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Universal Scaling Parameter in the Coil-to-Globule Transition

Il Hyun Park* **and Jae-Hoon Kim**

Department of Polymer Science and Engineering, Kum-Oh National Institute of Technology, Kumi, 730-301 Korea

Taihyun Chang

Department of Chemistry, Pohang Institute of Science and Technology, Pohang, 790-330 Korea

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ABSTRACT: The coil-to-globule transition of the radius of gyration of polystyrene (PS) samples (M_w: 3.84 × 10^6–8.42 × 10^6 g/mol) in methylcyclohexane (MCH) solvent has been measured by static light scattering below the Θ-temperature (Θ = 69.3 °C). In order to analyze our coil-to-globule data as well as already-reported data of polystyrene/cyclohexane (PS/CH) and polystyrene/methyl acetate (PS/MA) systems, $(M_w/R_o^2)^{3/2}|\tau|/\tau_c$ was introduced as a new scaling parameter. The master curve of each system overlapped in the plot of $\alpha_s^3(M_w/R_o^2)^{3/2}|\tau|/\tau_c$ versus $(M_w/R_o^2)^{3/2}|\tau|/\tau_c$. Thus this seems to be a universal parameter in coil-to-globule transition. On the basis of this observation, we concluded that the system dependence of the asymptotic height of the globular regime in the plot of $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ resulted mainly from the difference of the temperature width (i.e., $\Theta - T_c$) of the Θ-regime in the phase diagram of polymer solution. Here R_o, α_s [$=R_g(T)/R_g(\Theta)$], τ [$=(T-\Theta)/\Theta$], and τ_c [$=(\Theta - T_c)/\Theta$] are the unperturbed end-to-end distance, the expansion factor of the radius of gyration, the reduced temperature, and the reduced critical temperature, respectively.

I. Introduction

The transition of a flexible linear polymer chain from a random coil state in the Θ-condition to a globule (or collapsed) state in a poor solvent has attracted a great deal of attention both theoretically[1-15] and experimentally.[16-35] Although there were many theoretical controversies and conflicting experimental results concerning the existence and the type of coil-to-globule transition, this transition began to be understood more correctly through experimental results reported by Chu's group.[27-31] The important facts discovered so far are that, in the initial stage of contraction to the globule form, the static (or hydrodynamic) size of a single polymer chain could be represented by a master curve in a plot of $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ and that the hydrodynamic size approached the contracted globule state more slowly with temperature changes than the static size. In this particular experiment, the polymer samples should have very high molecular weights, each with a very narrow polydispersity. One example of this extreme condition was well described in ref 31, where it was reported that the globule state of hydrodynamic size could be observed only with a polystyrene (PS) sample of $M_w = 4.83 \times 10^7$ g/mol, M_w/M_n = 1.03.

If we examine thoroughly this coil-to-globule transition, there are still some unsolved problems. One of them is to find a true universal scaling variable. In order to show universality in the contraction (or expansion) of the polymer chain dimension in a given polymer/solvent system, a reduced blob parameter (N/N_c) has been used and accepted as a universal variable, where N and N_c are the number of monomer unit in a polymer chain and the number of monomer unit in one temperature blob, respectively. However, this reduced bolb parameter requires an empirical adjustable prefactor between the temperature blob theory and experimental results in the asymptotic collapsed regime. This adjustable parameter has no strong theoretical basis. In this paper, by combining the Shultz–Flory equation for the critical solution temperature (T_c) with the modified Flory equation for the expansion factor (α), we derive a universal parameter which can be interpreted easily as the ratio of ΔT (=Θ − T) to the temperature width (=Θ − T_c) of the Θ-regime in the phase diagram of the polymer solution. Also we measured the static size of linear polystyrene chains in methylcyclohexane (MCH) by static light scattering. In addition to reported data for the polystyrene/cyclohexane (PS/CH)[27] and polystyrene/methyl acetate (PS/MA)[28] systems, contraction of the static size of the PS/MCH system was analyzed by means of the new-derived parameter. The universality of this parameter was discussed in terms of the temperature width of the Θ-regime, the molar volume of solvent, and the scaling constant between M_w and the unperturbed mean square end-to-end distance R_o^2.

