Macromolecules **1984,** *17,* 1055–1059

Semidilute Region for Linear Polymers in Good Solvents

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ABSTRACT: Osmotic pressures of concentrated solutions of polystyrenes with different molecular weights in good solvents were determined by a vapor pressure method. The data obtained as well as the osmotic pressure data in the literature were analyzed based on the scaling theory and the theory of Flory and Huggins. It was shown that the crossover between semidilute and concentrated solutions takes place at a critical concentration C^{**} (0.15–0.2 g/cm^3), irrespective of molecular weight.

Introduction

In previous papers[1-3] osmotic pressures π of polymers in good solvents were studied over wide ranges of molecular weight M and segment concentration C (g/cm^3) and compared with the theories so far published.[4-7] The scaling theory[7-9] on the thermodynamic properties of semidilute solutions was found to be in excellent agreement with the experimental data. It was shown[1-3] that the reduced osmotic pressure $\pi M/CRT$ or the ratio of the apparent second virial coefficient S [$\equiv(\pi/CRT - 1/M)/C$] to the second virial coefficient A_2, S/A_2, can be expressed by a universal function of C/C^* in both dilute and semidilute solutions, where C^* is the critical concentration at which polymer coils begin to overlap, as defined by

$$C^* = \frac{3M}{4\pi\langle S^2\rangle^{3/2}N_A} \tag{1}$$

Here, $\langle S^2\rangle$ is the mean square radius of gyration of the polymer and N_A is Avogadro's number. C/C^* is the volume concentration of polymer coils or the degree of coil overlapping.

The thermodynamic properties of linear polymer solutions in good solvents are usually discussed from their dependences on two parameters: segment concentration C and molecular weight M. To specify the polymer solutions, however, it is equally reasonable to employ two concentrations, C and C/C^*, since C^* is a function of molecular weight. If we employ these two concentrations C and C/C^*, we can classify the polymer solutions into three different regions.

(1) In dilute solutions where the segment concentration C is low and the polymer coils do not overlap, i.e., in the region of $C < 1$ and $C/C^* < 1$, π and S depend on both M and C, and $\pi M/CRT$ and S/A_2 can be expressed as the following virial expansion forms of C/C^*, respectively.

$$\pi M/CRT = 1 + 3\pi^{1/2}\psi(C/C^*) + 9\pi\psi^2\gamma(C/C^*)^2 + ... \tag{2}$$

$$S/A_2 = 1 + 3\pi^{1/2}\psi\gamma(C/C^*) + ... \tag{3}$$

where ψ is the interpenetration function, defined by $\psi = A_2M^2/4\pi^{3/2}\langle S^2\rangle^{3/2}N_A$, and γ is a coefficient in the relationship between A_2 and the third virial coefficient A_3, $A_3 = \gamma A_2^2M$; ψ and γ may be nearly constant in good solvents.[2,10]

(2) In semidilute solution where the segment concentration is low but the polymer coils overlap, i.e., in the region of $C < 1$ but $C/C^* > 1$, π and S are practically independent of molecular weight, and $\pi M/CRT$ and S/A_2 are given by the following scaling law expressed as a power of C/C^* irrespective of molecular weight[1,2]

$$\pi M/CRT = K_\pi(C/C^*)^{1/(3\nu-1)} \tag{4}$$

$$S/A_2 = K_s\psi^{-1}(C/C^*)^{(2-3\nu)/(3\nu-1)} \tag{5}$$

where ν is the excluded volume exponent as defined in the radius of gyration–molecular weight relationship $\langle S^2\rangle \propto M^{2\nu}$, K_π and K_s being numerical constants.

(3) In concentrated solutions where both the segment concentration and the degree of coil overlapping are high, i.e., in the region of $C \simeq 1$ and $C/C^* > 1$, π and S are practically independent of molecular weight as in semidilute solutions but $\pi M/CRT$ and S/A_2 are not universal functions of C/C^*, in contrast to those in semidilute solutions. The osmotic pressure in this region may be satisfactorily expressed by the theory of Flory and Huggins.[11]

$$\pi/RT = -1/V_1[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi v_2^2] \tag{6}$$

where V_1 is the molar volume of solvent, v_2 is the volume fraction of polymer, x is the molar volume ratio of polymer to solvent, and χ is the thermodynamic interaction parameter, which may be independent of M but may depend on v_2.

