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Communications to the Editor

Application of a Modified Scaled Reduced Temperature Parameter to the Chemically Different Polymer Systems

Il Hyun Park

School of Polymer and Textile Design, Kumoh National University of Technology, Kumi, Kyungbuk, 730-301 Korea

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In order to analyze the excluded volume effect of a single polymer chain, the polymer scientists have used various theoretical approaches[1−10] such as the mean field theory,[1−5] the scaling theory,[3,6−9] the renormalization group theory,[10,11] etc. Especially, the blob theory, one of the scaling theories, seems to have the strong universality for the expansion of a polymer chain through a reduced blob parameter.[12,13] However, this reduced blob parameter has a weak point: it requires an empirical adjustable prefactor linking blob theory and experimental results. In the mean field theory, the excluded volume effect is described by the Flory equation (eq 1) for the expansion factor α [$=R(T)/R(\Theta)$], where the Flory entropy parameter ψ is strongly dependent on the polymer/solvent system.[1,2,5]

$$\alpha^5 - \alpha^3 = 2.846 \times 10^{-24}(v^{3/2}/V_1^{\ 1/2})(M/R_0^{\ 2})^{3/2}\psi\left(\frac{T-\Theta}{\Theta}\right)\sqrt{M} \quad (1)$$

where v, V_1, R_0, T, Θ, and M are the polymer partial specific volume, the solvent molar volume, the unperturbed mean square end-to-end distance, the solution temperature (K), the Flory Θ temperature, and the molecular weight, respectively. According to Daoud and Jannink's phase diagram of a polymer/solvent system,[14] the temperature width of the Θ regime, i.e., $\Theta - T_c$, scales with $M^{-1/2}$. The Flory−Shultz equation (eq 2) shows how the Flory entropy parameter ψ is involved in the scaling constant between $\Theta - T_c$ and $M^{-1/2}$. Thus, eq 3 can be derived easily by combining eqs 1 and 2.[15,16]

$$\frac{1}{T_c} = \frac{1}{\Theta}\left(1 + \frac{(V_1^{\ 1/2}/v)}{\psi\sqrt{M}}\right) \quad \text{if} \quad M \gg \sqrt{M} \quad (2)$$

$$\alpha^5 - \alpha^3 = 2.846 \times 10^{-24}(v^{3/2}/V_1^{\ 1/2})(M/R_0^{\ 2})^{3/2}(\tau/\tau_c) \quad (3)$$

where τ [$=(T - \Theta)/\Theta$] and τ_c [$=(\Theta - T_c)/T_c$] are defined as the reduced temperature and the reduced critical temperature, respectively. In our previous papers we investigated the application of *the scaled reduced temperature parameter* τ/τ_c to both the coil-to-globule transition below the Θ temperature[15] and the expansion above the Θ temperature.[16] Up to the present this scaled parameter of τ/τ_c has shown very good universality for the expansion (or contraction) of a single chain above (or below) the Θ temperature in many UCST (upper critical solution temperature) systems of polystyrene polymer. However, we have wondered whether the application of this parameter can be successfully extended to the chemically different polymer systems or not. In this paper we tried to test the universality of the τ/τ_c parameter in terms of the expansion factor α_H of the effective hydrodynamic radii R_H in several different polymer/solvent systems such as polystyrene/cyclohexane (PS/CH), polystyrene/cyclopentane (PS/CP), polystyrene/*trans*-decalin (PS/*t*-DC), and poly(methyl methacrylate)/*n*-butyl chloride (PMMA/BC).

The molecular weights, hydrodynamic radii, and radii of gyration (R_G) of PS and PMMA samples used in this study were measured by a commercial laser light scattering instrument (Brookhaven model BI-200SM Goniometer and model BI-9000AT Digital Correlator) operated with the $\lambda_0 = 632.8$ nm line of a He−Ne ion laser (Spectra Physics model 127) and are listed in Table 1. Since the radii of gyration and the effective hydrodynamic radii were measured at the very dilute concentration ($C < C^*/30$, where C^* is the overlap concentration), the concentration correction was not necessary for the determination of the radius of the polymer chain. The values of M_z/M_w were estimated approximately by assuming the relation of variance $\sim(M_z/M_w - 1)/4$, which is valid at $M_w/M_n < 1.25$.[17] The critical solution temperature was identified using a homemade tubidimeter. Solutions were cooled down by the rate of 2−3 °C/h. The cloud point was defined as the temperature where the beam intensity began to decrease abruptly. The critical concentrations of various molecular weight PMMA samples (M_w range: $3.30 \times 10^5 - 2.04 \times 10^3$) were estimated by the empirical relation ($\phi_c = 6.8M^{-0.37}$, reported by Xia et al.[18] Finally, the equation of T_c for the PMMA/BC system was given as $1/T_c = 3.175 \times 10^{-3} + 0.0855/M_w^{\ 1/2}$. The other corresponding equations for PS systems were reported in detail in the ref 15. The Θ temperature of each system was obtained from the critical temperature T_c of the polymer solution in the limit of infinite molecular weight.