II. Theoretical Background

IIa. Modified Flory Theory.[4,7] When the temperature of a polymer solution is decreased below the Θ-temperature, intramolecular interactions in polymer solution become more attractive and the polymer chain contracts. This contraction is well described using the modified Flory equation in terms of an expansion factor $\alpha = [R(T)/R(\Theta)]$:

$$\alpha^5 - \alpha^3 - \frac{w}{\alpha^3 a^6} = 2C_m\varphi\left(\frac{T-\Theta}{\Theta}\right)\sqrt{M} \qquad (1)$$

where M is the molecular weight of polymer chain with a monomer unit length a. The ternary cluster integral w is known to be proportional to a^6. Thus, the term w/a^6 is dependent only on the nature of the polymer chain and is independent of the solution temperature. The φ parameter is the Flory entropy parameter, which is strongly dependent upon the polymer/solvent system. It should be noticed that the original Flory equation had the term $(T - \Theta)/T$ instead of $(T - \Theta)/\Theta$ in eq 1. However, this differnce introduces only a few percent error in the high molecular weight polymer solution. The value of C_m can be calculated by eq 2,[36,37] where υ is the polymer partial specific volume, N_A is the Avogardro number, V_1 is the solvent molar volume, and R_o^2 is the unperturbed mean

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* To whom correspondence should be addressed.

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$$C_m = (27/2^{5/2}\pi^{3/2})(\upsilon^2/N_A V_1)(R_o^2/M)^{-3/2}$$
$$= 1.423 \times 10^{-24}(\upsilon^2/V_1)(R_o^2/M)^{-3/2} \qquad (2)$$

suare end-to-end distance of the polymer chain. To estimate the size of the polymer chain at temperature T in a given system, we should know the Flory entropy parameter φ of the system. This parameter can be determined from the Shultz–Flory equation showing the relation between the molecular weight and the critical solution temperature.[36]

$$\frac{1}{T_c} = \frac{1}{\Theta}\left(1 + \frac{b}{\sqrt{M}}\right) \quad \text{if } M \gg \sqrt{M} \qquad (3)$$

where $b = (V_1/\upsilon)^{1/2}/\varphi$. After arranging eq 3 with respect to $\sqrt{M}$ and introducing it into eq 1, we obtain a modified Flory equation where the terms φ and $\sqrt{M}$ were eliminated:

$$\alpha^5 - \alpha^3 - \frac{w}{\alpha^3 a^6} = 2C_m(V_1/\upsilon)^{1/2}\left(\frac{T-\Theta}{\Theta}\right)\left(\frac{T_c}{\Theta - T_c}\right) \qquad (4)$$

$$= 2.847 \times 10^{-24}(\upsilon^3/V_1)^{1/2}(M/R_o^2)^{3/2}(\tau/\tau_c) \qquad (4')$$

where τ [$=(\tau - \Theta)/\Theta$] and τ_c [$=(\Theta - T_c)/T_c$] are defined as the reduced temperature and the reduced critical temperature, respectively. If $\alpha \ll 1$, α^5 and α^3 are negligible compared with $w/\alpha^3 a^6$. Then, eq 4 becomes eq 5. In our

$$\alpha^{-3} = 2.847 \times 10^{-24}(a^6/w)(\upsilon^{3/2})(V_1^{-1/2})(M/R_o^2)^{3/2}(|\tau|/\tau_c) \qquad (5)$$

experimental temperature range, the term $(a^6/w)(\upsilon^{3/2})$ can be regarded as constant within a few percent error. Thus, the main part of the new universal variable of expansion factor becomes $(V_1^{-1/2})(M/R_o^2)^{3/2}(|\tau|/\tau_c)$ in a given polymer/solvent system.

IIb. Temperature Blob Theory.[38,39] In the temperature blob theory, the expansion factor of static size (i.e., radius of gyration) α_s can be described in the poor solvent limit as

$$\alpha_s = 1.161(N/N_c)^{-1/6} \quad \text{(poor solvent limit)} \qquad (6)$$

Here the relation between the theoretical blob parameter (N/N_c) and the experimentally measurable quantity $\tau^2 M_w$ can be written as eq 7, where M_o is the molecular weight

$$N/N_c = \frac{\tau^2 M_w}{M_o(AN_1)} \qquad (7)$$

of one monomer segment and N_1 is the number of monomers in a statistical segment. The prefactor (AN_1) should be determined from a comparison of theory and experiment. When we reach the globular regime, we can set the plateau height as H in a plot of $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$. Then, for the case of static size, by combining eqs 6 and 7, we get