The crossover between dilute and semidilute solution for linear polymers in good solvents was found to take place at a certain value of C/C^*, say, 1.5–2.[1,3] The distinction between semidilute and concentrated solutions, however, was not clearly shown in the previous paper.[1] In the present work, therefore, we studied the crossover between semidilute and concentrated solutions by using the thermodynamic data of polystyrenes reported in the literature[3,12-14] and also determined by a vapor pressure method in this work.

Experimental Section

Materials. Samples used were three polystyrenes having narrow molecular weight distributions. The sample PS-3 was purchased from Pressure Chemical Co. The other two samples were prepared by an anionic polymerization method in this laboratory. Their molecular characteristics are listed in Table I. Solvents used as good solvents for polystyrenes were benzene and toluene. They were purified as described previously.[10]

Measurements. Vapor pressures of concentrated polymer solutions were measured by a gravimetric technique, using the apparatus shown in Figure 1. About 0.45 g of a sample was placed on a thin glass dish H. The whole apparatus was evacuated to 10^{-2} mmHg and sealed off at J. A breakable seal F for pure solvent in a reservoir E was broken and the equilibrium vapor pressure was controlled by changing the temperature of a thermostat B for reservoir E. The vapor pressure of pure solvents at various temperatures can be found in a table.[15] The sample solution on dish H reached an equilibrium with the vapor within 5 days. The weight fraction w_2 of the sample solution was determined from the weight of polymer taken and the weight of the polymer solution measured by a quartz spring after the weight reached a constant value. The temperature of the sample solution was determined by a thermostat A. The temperature was 25 °C for sample PS-3 in toluene and 15, 30, 45, and 60 °C for samples K-40

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0024-9297/84/2217-1055$01.50/0

Table I
Molecular Characteristics of Polystyrenes

sample code	$M \times 10^{-4}$	$\langle S^2 \rangle \times 10^{-4}$, Å^2	$C^* \times 10^2$, g/cm^3	$A_2 \times 10^4$,[f] (cm^3 mol)/g^2	solvent
K-40	6.3[a]	0.76[d]	3.8	5.9	benzene
PS-3	90[b]	$16._8$[e]	0.52	2.9	toluene
μ-302	90_0[c]	27_8[d]	0.077	1.7	benzene

[a] Number-average molecular weight. [b] Weight-average molecular weight. [c] Calculated from $[\eta]$ using the following Mark–Houwink–Sakurada equation determined from data in the literature[20-23] by the least-squares method: $[\eta] = 9.06 \times 10^{-5}$ $10^{-5} M^{0.74}$. [d] Evaluated from $\langle S^2 \rangle = 1.47 \times 10^{-2} M^{1.19}$.[24] [e] Evaluated from $\langle S^2 \rangle = 1.38 \times 10^{-2} M^{1.19}$.[3] [f] Evaluated from the relationship between A_2 and M in the literature.[3,20-24]

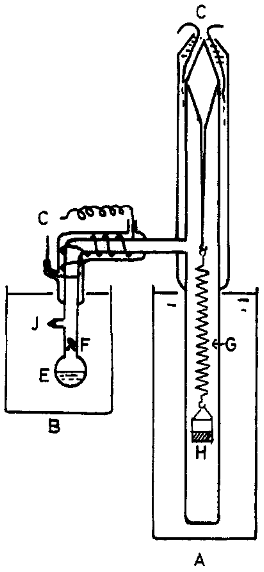

Figure 1. Apparatus for vapor pressure measurements: (A) thermostat for polymer solution; (B) thermostat for solvent; (C) heater; (E) solvent reservoir; (F) breakable seal; (G) quartz spring; (H) sample dish.

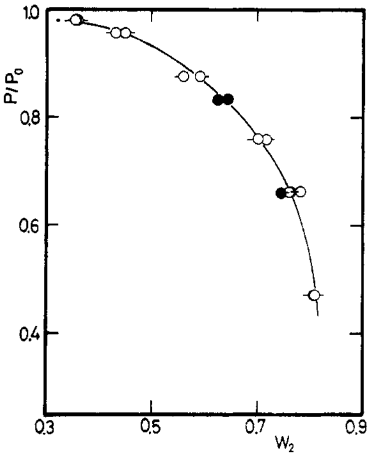

Figure 2. Polymer concentration dependence of equilibrium vapor pressure at 30 °C. P is the equilibrium vapor pressure, P_0 is the vapor pressure of pure solvent at 30 °C, and w_2 is the weight fraction of polymer. The open and filled circles show the data obtained in the absorption and desorption processes, respectively. The left and right pips show the data for samples K-40 and μ-302, respectively.

