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Notes

Application of a Scaled Reduced-Temperature Parameter to the Expansion of a Single Polystyrene Chain

Il Hyun Park

Department of Polymer Science and Engineering, Kumoh National University of Technology, Kumi, Kyungbuk 730-301, Korea

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Introduction

The expansion of a flexible linear polymer chain above the upper critical solution temperature has been studied by many polymer scientists.[1–10] In order to analyze the excluded-volume effect of a single polymer chain in this temperature regime, they have used various theoretical approaches such as the mean field,[1,2,11,12] the scaling,[3,13–15] the renormalization group theory,[16–17] etc. In the blob theory, one of the scaling theories, universality is introduced through a reduced blob parameter (N/N_τ) in the expansion of the dimension of polymer chain. Here N is the number of monomer units in a polymer chain and N_τ is a temperature-dependent cutoff separating the Gaussian and the excluded-volume regimes and is considered the number of monomers in a temperature blob.[14] However, this reduced blob parameter requires an empirical adjustable prefactor linking blob theory and experimental results.[9,14] It is a weak point in the blob theory that this adjustable parameter has no strong theoretical basis. In the mean-field theory, the excluded-volume effect is described by the Flory equation (eq 1), where the Flory entropy parameter ψ and the term $[(T-\Theta)/\Theta]M^{1/2}$ are strongly dependent on the polymer/solvent system. In our previous paper[18] we derived the scaled reduced-temperature parameter $[(T-\Theta)/\Theta]/[(\Theta-T_c)/T_c]$, where Θ and T_c are the Flory Θ temperature and the critical solution temperature, respectively, and investigated its use as a universal scaling parameter in the coil-to-globule transition below the Θ temperature. According to this new universal parameter, solvent quality not only depends on how far the solution temperature is from Θ but is mainly determined by the relative ratio of temperature distance from Θ temperature, ΔT $(=T-\Theta)$, to the temperature width of the Θ regime,[23] ΔT_c $(=\Theta-T_c)$, in the phase diagram of the polymer solution. When this parameter was first applied to the coil-to-globule transition in the systems of polystyrene/cyclohexane (PS/CH), polystyrene/methyl acetate, and polystyrene/methylcyclohexane (PS/MCH), we found that the universality in the contraction of a single linear polystyrene chain below the Θ temperature could be described successfully by the new scaling parameter.[18] In the present paper, we tried to apply this parameter to the expansion of a polymer chain above the Θ temperature and found its universality in various polystyrene/solvent systems.

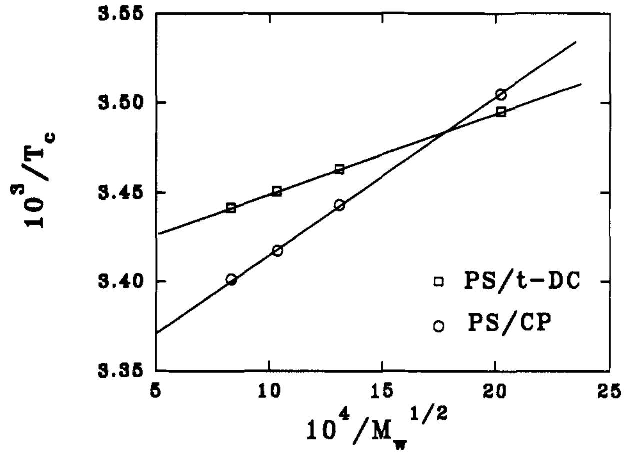

Figure 1. Molecular weight dependence of the critical solution temperature T_c in polystyrene/*trans*-decalin and polystyrene/cyclopentane.

Table 1. Characteristics of Polystyrene Samples

M_w ($\times 10^4$)	M_z/M_w	manufacturer	M_w ($\times 10^4$)	M_z/M_w	manufacturer
24.4	1.08	PC[a]	145	1.10	PC
58.2	1.05	PC	384	1.06	TS[b]
93.6	1.07	PC	548	1.12	TS

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

Table 2. Comparison between the Measured Kraemer Coefficients and the Calculated Kraemer Coefficients (Sample: Polystyrene $M_w = 3.84 \times 10^6$)

solvent	temp (°C)	α_η^3	$k_{1,\mathrm{mea}}'$	$k_{1,\mathrm{cal}}'$	$\Delta k_1'$
cyclohexane	45.0	1.36	0.05	0.10	–0.05
cyclohexane	55.0	1.61	0.12	0.15	–0.03
trans-decalin	43.6	1.60	0.12	0.15	–0.03