$$(AN_1) = H^2/(2.45M_o) \qquad (8)$$

Table I
Characterization Table of Polystyrene Samples

$10^{-4}M_w$ (g/mol)	10^8R_g (cm)	$10^{18}R_g^2/M_w$ ((cm^2 mol)/g)	plot used for R_g	M_w/M_n	maker
58.2	x	x	x	1.06	PC[a]
93.6	264	7.45	Berry	1.06	PC
142	x	x	x	1.12	PC
384	540	7.59	Berry	1.04	TS[b]
548	649	7.68	Berry	1.15	TS
842	822	8.02	Zimm	~1.2	TS

[a] Pressure Chemical Co. [b] Toyo Soda Co.

IIc. Intensity of Scattered Light. The excess Rayleigh ratio, R_{vv} (cm^{-1}), at a finite scattering angle θ in a diute solution of concentration C (g/cm^3) has an approximate form[40]

$$\frac{KC}{R_{vv}} = \frac{1}{M_w P(q)} + 2A_2C \qquad (9)$$

where K is equal to $4\pi^2 n^2(\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_o^4)$ with n, N_A, λ_o, and $\mathrm{d}n/\mathrm{d}C$ being, respectively, the refractive index, Avogadro's number, the wavelength of incident light in vacuo, and the specific refractive index increment. Subscript vv in R_{vv} indicates that both the incident and the scattered light are polarized vertically. A_2 ((mol cm^3)/g^2) is the second virial coefficient and q [$=(4\pi n/\lambda_o)\sin(\theta/2)$] is the magnitude of the momemtum transfer vector. $P(q)$ is the form factor of a single polymer chain and can be approximated as

$$P^{-1}(q) = [1 + (qR_g)^2/3] \quad \text{(Zimm plot)} \qquad (10)$$

$$P^{-1}(q) = [1 + (qR_g)^2/6]^2 \quad \text{(Berry plot)} \qquad (11)$$

III. Experimental Section

Static Light Scattering. The scattered intensity was measured by a commercial light scattering instrument (Malvern, Model 4700) operated with the λ_o = 488 nm line of an Ar ion laser (Coherent, Model 90-3). The radius of gyration, R_g was evaluated by the Berry plot except for the PS sample of $M_w = 8.42 \times 10^6$ g/mol, whose correct value of R_g was obtained by using the Zimm plot. The temperature was controlled within ±0.02 °C.

PS/MCH System. As coil-to-globule transition in PS/CH and PS/MA systems had already been studied thoroughly,[27-30] we chose the PS/MCH system. Another reason for choosing this PS/MCH system is the upper critical solution temperatures of this system have been well documented.[41-45] In order to determine the Θ-temperature by means of light scattering, dust-free polymer solution samples (M_w: 9.36×10^5 g/mol) with several different concentrations were prepared in the dry oven chamber at ~80 °C by filtering the solution quickly into the light scattering cell because of its high Θ-temperature (69.3 °C). However, for R_g measurements in the coil-to-globule transition, very dilute solution samples of high molecular weight PS were prepared as follows: first, a very small amount (~0.02 mg) of high molecular weight PS powder sample was poured into the dust-free light scattering cell and the proper amount of dust-free solvent was added into the cell up to roughly the desired concentration. The vial was then sealed with a Teflon-lined cap and inserted into a vat of a refractive index matching oil. We could reduce any possible polymer degradation by starting measurement as soon as the PS sample was dissolved. The inhomogeneity due to a very small amount of sampling was not observed in our experiments. The molecular weight, radius of gyration, polydispersity and source of the polystyrene samples used in this experiment are listed in Table I.

Physical Constants of PS and MCH. Physical constants of the organic solvent and polystyrene were calculated by the following equations where t stands for °C.