Table II
Vapor Pressure Data of Polystyrene in Toluene and Benzene

Sample K-40, Benzene

15 °C		30 °C		45 °C		60 °C	
P/P_0	w_2	P/P_0	w_2	P/P_0	w_2	P/P_0	w_2
0.592	0.802	0.572	0.806	0.609	0.817	0.617	0.805
0.660	0.769	0.661	0.779	0.722	0.742	0.747	0.729
0.734	0.724	0.761	0.700	0.818	0.663	0.866	0.599
0.815	0.702	0.874	0.610	0.887	0.572	0.931	0.492
0.904	0.565	0.956	0.458	0.923	0.515	0.965	0.386
0.951	0.476	0.978	0.358	0.961	0.421	0.931	0.498
0.951	0.470	0.835	0.645	0.980	0.351	0.835	0.650
0.858	0.612	0.661	0.763	0.818	0.662		

Sample μ-302, Benzene

15 °C		30 °C		45 °C		60 °C	
P/P_0	w_2	P/P_0	w_2	P/P_0	w_2	P/P_0	w_2
0.592	0.790	0.572	0.804	0.609	0.798	0.617	0.791
0.660	0.766	0.661	0.760	0.722	0.728	0.747	0.713
0.734	0.720	0.761	0.717	0.818	0.647	0.866	0.590
0.815	0.610	0.874	0.592	0.887	0.562	0.931	0.503
0.904	0.552	0.956	0.450	0.923	0.516	0.965	0.401
0.951	0.472	0.978	0.358	0.961	0.414	0.931	0.504
0.951	0.476	0.835	0.623	0.980	0.348	0.835	0.637
0.858	0.611	0.661	0.743	0.818	0.647		

Sample PS-3, Toluene (25 °C)

P/P_0	w_2	P/P_0	w_2
0.966	0.381	0.888	0.562
0.951	0.438	0.754	0.696
0.937	0.474		

and μ-302 in benzene. The equilibrium vapor pressure, and consequently, the concentration of the sample solution, was changed either by raising or by lowering the temperature of thermostat B. There was no hysteresis in the cycle.

The weight concentration of polymer C (g/cm^3) was converted from weight fraction w_2 by multiplying the density of the solution. The densities of toluene solutions of polystyrene were experimentally given by Scholte.[12,13] The densities of their benzene soltuions were evaluated by assuming addivity of specific volumes of solvent and solute. The densities of benzene and polystyrene at various temperatures can be found in the literature.[16] It was confirmed by analyzing the data of Scholte[12,13] for toluene solutions of polystyrenes that the assumption of additivity concerning the specific volumes is a sufficient approximation for our present purpose.

Results

Figure 2 shows an example of the relationship between equilibrium vapor pressure P and weight fraction of polymer w_2 for samples K-40 and μ-302 in benzene at 30 °C. In the figure it can be observed that both series of data obtained from absorption and desorption processes fit the same line. All data concerning equilibrium vapor pressure are listed in Table II.

Vapor pressure P is related to osmotic pressure π as

$$\pi V_1 = -RT \ln (P/P_0) \qquad (7)$$

where P_0 is the vapor pressure of pure solvent. The osmotic pressures π/C of toluene solutions of polystyrene at 25 °C, thus evaluated from vapor pressure, are double-logarithmically plotted against C in Figure 3. The data determined by direct measurements of osmotic pressure[3] and the data reported by Scholte[12,13] are also shown in Figure 3. All data are found to be consistent. The π/C vs. C relationship differs with different molecular weights

