almost independent of the molecular weight of the polymer, conversely ensuring that $g_m/g_{m\Theta}$ is a universal function of τ/c.

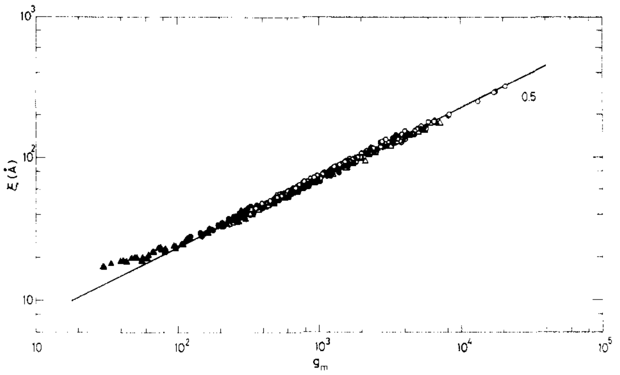

Figure 10. Double-logarithmic plots of ξ and g_m for different molecular weights. All the data obtained in the present study are included. The straight line, whose slope is 0.5, gives a value of 0.76 Å for the characteristic ratio A (see eq 22).

Turning now to the observed values of the scaling exponents of g_m and ξ, we easily notice that the values for g_m are almost twice those for ξ. This suggests that ξ^2 is proportional to g_m; i.e., $\xi^2 \propto g_m$, which is analogous to the well-known relation $\langle S^2 \rangle_0 \propto M$. As a matter of fact, according to mean-field theories,[6,41] we can obtain

$$\xi^2 = (A^2 M_u/12) g_m \tag{22}$$

It is worth mentioning that eq 22 predicts not only proportionality between g_m and ξ^2 but also an exact value of the proportionality constant. It is also important to note that the characteristic ratio A, appearing in the relation $\langle S^2 \rangle_0 = MA^2/6$, can be determined by other experimental methods such as light scattering operated in the dilute–Θ region. For example, Miyaki et al.'s eq 8 gives $A = 0.73$ Å. In the previous paper,[17] we verified eq 22 by measuing SAXS applied to semidilute solutions of low-molecular-weight polystyrene in toluene: the value of A observed in the experiment is 0.71 Å, in excellent agreement with the results obtained from unperturbed chain dimension $\langle S^2 \rangle_0{}^{1/2}$, which range from 0.68 to 0.77 Å.[21,38,43]

Figure 10 shows double-logarithmic plots of ξ vs. g_m for all the data we obtained in this study for all the molecular weights. As clearly shown in the figure, almost all the data fall on a single straight line whose slope is approximately 0.5, confirming the proportionality between ξ^2 and g_m. Moreover, the value of A determined by the line is 0.76 Å, in excellent agreement with other experimental values mentioned above. Hence the results of ξ and g_m give evidence for the validity for eq 22 or mean-field theories and indicate that most of our data are in poor solvent regions. According to the recent thermal blob hypothesis,[9,44] the mean-field result $\xi^2 \propto g_m$ can also be expected when the correlation length ξ is less than the radius ξ_τ of a thermal blob. Recently, based on a procedure similar to that of Akcasu and Han,[44] we have derived a semiempirical equation giving the value of ξ_τ as a function of only the reduced temperature τ for polystyrene in various solvents, including cyclohexane.[45] In part 1 of this series,[17] applying this equation to polystyrene in toluene, we have estimated the value of ξ_τ for this system and found the proportionality $\xi^2 \propto g_m$ for the data satisfying $\xi < \xi_\tau$. Using the same equation for the present system, we have calculated values of ξ_τ at different temperatures and then found that almost all the data satisfy $\xi < \xi_\tau$. As an example, we have obtained ξ_τ = 117 Å for t = 60.8 °C, which is larger than any value of ξ observed at this temperature. On the other hand, as we have shown in part 1 of this series,[17] another relation, $\xi^2 \propto g_m^{2\nu}$, predicted by the blob hypothesis would be observed also for the present system when $\xi > \xi_\tau$.