In Figure 1, α_H data of only two systems of PS/*t*-DC and PMMA/BC were plotted as a function of the reduced temperature τ [$=(T - \Theta)/\Theta$] to see the molecular weight effect on α_H. The polymer chain of high molecular weight expanded more than that of low molecular weight at the same reduced temperature. This shows that the solvent quality is not simply dependent on how far the solution temperature is from the Θ temperature. Since, according to eq 1, the molecular weight dependence of solvent quality is introduced through the term $\tau M_w^{\ 1/2}$ of the same polymer/solvent system, experimental data were thus plotted as a function of $\tau M_w^{\ 1/2}$ in Figure 2. Expansion factors obtained for the different molecular weight PS (or PMMA) samples in the same

Table 1. Characteristics of Polystyrene and Poly(methyl methacrylate) Samples

polymer	$10^{-4} M_w$	M_z/M_w	$R_{G,0}$[a] (nm)	$R_{H,0}$[a] (nm)	maker
PS	384	1.06	57.0	42.4	TS[b]
PS	842	1.14	86.0	65.5	TS
PMMA	106	1.18	25.5	22.3	PC[c]
PMMA	156	1.09	30.7	24.0	PC
PMMA	204	1.08	35.5	28.0	PC

[a] PS and PMMA samples are measured at cyclohexane (35 °C) and *n*-butyl chloride (41.8 °C), respectively. [b] Toyo Soda Co. [c] Pressure Chemical Co.

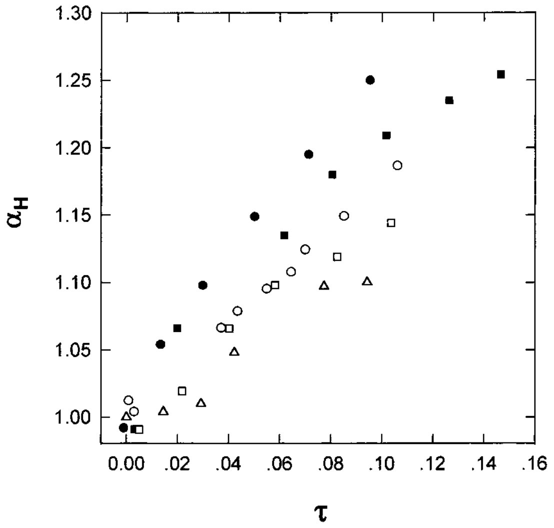

Figure 1. Plots of the expansion factor α_H versus τ at two different systems of polystyrene/*trans*-decalin and poly(methyl methacrylate)/*n*-butyl chloride. Symbols: filled circles, PS ($M_w = 8.42 \times 10^6$)/*t*-DC; filled squares, PS ($M_w = 3.84 \times 10^6$)/*t*-DC; open circles, PMMA ($M_w = 2.04 \times 10^6$)/BC; open squares, PMMA ($M_w = 1.56 \times 10^6$)/BC; open triangles, PMMA ($M_w = 1.06 \times 10^6$)/BC.

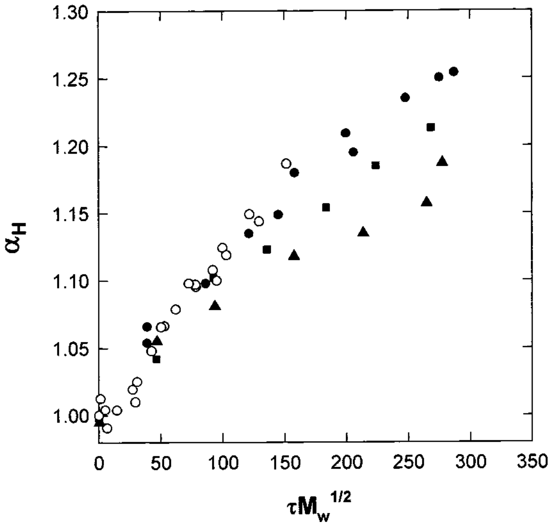

Figure 2. Plots of the expansion factor α_H versus $\tau M_w^{1/2}$ at several systems of polystyrene and poly(methyl methacrylate). Symbols: open circles, PMMA ($M_w = 2.04 \times 10^6$, 1.56×10^6, 1.06×10^6)/*n*-butyl chloride; filled circles, PS ($M_w = 8.42 \times 10^6$, 3.84×10^6)/*trans*-decalin; filled squares, PS ($M_w = 8.42 \times 10^6$)/cyclohexane; filled triangles, PS ($M_w = 8.42 \times 10^6$)/cyclopentane.