Theoretical Background

When the temperature of the polymer solution increases above the Θ temperature, intramolecular interactions in the polymer chain become more repulsive and the polymer chain expands. This expansion is well described by the Flory equation[1,2,12] for the expansion factor $\alpha = [R(T)/R(\Theta)]$

$$\alpha^5 - \alpha^3 = 2C_m\psi[(T-\Theta)/\Theta]M^{1/2} \tag{1}$$

where C_m $[=1.423\times10^{-24}(v^2/V_1)(R_0^2/M)^{-3/2}]$ is the system-dependent constant and v, V_1, R_0^2, and M are the polymer partial specific volume, the solvent molar volume, the unperturbed mean-square end-to-end distance, and the molecular weight, respectively. The Flory entropy parameter ψ can be determined experimentally using the Schultz–Flory equation[1] which relates the critical solution temperature, T_c to the molecular weight, M:

$$\frac{1}{T_c} = \frac{1}{\Theta}\left(1 + \frac{b}{M^{1/2}}\right) \quad \text{if } M \gg M^{1/2} \tag{2}$$

where $b = (V_1/v)^{1/2}/\psi$. Equations 1 and 2 lead to eq 3 in terms of universal scaling parameter τ/τ_c:

$$\alpha^5 - \alpha^3 = 2.846\times10^{-24}(v^{3/2}/V_1^{1/2})(M/R_0^2)^{3/2}(\tau/\tau_c) \tag{3}$$

where τ $[=(T-\Theta)/\Theta]$ and τ_c $[=(\Theta-T_c)/T_c]$ are defined

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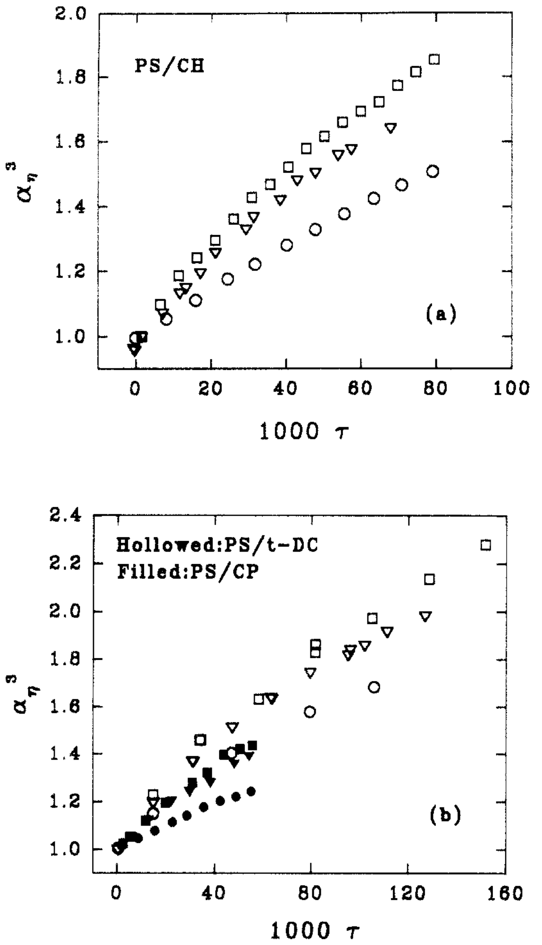

Figure 2. Plots of the expansion factor α_η^3 versus the reduced temperature τ at three different polystyrene/solvent systems: (a) polystyrene/cyclohexane; (b) polystyrene/*trans*-decalin (open symbols); polystyrene/cyclopentane (filled symbols). Circles: $M_w = 1.45 \times 10^6$ for PS. Triangles: $M_w = 3.84 \times 10^6$ for PS. Squares: $M_w = 5.48 \times 10^6$ for PS.