Partial specific volume of PS[46]

$$\upsilon = 0.9336 + 5.34 \times 10^{-4}(t - 25) \quad \text{(mL/g)}$$

Density and refractive index of methylcyclohexane[40,47]

$$d = 0.7867 - 8.66 \times 10^{-4}t \quad \text{(g/mL)}$$

$$n = 1.4260 - 5 \times 10^{-4}(t - 25) \quad (\text{at } \lambda_o = 488 \text{ nm})$$

The scaling constants (i.e., the ratio of the unperturbed dimension to moelcular weight in various PS/solvent systems) were listed in Table II where the values of R_g^2/M_w in the PS/MCH system

Table II
List of the Scaling Constants between the Unperturbed Size and the Molecular Weight in Several PS/Solvent Systems

system	$10^{18}R_g(\Theta)^2/M_w$ [a] ((cm^2 mol)/g)	$10^{-24}(M_w/R_o^2)^{3/2}$ [b] (g$^{3/2}$/(mol$^{3/2}$ cm^3))	ref
PS/CH	9.36	2.37	49
	9.80	2.22	27
	8.80	2.61	50
	9.00	2.50	51
	8.40	2.80	52
PS/MCH	7.60	3.25	our work
PS/MA	8.90	2.57	28

[a] Here $R_g(\Theta)$ means R_g measured at the Θ-temperature. [b] Relation $R_g(\Theta)^2 = R_o^2/6$ was used to calculate this column.

were obtained by averaging the values of several PS samples, except for one PS sample ($M_w = 8.42 \times 10^6$ g/mol) which had a higher polydispersity. Here we do not intend to list all reported literature values of the scaling constant in the PS/CH system.

IV. Results and Discussion

Θ-Temperature Measurement. First, the Θ-temperature of a linear polymer chain in a given solvent was identified as the critical solution temperature T_c of the polymer solution in the limit of infinite molecular weight. Critical concentration samples of four different molecular weight PS in methylcyclohexane solvent were prepared. The corresponding critical concentration of a given PS sample could be calculated from the empirical relationship between molecular weight and the critical concentration in the PS/MCH system.[31]

$$\phi_c = (6.68 \pm 0.02)M_w^{-0.38\pm0.01} \tag{12}$$

where ϕ_c is the critical concentration expressed by volume fraction. We tried to estimate how much the measured phase separation temperature deviated from the critical solution temperature T_c by using eq 13.[31] where $\Psi = \phi/(\phi + r(1 - \phi))$ (if $\phi = \phi_c$, then $\Psi = \Psi_c$), $r = 32.9M_w^{-0.38}$, and $X = [(T_c - T)/T_c](M_w/M_o)^{0.31}$.

$$\Psi_c - \Psi = 0.425X^{0.327} - 0.252X^{0.827} \tag{13}$$

Here r and M_o are the adjustable parameters depending on the system and the molecular weight of monomer unit, respectively. For example, with $M_w = 1 \times 10^6$ g/mol, the phase separation temperature at the concentration $\phi = 0.95\phi_c$ was off by less than 0.01 °C from T_c. Such a deviation from the critical temperature due to the incorrect critical concentration sample could be negligible when compared with our temperature measurement error of ±0.02 °C. Therefore, the critical temperature was considered as the temperature where the turbidity increased suddenly in the cooling rate of ~4 °C/h. In Figure 1, $1/T_c$ was plotted against $1/M_w^{1/2}$. The Θ-temperature calculated from the y-axis intercept was about 69.4 °C.

Another definition of the Θ-temperature is the temperature at which the second virial coefficient A_2 becomes zero. Since the value of A_2 was proportional to the initial slope $[=\Delta I(\theta = 0)/\Delta C]$ of the variation of excess scattered intensity against polymer concentration at the zero scattering angle limit, we tried to plot the initial slope $\Delta I(\theta = 0)/\Delta C$ versus temperature in Figure 2. The Θ-temperature obtained from our light scattering experiments was 69.2 °C. The different methods showed almost the same value of Θ-temperature in the PS/MCH system. It agreed well with the Θ-temperature (69.2 °C) reported by Dobashi et al.,[44,45] but there was a difference between ours and Kuwahara's value (70.8 °C).[41]