Conclusion

Data of both ξ and g_m gathered by SAXS measurements have been analyzed and discussed in connection with scaling theories and mean-field theories proposed for semidilute polymer solutions. First, we have examined Daoud and Jannink's tricritical theory or scaling theory.[1,5] It is found that the temperature and concentration dependences of g_m can be described by the theory: observed temperature and concentration exponents of g_m agree well with those predicted by the theory in both the semidilute–good and semidilute–poor regions. Additionally, the concentration dependence of ξ observed at the Θ-temperature is found to agree with the power law predicted by the theory. However, on the other hand, neither the temperature nor the concentration exponent for ξ observed at high temperatures agrees with the prediction of the theory. Although no distinct $c^\dagger$ crossover is observed, this disagreement implies that all the power laws observed at higher temperatures are apparent: the agreement between the observed exponents of g_m and the predicted scaling laws for good solvents may be fortuitous. Second, universal properties of ξ and g_m have been examined. Instead of finding c/c^* universality, we have demonstrated that a reduced variable $c\xi$ or $c^2 g_m$ for a given molecular weight is a universal function of τ/c in semidilute regions. In particular, $g_m/g_{m\Theta}$ has been given as a universal function of τ/c only, irrespective of the molecular weight of the polymer. Finally, we have examined Moore's mean-field theory[6] for poor solvents. In the semidilute–poor region ($\tau/c \ll 1$), the variation of g_m and ξ with both temperature and concentration is found to be well described quantitatively by the mean-field theory rather than Daoud and Jannink's theory.

Appendix A

Daoud and Jannink[5] have indicated that the scaling law for the correlation length ξ near the tricritical point may be written as

$$\xi^2(\mu,\upsilon) = \upsilon^{-2\nu_t/\phi_t} f_\xi(\mu/\upsilon^{1/\phi_t}) \qquad \text{(A1)}$$

where μ is a reduced temperature of the magnetic analogue and ν_t and ϕ_t are the tricritical exponents whose values are close to $^1/_2$ for the dimensionality of space d = 3. The function $f_\xi(x)$ has a limiting power law $f_\xi(x) \propto x^{-2\nu}$ or $f_\xi(x) \propto c^{-2\nu_t}$, according as $x \ll 1$ or $x \gg 1$. In the semidilute–good region (II), $\mu/\upsilon^{1/\phi_t} \ll 1$ and $\mu \propto c^{1/(\nu d-1)} \upsilon^{(\nu-\nu_t)d/(\nu d-1)}$, while in the semidilute–poor region (III), $\mu/\upsilon^{1/\phi_t} \gg 1$ and $\mu \propto c^{1/(\nu_t d-1)}$. When $d = 3$ and $\nu_t = \phi_t = {}^1/_2$, we thus obtain

$$\mu/\upsilon^{1/\phi_t} \propto x^{-1/(3\nu-1)} \qquad (x \gg 1;\ \text{region II}) \qquad \text{(A2)}$$

$$\mu/\upsilon^{1/\phi_t} \propto x^{-2} \qquad (x \ll 1;\ \text{region III}) \qquad \text{(A3)}$$

Here we introduce a reduced variable x, which is defined as

$$x = \upsilon/c \qquad \text{(A4)}$$

Combination of eq A1 and A2 or eq A1 and A3 gives

$$c^2\xi^2 \propto c^{-(4\nu-2)/(3\nu-1)} \qquad (x \gg 1) \qquad \text{(A5)}$$

$$c^2\xi^2 \propto \text{constant} \qquad (x \ll 1) \qquad \text{(A6)}$$

Recently, Schäfer[8] derived the same limiting law as eq A5 by applying renormalization group theory. The crossover between the semidilute regions II and III takes place when $x = x^{**}$ ($\cong$1), which corresponds to c^{**} in the DJ diagram.

In a similar way, we may derive the following universal formula for g_m from the predicted power laws for II:[5]

$$c^2 g_m \propto x^{-(6\nu-3)/(3\nu-1)} \qquad (x \gg 1) \qquad \text{(A7)}$$

$$c^2 g_m \propto \text{constant} \qquad (x \ll 1) \qquad \text{(A8)}$$

According to Moore's mean-field theory for the semidilute–poor region (III),[6] an explicit formula for g_m can be obtained:[18]

$$1/g_m = M_u N_A B_1 c + 3M_u N_A{}^2 B_2 c^2 \qquad (c > c^*) \qquad \text{(A9)}$$

where B_1 and B_2 are the parameters that are related to the binary and ternary cluster integrals, respectively.[18,38,42] Frequently, the temperature variation of B_1 is approximated near the Θ-temperature as[38]