Table 3. Cloud Points at Various Concentrations in the System of Polystyrene/*trans*-Decalin (PS $M_w = 1.45 \times 10^6$)

conc (10^{-2} g/g)	cloud point (°C)[a]	conc (10^{-2} g/g)	cloud point (°C)[a]
5.04	17.40	1.94	17.27
3.97	17.42	0.871	16.78
2.94	17.38		

[a] The measurement error of the cloud point is about ±0.03 °C.

as the reduced temperature and the reduced critical temperature, respectively. In this study we investigated the expansion of the hydrodynamic size of the polymer chain by means of viscometry with increasing solution temperature. The expansion factor of intrinsic viscosity α_η^3 is defined as the ratio of the intrinsic viscosity at a given temperature, $[\eta]_T$, and at the Θ temperature, $[\eta]_\Theta$.

$$\alpha_\eta^3 = [\eta]_T/[\eta]_\Theta \qquad (4)$$

In this particular case, the intrinsic viscosity of the polymer chain at each solution temperature was estimated from a single inherent viscosity (η_{inh}) by correcting for the finite concentration term ($k_1'[\eta]c$ in eq 5) in the Kraemer equation.[19]

$$\ln(\eta/\eta_0)/c = \eta_{\text{inh}} \cong [\eta](1 - k_1'[\eta]c) \qquad (5)$$

The value of Kraemer coefficient k_1' was estimated using the Sakai equation,[19] eq 6, relating the Kraemer coefficient k_1' to the expansion factor α_η^3.

$$k_1' = (3/4)(\alpha_\eta^2 - 1)/\alpha_\eta^4 \qquad (6)$$

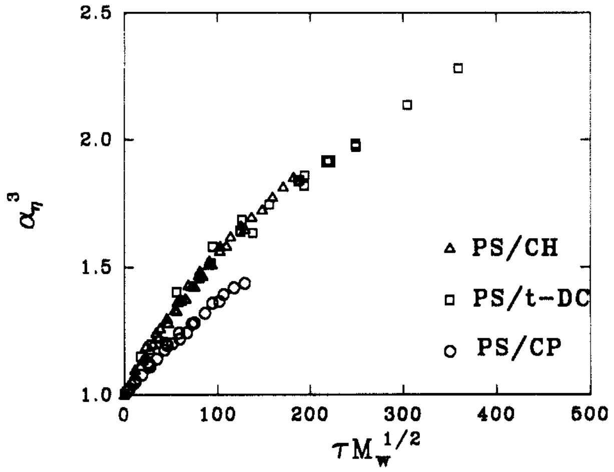

Figure 3. Plots of the expansion factor α_η^3 versus $\tau M_w^{1/2}$ at three different polystyrene/solvent systems. Triangles: polystyrene/cyclohexane. Squares: polystyrene/*trans*-decalin. Circles: polystyrene/cyclopentane.

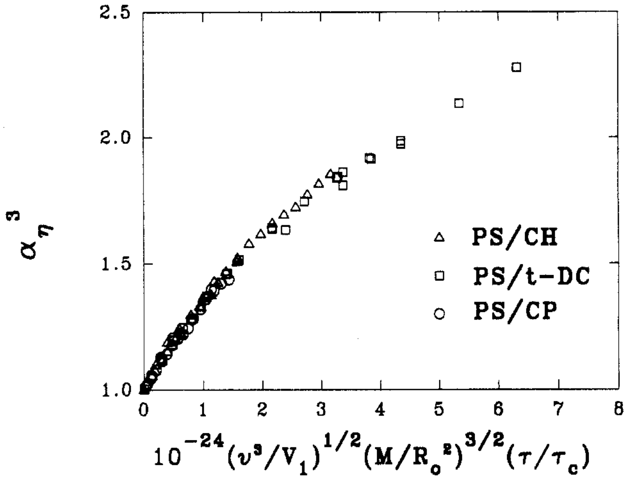

Figure 4. Plots of the expansion factor α_η^3 as a function of $(v^3/V_1)^{1/2}(M_w/R_0^2)^{3/2}(\tau/\tau_c)$ at three different polystyrene/solvent systems. Symbols have the same significance as in Figure 3. The values of $(M_w/R_0^2)^{3/2}$ (for example: PS/CH, 2.81×10^{24}; PS/t-DC, 2.83×10^{24}; PS/CP, 3.05×10^{24}, unit = $g^{3/2}/mol^{3/2}\,cm^3$) were computed approximately from the relation of $(M_w/R_0^2)^{3/2} = M_2^{1/2}\Phi_0/[\eta]_\Theta$ using the well-known intrinsic viscosity constant, Φ_0 ($=2.55 \times 10^{23}$ mol^{-1}), and the measured intrinsic viscosity under Θ conditions of polystyrene.[25]