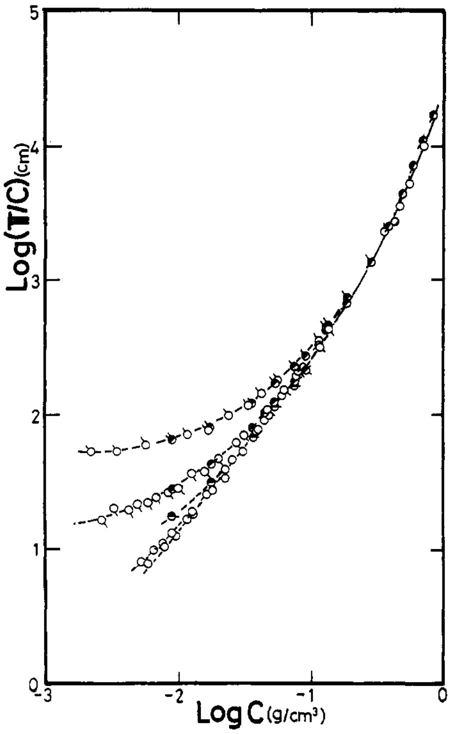

Figure 3. Polymer concentration dependence of osmotic pressure of toluene solutions of polystyrenes at 25 °C. (○) denotes the values for PS-3 evaluated from vapor pressure data. (○), (○), (○), and (○) denote the data for PS-1, PS-2, PS-3, and PS-4, respectively, reported previously.[3] (●), (●), (●), and (●) denote the data of Scholte.[12,13] The full line denotes the calculated values of eq 6 with χ values of eq 8.

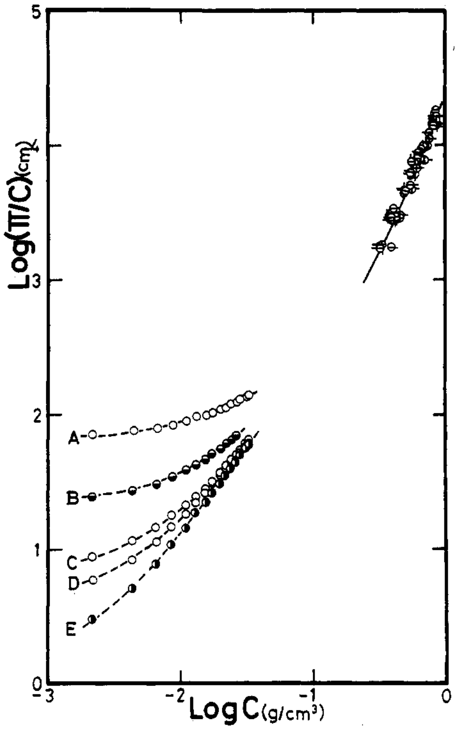

Figure 4. Polymer concentration dependence of osmotic pressure of benzene solutions of polystyrenes at various temperatures. (Φ), (φ), (Φ), and (Φ) denote the data for K-40 at 15, 30, 45, and 60 °C, respectively. (Θ), (θ), (Θ), and (Θ) denote the data for μ-302 at 15, 30, 45, and 60 °C, respectively. Curves A, B, C, D, and E denote the data of Chu and Munk for polystyrenes with various molecular weights.[14] The full line denotes the calculated values of eq 6 with χ values of eq 9.

in the dilute region but converges on a single line as the polymer concentration increases.

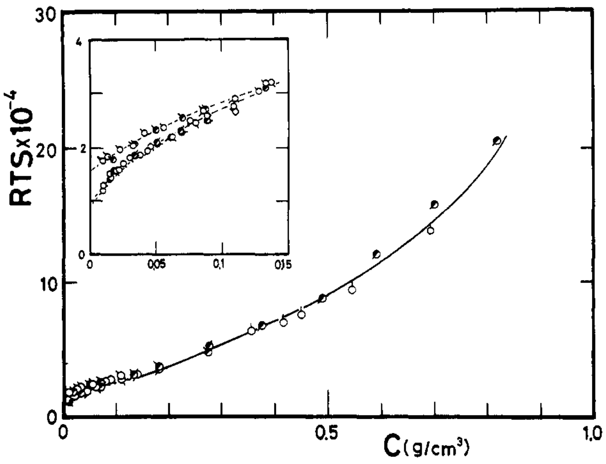

Figure 5. Polymer concentration dependence of apparent second virial coefficient S of toluene solutions of polystyrenes at 25 °C. Symbols are the same as in Figure 3.