$$B_1 = B_{10}\tau \qquad \text{(A10)}$$

and B_2 is assumed to be independent of the temperature.[39] Substituting eq A10 in eq A9, we obtain

$$1/c^2 g_m = 3M_u N_A{}^2 B_2 + M_u N_A B_{10}(\tau/c) \qquad (x \ll 1) \qquad \text{(A11)}$$

which corresponds to an expression at $x \ll 1$ to the first order of x. Equation A11 can also be reproduced from the recent Benoit–Benmouna theory.[41] From their theory, we can derive an expression of g_m up to the order of c^2:

$$1/g_m = 2A_2 M_u c + A_3 M_u c^2 \qquad (c > c^*) \qquad \text{(A12)}$$

If we assume single-contact approximations, i.e.

$$A_2 = N_A B_1/2 \qquad \text{(A13)}$$

$$A_3 = N_A{}^2 B_2 \qquad \text{(A14)}$$

then eq A12 reduces to eq A9 and finally to eq A11.

Additionally, mean-field theories give another important result for ξ and g_m:[6,41] between ξ and g_m

$$\xi^2 = (A^2 M_u/12) g_m \qquad \text{(A15)}$$

where A is a characteristic ratio appearing in the relation $\langle S^2\rangle_0 = A^2 M/6$. Combining eq A11 and A15, we obtain an expression for ξ at $x \ll 1$ to the first order of x:

$$c^2\xi^2 = A^2[36 N_A{}^2 B_2 + 12 N_A B_{10}(\tau/c)]^{-1} \qquad (x \ll 1) \qquad \text{(A16)}$$

Appendix B

On the basis of the SJP theory,[9] we can easily show that g_m/N_m is a function of ϕN_m and $\upsilon N_m{}^{1/2}$ in the two mean-field regions:

$$g_m/N_m = a^3[(\phi N_m{}^{1/2})(\upsilon N_m{}^{1/2}) + 3wa^{-3}(\phi N_m{}^{1/2})^2]^{-1} \qquad \text{(B1)}$$

where ϕ is the volume fraction of the polymer and a is the bond length. Here the ternary cluster integral w is assumed to be independent of temperature.[39] This equation corresponds to Moore's equation (eq A9). In the present paper we define the crossover concentration ϕ^* by the equation

$$\phi^* = N_m a^3/\langle S^2\rangle^{3/2} = \alpha_S{}^{-3} N_m{}^{-1/2} n^{-3/2} \qquad \text{(B2)}$$

where we use the relation $\langle S^2\rangle = \alpha_S{}^2\langle S^2\rangle_0$ with $\langle S^2\rangle_0 =$

$nN_m a^2$.[9] This equation leads to

$$\phi N_m^{1/2} = \alpha_S^{-3} n^{-3/2} (\phi/\phi^*) \tag{B3}$$

Substituting eq B3 into B1, we obtain $g_m/g_{m\Theta}$ as a function of ϕ/ϕ^* and $vN_m^{1/2}$:

$$g_m/N_m = \alpha_S^3 n^{3/2} [(\phi/\phi^*)(vN_m^{1/2}) + 3\alpha_S^{-3/2} w n^{-3/2} a^{-3} (\phi/\phi^*)]^{-1} \tag{B4}$$

where α_S is a universal function of the excluded volume parameter or $vN_m^{1/2}$.[21,38]

For the correlation length ξ, we can also show that $\xi/\langle S^2\rangle^{1/2}$ is a function of these two reduced variables: combining eq A15 and B4, we obtain

$$\xi/\langle S^2\rangle^{1/2} = \alpha_S^{-1/2} n^{-3/4} a^{-3/2} [(\phi/\phi^*) \times (vN_m^{1/2}) + 3w\alpha_S^{-3/2} n^{-3/2} a^{-3} (\phi/\phi^*)]^{-1/2} \tag{B5}$$

Registry No. Polystyrene, 9003-53-6.