Experimental Section

The molecular weights and the polydispersity indices of polystyrene samples used were measured by a commercial light scattering instrument (Brookhaven Model BI-200SM goniometer and Model BI-9000AT digital correlator) operated with the λ_0 = 632.8 nm line of a He–Ne ion laser (Spectra Physics Model 127) and were listed in Table 1. The values of M_z/M_w were estimated approximately by assuming the relation of Varience $\sim (M_z/M_w - 1)/4$ which is valid in the condition of $M_w/M_n < 1.25$.[24] Viscosities were measured with an Ubbelohde type capillary viscometer and a Jupiter automatic optical measurement system (Model 821, time resolution ±0.01 s). The solvent flow time was determined within ±0.04 s. In estimating $[\eta]$ for the polymer solution, the correction of the second term in eq 5 was no larger than 2.5%. In order to test the applicability of the Sakai equation to our systems, we compared the measure value of the Kraemer coefficient with the calculated one under several different conditions. As shown in Table 2, the difference between the two values of k_1' was on the order of only 0.04, justifying the

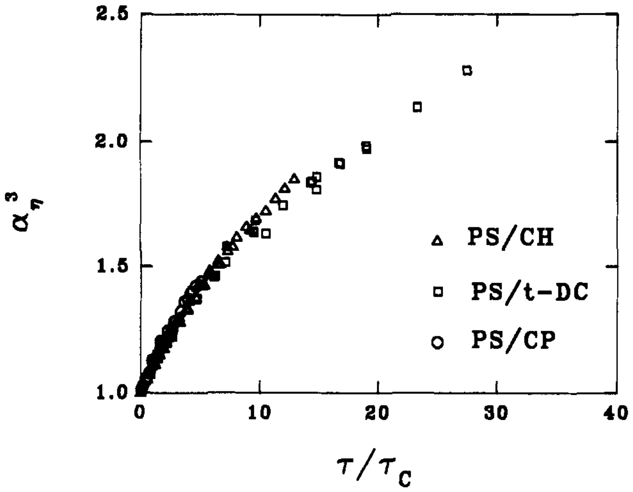

Figure 5. Plots of the expansion factor α_η^3 versus the scaled reduced temperature τ/τ_c at three different polystyrene/solvent systems. Symbols have the same significance as in Figure 3.

role of the approximately 0.6% error in $[\eta]$ ($\Delta k_1'[\eta]c \sim 0.04 \times 0.15 \sim 0.006$). We could accept the use of the Sakai equation. The critical solution temperature was identified using a homemade turbidimeter. Solutions were cooled off about 2–3 °C/h. The cloud point was defined as the temperature where the beam intensity began to decrease abruptly.

Results and Discussion

The Θ temperature of each PS/solvent system was obtained from the critical temperature T_c of the polymer solution in the limit of infinite molecular weight as shown in Figure 1. The corresponding critical concentrations of various molecular weight PS samples in *trans*-decalin or cyclopentane were estimated by the empirical relation eq 7, established originally for the PS/CH system.[20]

$$\phi_c = 7.13 M_w^{-0.38} \tag{7}$$

where ϕ_c is the critical concentration expressed by volume fraction. To estimate the error caused by using the incorrect critical concentration, we measured the phase separation temperature at various concentrations in the PS/t-DC system and listed the results in Table 3. On the basis of the results in Table 3, we concluded that eq 7 could be also applied to the PS/*trans*-decalin and PS/cyclopentane systems as well as the PS/CH system within a ±0.03 °C error in T_c measurement. Finally, our experiments on T_c were summarized in eq 8, and these equations were used to evaluate the scaled reduced-temperature parameters.

$$1/T_c = 3.245 \times 10^{-3} + 4.61 \times 10^{-2}/M_w^{1/2} \text{ (PS/CH)}^{18}$$

$$1/T_c = 3.404 \times 10^{-3} + 4.51 \times 10^{-2}/M_w^{1/2} \text{ (PS/t-DC)}$$

$$1/T_c = 3.328 \times 10^{-3} + 8.72 \times 10^{-2}/M_w^{1/2} \text{ (PS/CP)} \tag{8}$$