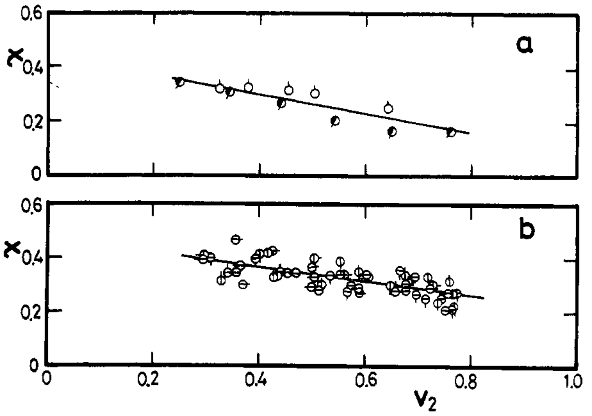

Figure 6. Plots of the χ parameter for polystyrene against volume fraction of polymer v_2. (a) In toluene; symbols are the same as in Figure 3. The full line denotes eq 8. (b) In benzene; symbols are the same as in Figure 4. The full line denotes eq 9.

Figure 4 also shows double-logarithmic plots of π/C vs. C for polystyrene in benzene at various temperatures. All data at high polymer concentrations were evaluated from vapor pressure data in this work, while the data at low concentrations were given for the samples with various molecular weights by Chu and Munk.[14] The temperature dependence of osmotic pressure at high concentrations is rather small in the good solvent.

The values of RTS evaluated from the data in Figure 3 are plotted against polymer concentration in Figure 5.

The thermodynamic interaction parameter of Flory χ can be evaluated from vapor pressures of concentrated solutions by using eq 6 and 7. Figure 6a shows the χ parameters in toluene at 25 °C as calculated from the present data and also from the data reported by Scholte. The concentration dependence of the χ parameter is similar to that reported in the literature.[11] Figure 6b shows the χ parameters in benzene at various temperatures. The values appear to be independent of temperature as reported previously.[17] Although the concentration dependence of the χ parameters may be rather complex, we can assume the following linear relationships betwreen χ and v_2 as denoted by the full lines in Figure 6, parts a and b.

$$\chi = 0.44_0 - 0.34_5 v_2 \quad \text{in toluene} \quad (8)$$

$$\chi = 0.47_5 - 0.26_5 v_2 \quad \text{in benzene} \quad (9)$$

Figure 7 shows double-logarithmic plots of $\pi M/CRT$ vs. C/C^*, which include both the data in toluene at 25 °C (Figure 3) and the data in benzene at various temperatures

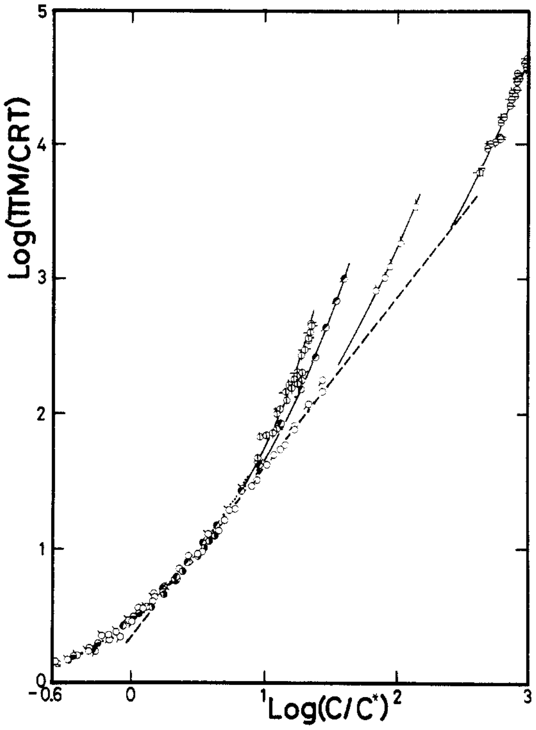

Figure 7. Double-logarithmic plots of reduced osmotic pressure ($\pi M/CRT$) vs. degree of coil overlapping (C/C^*). Symbols are the same as in Figures 3 and 4. The data of Scholte[12,13] shown by (●) and (⊖) in Figure 3 and the data of Chu and Munk[14] in curves A, C, and D of Figure 4 are not plotted in this figure. The dotted, broken, and full lines denote the calculated values of eq 2, 4, and 6, respectively.