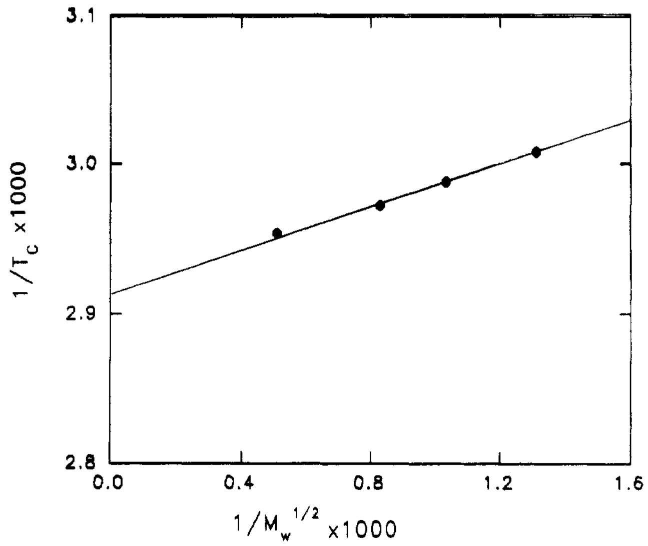

Figure 1. Molecular weight dependence of the critical solution temperature (T_c) in the polystyrene/methylcyclohexane system. The Θ-temperature estimated from the y-axis intercept was about 69.4 °C.

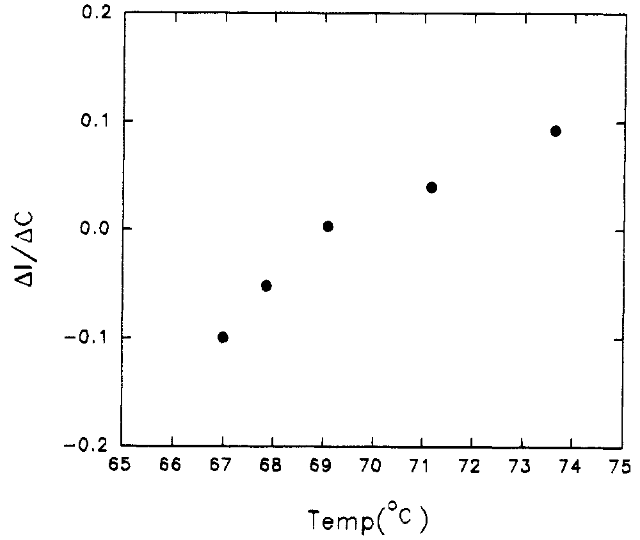

Figure 2. Plot of the initial slope ($\Delta I/\Delta C$) of excess scattered intensity against polymer concentration at various temperatures. The Θ-temperature estimated from ($\Delta I/\Delta C$) = 0 was about 69.2 °C.

In Figure 3, we plotted $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ for the PS/MCH system. The linear line of $\alpha_s = 1$ means that the polymer chain keeps the ideal size even though polymer solution temperature is decreased. If the polymer chain starts to contract with decreasing solution temperature, the data deviate downward from the $\alpha_s = 1$ line. When the value of $\alpha_s^3|\tau|M_w^{1/2}$ becomes constant, we can say the polymer chain has reached a globular regime. We observed (i) the contraction data of three different molecular weight PS samples could be expressed by one master curve and (ii) the asymptotic height of $\alpha_s^3|\tau|M_w^{1/2}$ in the globular regime was ~25.8. Also, all data of the PS/CH and PS/MA systems as well as our data of PS/MCH system were shown in Figure 3. It was found that $|\tau|M_w^{1/2}$ used as the x-axis was no longer the universal variable. As shown in Figure 3, the three systems had their own master curves and those curves did not overlap one another except in the Θ-regime ($|\tau|M_w^{1/2} < 10$). If we compare the asymptotic height levels of these three systems, PS/CH:PS/MCH:PS/MA is 20.1:25.8:50.3. The PS/MA system (50.3) had a ~2.5 times higher value than the PS/CH system. Figure 4 showed a plot of $\alpha_s(N/N_c)^{1/6}$ as a function of the reduced