References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, and London, 1979.
(2) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(3) Cotton, J. P.; Nierlich, M.; Boué, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976**, *65*, 1101.
(4) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 281.
(5) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(6) Moore, M. A. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 265.
(7) Muthukumar, M.; Edwards, S. F. *J. Chem. Phys.* **1982**, *76*, 2720.
(8) Schäfer, L. *Macromolecules* **1984**, *17*, 1357.
(9) Schaefer, D. W. *Polymer* **1984**, *25*, 387.
(10) Nakanishi, A.; Ohta, T. *J. Phys. A* **1985**, *18*, 127.
(11) Chu, B.; Nose, T. *Macromolecules* **1980**, *13*, 122.
(12) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, *14*, 668.
(13) Richards, R. W.; Maconnachie, A.; Allen, G. *Polymer* **1981**, *22*, 147.
(14) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983**, *51*, 1183.
(15) Stepanek, P.; Perzynski, R.; Delsanti, M.; Adam, M. *Macromolecules* **1984**, *17*, 2340.
(16) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(17) Hamada, F.; Kinugasa, S.; Hayashi, H.; Nakajima, A. *Macromolecules* **1985**, *18*, 2290.
(18) Okano, K.; Wada, E.; Kurita, K.; Fukuro, H. *J. Appl. Crystallogr.* **1978**, *11*, 507.
(19) Schaefer, D. W.; Lin, J. S. *Macromolecules* **1983**, *16*, 1015. Pecora, R., Ed. *Dynamic Light Scattering*; Plenum: New York and London, 1985; Chapter 5. Schaefer, D. W. *J. Polym. Sci., Polym. Symp.* **1985**, *No. 73*, 121.
(20) In the scaling theory, the reduced temperature τ is usually defined as $\tau = (T - \Theta)/\Theta$ on the analogy of critical phenomena. In the present study, however, we define it by $\tau = (T - \Theta)/T$ simply because the temperature dependence of the binary cluster integral B_1 is usually approximated by $B_1 \propto \tau$ near the Θ-temperature.
(21) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(22) The scattering law $S_m(h)$ is related to the Rayleigh ratio $R(h)$ by the equation $S_m(h) = R(h)/KcM_u$, where K is an optical constant and M_u is the molecular weight of the monomeric unit.
(23) Edwards, S. F. *Proc. Phys. Soc. London* **1966**, *88*, 265.
(24) Scholte, Th. G. *J. Polym. Sci., Part A-2* **1970**, *8*, 841.
(25) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(26) Krigbaum, W. R.; Carpenter, D. K. *J. Phys. Chem.* **1955**, *59*, 1166.
(27) McIntyre, D.; Wims, A.; Williams, L. C.; Mandelkern, L. *J. Phys. Chem.* **1962**, *66*, 1932.
(28) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J. (Tokyo)* **1971**, *2*, 799.
(29) Oyama, T.; Shiokawa, K.; Baba, K. *Polym. J. (Tokyo)* **1981**, *13*, 167.
(30) Miyaki, Y.; Fujita, H. *Polym. J. (Tokyo)* **1981**, *13*, 749.
(31) Glatter, O. *J. Appl. Crystallogr.* **1974**, *7*, 147.
(32) Kratky, O.; Pilz, I.; Schmitz, P. J. *J. Colloid Interface Sci.* **1966**, *21*, 24. Pilz, I.; Kratky, O. *J. Colloid Interface Sci.* **1967**, *24*, 211.
(33) Hara, M.; Nakajima, A. *Polym. J. (Tokyo)* **1980**, *12*, 711.
(34) Guenet, J. M.; Willmott, N. F. F.; Ellsmore, P. A. *Polym. Commun.* **1983**, *24*, 230.
(35) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(36) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(37) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. B* **1980**, *B21*, 3976.
(38) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(39) Vink, H. *Eur. Polym. J.* **1974**, *10*, 149. In the Flory–Huggins lattice theory, the ternary cluster integral w is expressed as $w = \bar{v}_2^3 M_u^3 / 3N_A^2 V_1$, where V_1 is the molar volume of the solvent. This equation shows that w is almost independent of temperature. In fact, Vink shows that the third virial coefficient A_3 ($\propto w$) depends slightly on τ compared with A_2.
(40) Ito, H.; Koyama, O.; Chiba, A. *J. Chem. Phys.* **1984**, *81*, 1504.
(41) Benoit, H.; Benmouna, M. *Polymer* **1984**, *25*, 1059.
(42) The parameters B_1 and B_2 are respectively related to v and w as follows: $B_1 = vM_u^{-2}$ and $B_2 = wM_u^{-3}$.
(43) Orofino, T. A.; Mickey, J. W., Jr. *J. Chem. Phys.* **1963**, *38*, 2512.
(44) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(45) Kinugasa, S.; Hayashi, H.; Hamada, F.; Nakajima, A. *Polymer*, to be published.