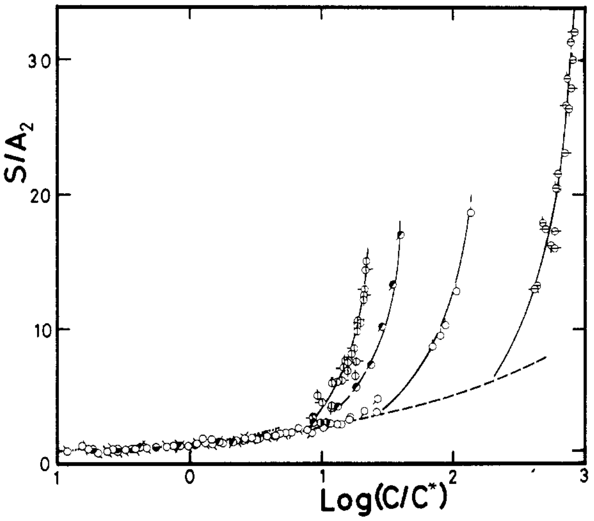

Figure 8. Plots of S/A_2 vs. log (C/C^*). The symbols are the same as in Figure 7. The dotted, broken, and full lines denote the calculated values of eq 3, 5, and 6, respectively.

(Figure 4). In this form of plots, no practical difference is found between the data in benzene and in toluene since both solvents are good. Figure 8 shows plots of S/A_2 vs. C/C^* for both toluene and benzene solutions. The dotted, broken, and full lines in Figures 7 and 8 denote the virial expansion forms (eq 2 and 3) in dilute solutions, the scaling law (eq 4 and 5) in semidilute solutions, and the theory of Flory and Huggins (eq 6) in concentrated solutions, respectively. Here, we used $\psi = 0.25$ and $\gamma = 0.25$ in eq 2 and 3, $\nu = 0.595$, and $K_\pi = 2.2$ and $K_s = 0.36$ in eq 4 and 5. Also, eq 8 or 9 was inserted into eq 6 in calculating the solid lines.

It was already reported[1,3] that both $\pi M/CRT$ and S/A_2 of poly(α-methylstyrenes) and polystyrenes in the dilute and semidilute solutions are expressed as functions of C/C^* but the functional forms in the two regions are different. The crossover between the two regions occurs at a constant value of C/C^*. The same phenomenon can be found in Figure 7.

Moreover, Figures 7 and 8 show that $\pi M/CRT$ or S/A_2 deviates from the universal function of C/C^* at a concentration C^{**}. The critical concentration C^{**} is found to be 0.15–0.2 g/cm^3 irrespective of molecular weight. Above C^{**}, π/C can well be expressed by the theory of Flory and Huggins.[11]

The fact that the crossover takes place at 0.15–0.2 g/cm^3 is consistent with the fact that the correlation length of polystyrene in good solvent becomes comparable to the segment length at such high concentration.[8]

Discussion

If the thermodynamic properties of linear polymers in good solvents are discussed from their dependences on segment concentration C and molecular weight M, it is reasonable to classify polymer solutions into two regimes: the dilute region and the Flory–Huggins region, which covers both the semidilute and concentrated solutions defined in this paper. In the dilute solution π depends on both M and C while in both the semidilute and concentrated solutions, π is practically independent of M and is a function of C only. The equation of Flory and Huggins can cover not only the concentrated solution but also the semidilute solution if the χ parameter is used as an adjustable parameter. On the basis of the concentration–molecular weight scheme, therefore, the crossover between the semidilute and concentrated solutions may appear arbitrary.

In the dilute region theoretical equations[18] of the second virial coefficient can be expressed as $A_2 = N_A\beta h(\bar{z})/2m_s^2$, where β is the binary cluster integral for the interaction of segments and m_s is the molecular weight of segment. All the theories published[18] differ only in the functional form of $h(\bar{z})$, and $h(\bar{z})$ is generally much lower than unity in good solvents if the molecular weight is high. In the theory of Flory and Huggins,[11,18] on the other hand, the second virial coefficient is given by $A_2 = (\bar{v}^2/V_1)(^1/_2 - \chi_1) \equiv N_A\beta/2m_s^2$, where $\bar{v}$ is the partial specific volume of polymer and χ_1 is the first term in the concentration expansion form of χ. Since the apparent second virial coefficients around C^* are almost equal to A_2 for high molecular weight samples, there is a big discrepancy between two values of β, estimated by applying the virial expansion form in dilute solutions and by applying the theory of Flory and Huggins to the value of S around C^*.