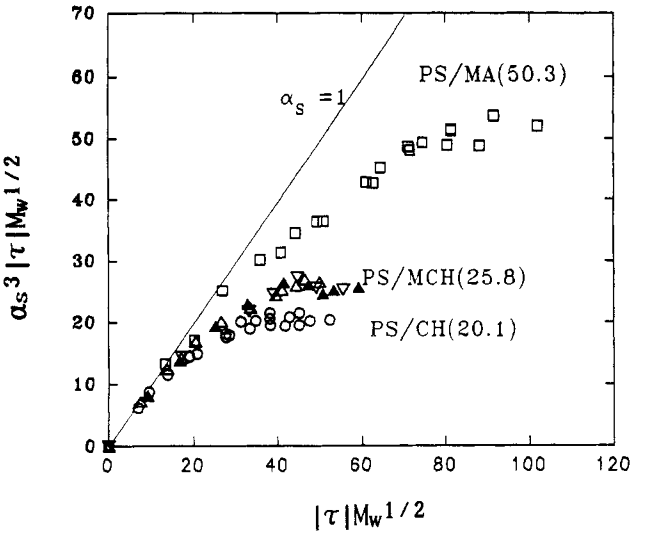

Figure 3. Plots of $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ at three different solvent systems. In PS/MCH system, (▽) $M_w = 3.84 \times 10^6$, (△) $M_w = 5.48 \times 10^6$, and (▲) $M_w = 8.42 \times 10^6$. This figure shows us that $|\tau|M_w^{1/2}$ is no longer the universal variable in various polystyrene/solvent systems.

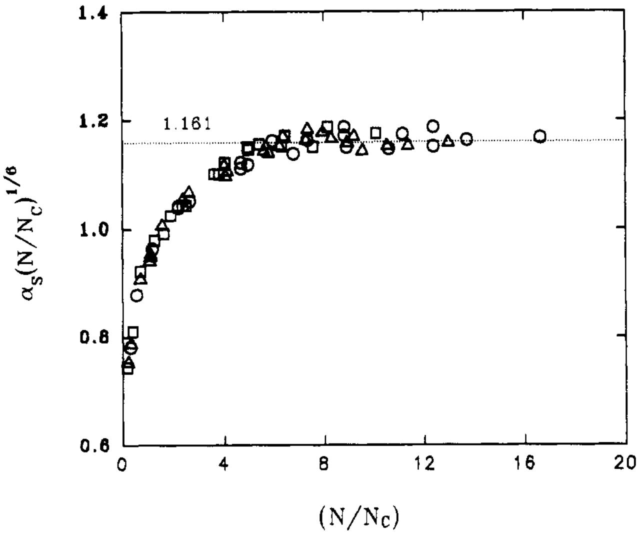

Figure 4. Universal plot of $\alpha_s(N/N_c)^{1/6}$ versus the reduced blob parameter (N/N_c) in various polystyrene/solvent systems: (○) PS/cyclohexane; (□) PS/methyl acetate; (△) PS/methylcyclohexane.

blob parameter N/N_c for all three systems. In order to convert the $|\tau|M_w^{1/2}$ variable to the N/N_c blob parameter, the prefactor AN_1 for each system should be estimated. It could be done by using eq 8. The values of this prefactor in our systems are as follows: PS/MA, ~9.9; PS/MCH, ~2.6; PS/CH, ~1.6. As shown in Figure 4, all data points were well superposed not only in the globular regime but also in the crossover regime ($0 < N/N_c < 5$), indicating that a reduced blob parameter seems like a universal and system-independent variable regarding the contraction of polymer sizes. However, we should recall that it needed an empirically adjustable prefactor AN_1 between theory and experiment in the asymptotic globular regime.

As discussed in the Theoretical Background, we tried to test the universality of the variable $(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$ introduced as the new x-axis instead of $|\tau|M_w^{1/2}$. In order to calculate the variable, we should know the correct value of the critical reduced solution temperature τ_c and the scaling constant M_w/R_o^2 for each system. The scaling constants are listed in Table II. It should be noticed that Fujita's scaling constant[46-50] ($R_g^2/M_w = 8.80 \times 10^{-18}$ (cm^2 mol)/g) was used to analyze the data of the PS/CH system because his value was accepted as one of the most reliable ones. The values of the b parameter which is necessary for calculation of the reduced critical solution temperature τ_c also are listed in Table III. As shown in Table III, our experimental value ($b = 22.7$) in the PS/MCH system was about 5–10% higher than other reference values. In the PS/CH system, there was ~7% difference between the Chu group[31] and Kuwahara group.[41] For data analysis of the PS/MCH system, we used our measurement value ($b \sim 22.7$). But for data analysis of the other systems, the average values were used ($b \sim 14.2$ for PS/CH, $b \sim 36.4$ for PS/MA). In Figure 5, we plotted $\alpha_s^3(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$ versus $(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$. Surprisingly, almost all data points both in the ideal regime and in the crossover region fell on one master curve when compared with Figure 3. Only a minor difference in the value of the asymptotic height of each system was observed in the globular regime. For example, the highest asymptotic value from the PS/MA system is $\sim 3.63 \times 10^{23}$ and the lowest value from PS/MCH is $\sim 3.05 \times 10^{23}$. Thus, the ratio of these is $H(\max)/H(\min) = 1.19$ [$= 3.63 \times 10^{23}/3.05 \times 10^{23}$] and is much improved when compared with the ratio of 2.50 [=50.3/20.1] in Figure 3. Here $H(\max)$ and $H(\min)$ mean the highest asymptotic value and the lowest one, respectively, among the three systems. When analyzing the x-axis variable $(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$ carefully, we find that it consists of three parts such as the molar volume of solvent V_1, the scaling constant of R_o^2 with respect to M_w, and the rescaled reduced temperature $|\tau|/\tau_c$. Next, in order to examine the role of the molar volume of solvent V_1 in the universality of this variable, we used $(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$ as the x-axis in Figure 6. The new x-axis variable does not contain the molar volume of solvent V_1 and the specific