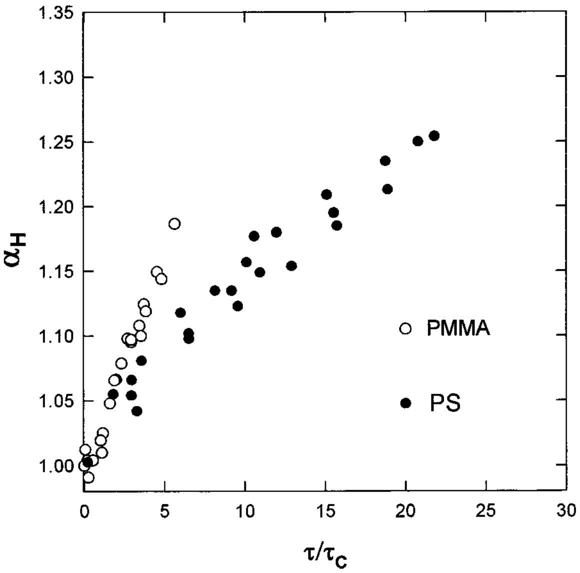

Figure 3. Plots of the expansion factor α_H as a function of τ/τ_c at chemically different polymer systems of polystyrene and poly(methyl methacrylate).

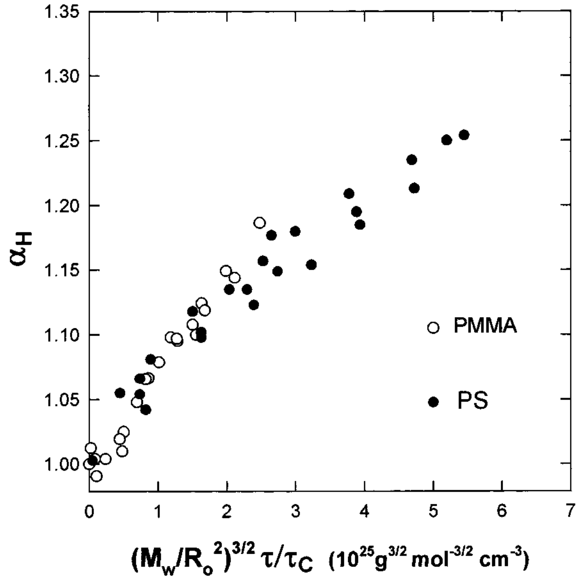

Figure 4. Plots of the expansion factor α_H as a function of $(M_w/R_0^2)^{3/2}(\tau/\tau_c)$ at chemically different polymer systems of polystyrene and poly(methyl methacrylate).

solvent fell on one curve. However, these curves for the different solvent systems of PS did not overlap one another. Thus, $\tau M_w^{1/2}$ cannot be a universal parameter for different solvent systems of a given polymer. It seems that the overlapping of two curves for PMMA/BC and PS/*t*-DC systems occurs by chance. When the values of α_H were plotted as a function of the τ/τ_c parameter in Figure 3, all data points from different solvent systems of PS fell on one master curve. Next, in order to examine whether this parameter had the universality even for the chemically different polymer systems or not, the data of PMMA/BC were also plotted in the same figure. As show in Figure 3, the τ/τ_c parameter lost its universal character for the chemically different polymer systems. As a matter of fact, eq 3 shows a guide line for what is the correct form of the universal scaling parameter. The scaled reduced temperature parameter can be modified by simply multiplying the τ/τ_c parameter by the term $(M/R_0^2)^{3/2}$. The important thing is that the term $(M/R_0^2)^{3/2}$ has a strong system dependence but very weak Θ temperature dependence. Here, the unperturbed end-to-end distance R_0 can be easily calculated from the unperturbed radius of gyration $R_{G,0}$ measured at the Θ temperature using the relation of $R_{G,0}^2 = R_0^2/6$. From Table 1 and some reference values,[15,19] the values of $(M_w/R_0^2)^{3/2}$ for PS and PMMA systems are given as $(2.60 \pm 0.2) \times 10^{24}$ and $(4.39 \pm 0.2) \times 10^{24}$ g$^{3/2}$ mol$^{-3/2}$ cm^{-3}, respectively. When our experimental data were replotted as a function of $(M_w/R_0^2)^{3/2}(\tau/\tau_c)$ in Figure 4, surprisingly all data points of PS and PMMA systems fell on one master curve within experimental error.

Recently, Dondos proposed a universal molecular blob parameter N/N_c, which is identical with the original thermal blob parameter but can be obtained using the empirical relation $N_c = 0.37a^{-7.7}$ from the exponent of the Mark–Houwink equation a, without introducing any adjustable parameter.[20,21] The limit of this approach is that in order to get the value of a at a given solution temperature, a rather tedious experiment should be done with a series of monodisperse polymer samples of different molecular weights. Although our approach based upon the phase diagram needs some quantities such as the critical solution temperature, the Flory Θ temperature, and the scaling constant of the unperturbed dimension, they can be obtained experimentally from only one monodisperse polymer sample.

In conclusion, two points should be noticed: first, $(M_w/R_0^2)^{3/2}(\tau/\tau_c)$ in eq 3 seems to play a leading role as a universal character for the expansion of the linear flexible polymer chains such as PS and PMMA. Even though the specific volume of the polymer and the molar volume of the solvent appeared as a term of $(v^{3/2}/V_1^{1/2})$ in eq 3, there was no universality in this term, as we had already discussed in the previous papers.[15,16] Second, it interested me that some universal character contained implicitly in the phase diagram can be disclosed even by the simple approach of mean field type equations. In future work we will examine the universality of this modified parameter for the linear polymer systems with very different flexibility and/or polarity from PS (or PMMA).

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