Several theories[4-6] were published to connect the two concentration regions but were not successful to overcome this contradiction as shown in the previous paper.[1] It was pointed out in the previous paper[1] that the reason for their failure is in their assumptions that the polymer solutions should cross over from the dilute region directly to the region of Flory and Huggins. Considering the model of Flory and Huggins,[11] it is not reasonable to extend the theory to the semidilute region where the segment concentration C is low and the excluded volume effects still work between segments, though the polymer coils overlap each other if the molecular weight is high.

If we stand on the C and C/C^* scheme, however, the semidilute region can be observed as an independent region between the dilute and concentrated solutions. Then, the crossover between the dilute and semidilute regions and that between the semidilute and concentrated regions can be understood with no contradiction. To explain the thermodynamic properties of linear polymer solutions over

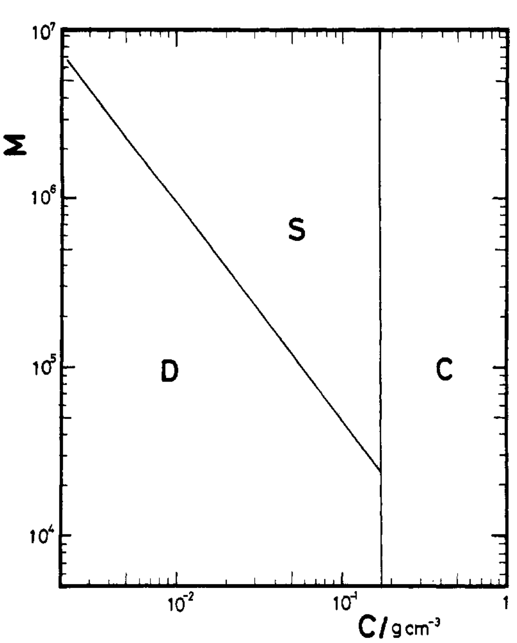

Figure 9. Molecular weight–concentration diagram for polystyrene in toluene or benzene. D, dilute solution; S, semidilute solution; C, concentrated solution.

the entire range of polymer concentration and molecular weight, it is our opinion that we should recognize the existence of the semidilute region to which neither the virial expansion form nor the theory of Flory and Huggins should be applied.

The scaling theory[19] predicts that π/C is proportional to C^2 in concentrated solutions. The experimental data of π/C appear to agree with this prediction in the concentration range 0.3–0.6 g/cm^3 as shown in Figure 3. If we compare the data with the theory of Flory–Huggins, however, we may see that π/C is almost proportional to C^2 in this concentration region owing to the fact that the third term in the expansion form of the equation of Flory and Huggins (eq 6) is relatively large and the second and fourth terms compensate each other though they still contribute to π. In the more concentrated solution the higher terms predominate and the concentration dependence becomes larger as shown in Figure 3.

In sum, we have a molecular weight–concentration diagram for polystyrene in toluene or benzene as shown in Figure 9. The lines dividing the regions do not mean that the thermodynamic properties change discontinuously at the lines but mean that the molecular weight and concentration dependences of the thermodynamic properties of linear polymers solutions are different in these regions.

Acknowledgment. We thank Professor M. Nagasawa of Nagoya University for helpful discussion and comments on the manuscript and Mr. N. Miyahara for help in measurements of vapor pressures.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Generalization of the Zimm Equation for Scattering from Concentrated Solutions

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ABSTRACT: The Zimm equation for solution light scattering is normally restricted to dilute solution studies and serves to characterize the solute molecular weight and radius of gyration, and its second virial coefficient describes the solute–solvent interaction. By extending our recent result obtained through use of the Flory–Huggins activity coefficient in the Einstein scattering equations, we show how a modified Zimm equation may be obtained which serves to characterize the Flory interaction parameter χ_{AB} in concentrated solutions. This approach proves useful in the analysis of neutron scattering data from polymer blends.

The Zimm equation[1] is well-known for light scattering measurements of molecular weight in dilute solution. At $q = 0$ [$q = (4\pi/\lambda) \sin (\theta/2)$, where λ is the wavelength of radiation and θ is the scattering angle], this may be written

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