Table III
List of Θ-Temperature and *b* in Various PS/Solvent Systems

system	Θ-temp (°C)	b^a	ref
PS/CH	34.0	14.6	31a
	34.0	13.7	41
PS/MCH	69.2	20.2	44, 45, 31a
	70.8	21.1	41
	69.4	22.7	our work
PS/MA	43.0	36.4	42

^{a} b was defined as $(V_1/v)^{1/2}/\varphi$ in eq 3.

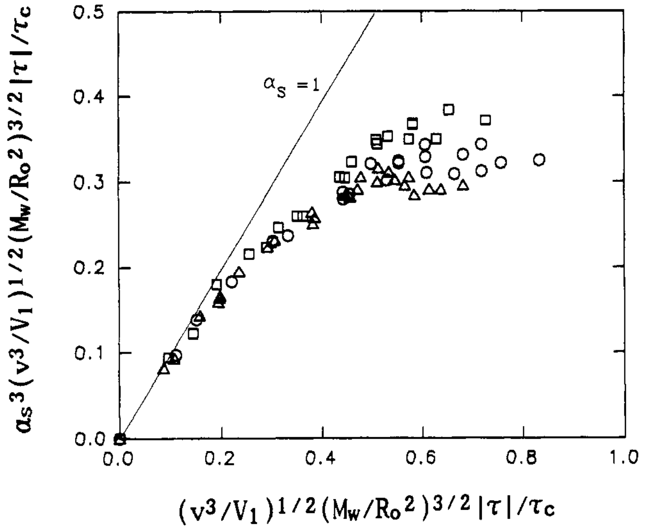

Figure 5. Plots $\alpha_s^3(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$ versus $(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$. Symbols have the same significance as in Figure 4. In order to get the actual value in g/mol units, multiply the reading value by a factor of 10^{24}.

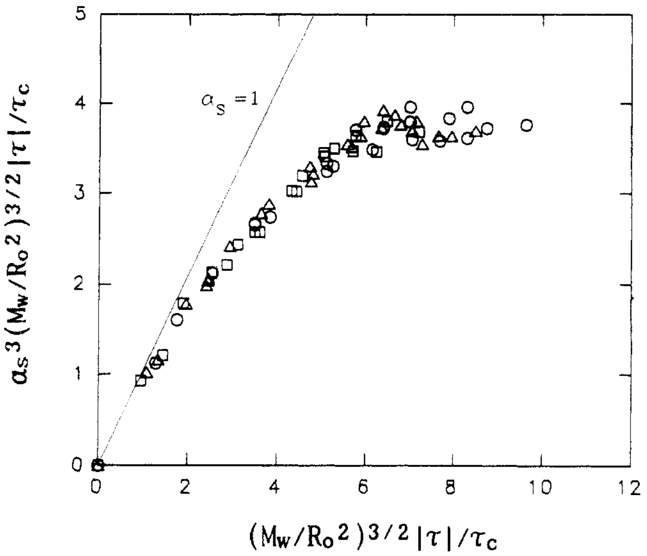

Figure 6. Plots $\alpha_s^3(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$ versus $(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$. Symbols have the same significance as in Figure 4. In order to get the actual value in $g^{3/2}/(\mathrm{mol}^{3/2}\,\mathrm{cm}^3)$ units, multiply the reading value by a factor of 10^{24}.