In Figure 2, α_η^3 was plotted as a function of the reduced temperature τ. The polymer chain of high molecular weight expanded more than that of low molecular weight even at the same reduced temperature. This shows that the solvent quality is not only a function of the temperature distance from Θ. Since according to eq 1, the molecular weight dependence of solvent quality is introduced through the term of $\tau M_w^{1/2}$ in Figure 3. Expansion factors obtained for the different molecular weight PS samples in the same solvent fell on one master curve. However, the master curves of different solvent systems did not overlap. Thus, $\tau M_w^{1/2}$ cannot be a universal parameter for polystyrene. Although the master curves for PS/CH and PS/t-DC seem to overlap, this is because its values of b/Θ in eq 8 are almost identical. When we plotted α_η^3 as a function of $(v^3/V_1)^{1/2}(M_w/R_0^2)^{3/2}(\tau/\tau_c)$ in Figure 4, all data points even from different solvent systems fell on the same master curve. Next, in order to examine the roles of the molar volume of the solvent, V_1, and the scaling constant, M_w/R_0^2, in the universality of this variable, we used only the τ/τ_c part as the x-axis in Figure 5. Almost the same universality was obtained through this simple parameter τ/τ_c when compared with Figure 4. Thus we could conclude that τ/τ_c is a universal scaling parameter in the expansion of a polymer chain above its Θ temperature as well as in the contraction of a polymer chain below Θ.[18] It should be noted that this scaled reduced temperature τ/τ_c can play a role as a universal scaling parameter in representation of the phase diagram of the polymer solution. For example, Izumi et al.[21] reported that the coexistence curve of the polymer solution showed universality in two different systems (PS/CH and PS/MCH) when τ/τ_c was plotted against ϕ/ϕ_c. According to Perzynski et al.,[22] A_2/A_2^c (i.e., the ratio of the second virial coefficient, A_2, at a given temperature and at its critical temperature, A_2^c) was also known to be a function of the scaled reduced temperature τ/τ_c in poor solvent. So far we dealt with the behavior of only PS, and it will be interesting to find whether τ/τ_c can also be applied to chemically different linear or branched polymers.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(2) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(3) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(4) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(5) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 1122.
(6) Pritchard, M. J.; Caroline, D. *Macromolecules* **1980**, *13*, 957; **1981**, *14*, 424.
(7) Adam, M.; Delsanti, M. *J. Phys. Fr.* **1980**, *41*, 713.
(8) Francois, J.; Schwartz, T.; Weill, G. *Macromolecules* **1980**, *13*, 564.
(9) Vidakovic, P.; Rondelez, F. *Macromolecules* **1983**, *16*, 253.
(10) Tanaka, G. *Macromolecules* **1982**, *15*, 1028.
(11) de Gennes, P.-G. *J. Phys. Lett.* **1975**, *36*, L55; **1978**, *39*, L299.
(12) Sanchez, I. C. *Macromolecules* **1978**, *18*, 1487; **1982**, *21*, 2123.
(13) Farnoux, B.; et al. *J. Phys. Fr.* **1978**, *39*, 77.
(14) Ackasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(15) Ackasu, A. Z.; Benmouna, M.; Alkhafaji, S. *Macromolecules* **1981**, *14*, 147.
(16) Oono, Y.; Kohmoto, M. *J. Chem. Phys.* **1983**, *78*, 520.
(17) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854, 2344, 2354.
(18) Park, I. H.; Kim, J.-H.; Chang, T. *Macromolecules* **1992**, *25*, 7300.
(19) Bohdanecky, M.; Kovar, J. *Viscosity of Polymer Solutions*; Elsevier: New York, 1982; Chapter 3.
(20) Chu, B.; Wang, Z. *Macromolecules* **1988**, *21*, 2283.
(21) Izumi, Y.; Miyake, Y. *J. Chem. Phys.* **1984**, *81*, 1501.
(22) Perzynski, R.; Delsanti, M.; Adam, M. *J. Phys. Fr.* **1987**, *48*, 115.
(23) Daoud, M.; Jannink, G. *J. Phys. Fr.* **1978**, *39*, 331.
(24) Stepanek, P. In *Dynamic Light Scattering, The method and some applications*; Brown, W., Ed.; Clarendon Press: Oxford, U.K., 1993; Chapter 4.
(25) Miyaki, Y.; Finaga, Y.; Fujita, H.; Fukuda, M. *Macromolecules* **1980**, *13*, 588.