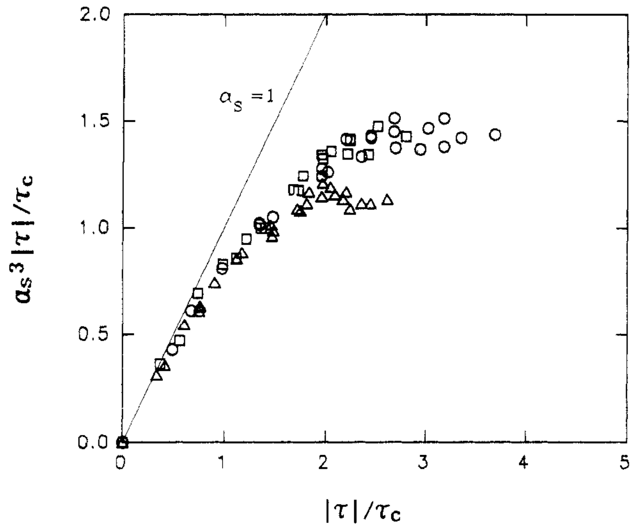

Figure 7. Plots of $\alpha_s^3(|\tau|/\tau_c)$ versus $|\tau|/\tau_c$. Symbols have the same significance as in Figure 4.

volume of polymer v. We guessed that a poorer universality would be obtained from such a parameter. On the contrary, a better universality was obtained, as shown in Figure 6. In this particular plotting, the difference between the highest value of asymptotic heights and the lowest one is only ~7%. If we recall that the relative experimental error (2σ) of the asymptotic height in the globular regime is about 10%, the 7% difference in asymptotic height is within the error range. When we replot again our data using the simplest form ($|\tau|/\tau_c$) as the x-axis, we obtained $H(\max)/H(\min)$ ~1.23 (Figure 7). This value is almost same as that (~1.19) obtained through the original parameter $(v^3/V_1)^{1/2}(M_w/R_o^2)^{3/2}(|\tau|/\tau_c)$. It can be interpreted that two different variables show the same level of universality. To investigate precisely the effects of molar volume of solvent and the w/a^6 term in the coil-to-globule transition, one needs to carry out this experiment with some other polymer sample soluble in a solvent of very small (or large) molar volume. For example, water (V_1, ~18 mL/mol) is one good candidate, as its molar volume is much less than that of ordinary organic solvent.

V. Conclusions

When the reduced temperature $|\tau|$ is scaled with the critical reduced temperature τ_c, contraction of the polymer dimension with respect to decrease of solvent quality can be expressed by a universal master curve. The background of this universality is based upon the principle of the corresponding state and scaling concepts. Now, we are trying to check whether this scaled reduced temperature $|\tau|/\tau_c$ can be applied not only to the poor solvent regime below the Θ-temperature but also to the good solvent regime above the Θ-temperature where an expansion of polymer chain dimension occurs. There are some reports that this scaled reduced temperature $|\tau|/\tau_c$ can play a role as a useful parameter in the field of polymer solution. For instance, Izumi et al.[48] reported that the coexistence curve in polymer solution showed universality in two different systems (PS/CH, and PS/MCH) when $|\tau|/\tau_c$ and ϕ/ϕ_c were used as the y-axis and x-axis in the phase diagram of polymer solution. Here τ is a reduced temperature at which phase separation started to occur at a given polymer volume fraction ϕ. Although our experiment was carried out in the thermodynamically stable regime located above the binodal curve, recently Chu's group[35] studied the kinetics of coil-to-globule transition in the thermodynamically metastable regime located just below the binodal. They observed a two-stage contraction process, i.e., crumpled globule and spherical globule, after an abrupt decrease of temperature. They claimed that the observed two-stage collapse process was very similar to the kinetic theory of a polymer chain proposed by de Gennes[10] and Grosberg et al.[11-15] One of their important results was that the polymer size at the first contraction stage obeyed the scaling concept even if that stage was located in the metastable regime. Thus, we believe that our parameter $|\tau|/\tau_c$ can apply only to the first stage contraction and that the second contraction is beyond this parameter. It will be challenging to develop a new universal parameter which can explain the final compact polymer size after the second contraction process.

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References and Notes

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