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Communications to the Editor

Application of a Modified Scaled Reduced Temperature Parameter to Polybutadiene/*n*-Propyl Acetate System

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For several decades, many polymer scientists have attempted to describe the excluded-volume effect in isolated polymer chains in terms of a single universal parameter.[1−24] Recently, there have been several new approaches to this such as a reduced blob parameter in the thermal blob theory,[12−16] a universal molecular blob parameter proposed by Dondos,[17−19] the normalized molecular weight parameter reported by Graessley et al.,[20,21] and a modified scaled reduced temperature parameter reported by Park.[22−24] Here Dondos' or Graessley's universal parameter can be regarded as an advanced form of the reduced blob parameter but requires a critical chain length which is a cutoff between the Gaussian and the excluded-volume regime. First, in the case of Dondos molecular blob parameter N/N_C, such a cutoff chain length N_C can be determined experimentally from the exponent a of the Mark−Houwink equation using the empirical relation $N_C = 0.37a^{-7.7}$, without introducing any adjustable parameter.[17−19] We should note two aspects of this Dondos parameter: (i) The very large exponent value of $|-7.7|$ in his equation gives rise to a large uncertainty in N_C. Typical uncertainty in a is of the order of $\pm 1.4\%$ (say $a = 0.7 \pm 0.01$) so that the relative uncertainty in N_C becomes approximately $\pm 12\%$. (ii) It also needs some tedious experimental work with several monodisperse polymer samples to get the Mark−Houwink exponent unless one uses a light scattering GPC on-line instrument setup. Second, recently Graessley and co-workers have introduced a universal molecular weight parameter M/M^* where M^* is a kind of cutoff molecular weight like N_C.[20,21] It is experimentally obtained as the molecular weight at $\alpha_\eta^3 \rightarrow 1$ in the plot of expansion factor against the molecular weight at good solvent condition. Thus, it surely needs some monodisperse polymer samples ranging from the very low to high molecular weight.

In contrast, the $(M/R_0^2)^{3/2}(\tau/\tau_C)$ parameter suggested by Park et al.[22−24] has a stronger theoretical basis and is obtained from measurable physical quantities with much less experimental error. This modified scaled reduced temperature parameter $(M/R_0^2)^{3/2}(\tau/\tau_C)$ of eq 1 can be derived easily from the Flory equation (eq 2) for the expansion factor $\alpha = [R(T)/R(\Theta)]$ and Flory−Shultz equation (eq 3) of the critical solution temperature T_C.

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

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

$$\frac{1}{T_C} = \frac{1}{\Theta}\left(1 + \frac{(V_1/v)^{1/2}}{\varphi\sqrt{M}}\right) \quad \text{if } M \gg M^{1/2} \quad (3)$$

where v, V_1, R_0, T, T_C, Θ, φ, and M are the polymer partial specific volume, the solvent molar volume, the unperturbed end-to-end distance, the solution temperature, the critical solution temperature, the Flory Θ temperature, the Flory entropy parameter, and the molecular weight, respectively. Here τ $[=(T-\Theta)/\Theta]$ and τ_C $[=(\Theta - T_C)/T_C]$ are defined as the reduced temperature and the reduced critical temperature, respectively.

We have already shown that this scaled parameter τ/τ_C exhibits good universality for the expansion (or contraction) of a single chain above (or below) the Θ temperature in lots of UCST (upper critical solution temperature) systems involving polystyrene.[22,23] Next we investigated whether the application of this parameter could be successfully extended to chemically different polymer systems such as polystyrene (PS) and

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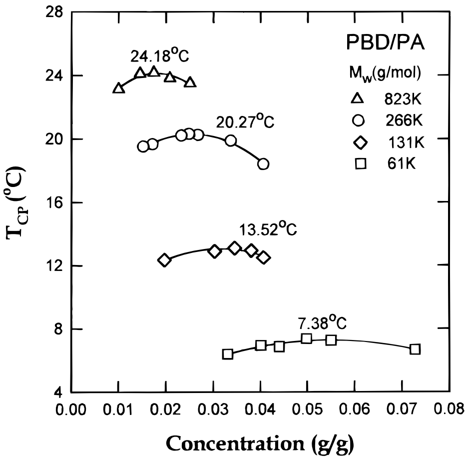

Figure 1. Plots of cloud point temperatures T_{CP} versus polymer concentration in the various molecular weight polybutadiene (PBD)/*n*-propyl acetate (PA) systems. The temperature noted in the figure is the critical solution temperature for each molecular weight of PBD.

poly(methyl methacrylate) (PMMA)[24] and showed that the modified scaled reduced parameter $(M/R_0^2)^{3/2}(\tau/\tau_C)$ can successfully and universally describe the expansion behavior of two kinds of polymer chains with different chemical structures. As however PS and PMMA are known as the vinyl type polymer and their backbone consists of only single C−C bonds, it would be very interesting to know whether this modified scaled reduced parameter can be still applied to non-vinyl-type polymers, such as polybutadiene (PBD) which is different from PS and PMMA in some aspects of chain flexibility and polarity due to double bonds in the backbone. Thus, in this study we measured the expansion factor of the intrinsic viscosity above the Θ temperature in the polybutadiene/*n*-propyl acetate (PBD/PA) system and compared these results with the other data of PS and PMMA systems. Four different weight-average molecular weight PBD samples ($M_w = 61.0 \times 10^3$, 131×10^3, 266×10^3, and 823×10^3 g/mol, Polymer Source, Inc., uncertainty of molecular weight determination ≈ 3%, 1,4-addition of more than 90%) were used in this experiment, and all had polydispersity indices M_w/M_n less than 1.1. Under the assumption that the cloud point curve near the critical point is almost identical to the coexistence curve, we analyzed the cloud point curves as shown in Figure 1 by mathematical regression and obtained the critical solution temperature T_C and the critical concentration ϕ_C from the maximum point. Thus, the molecular weight dependency of ϕ_C and T_C is given by

$$1/\phi_C = (7.61 \pm 0.68)M_w^{-0.43 \pm 0.02} \quad \text{(PBD/PA system, unit: g/g)} \quad (4)$$

$$1/T_C = (3.283 \pm 0.014) \times 10^{-3} + (7.027 \pm 0.529) \times 10^{-2}/M_w^{1/2} \quad \text{(PBD/PA system)} \quad (5)$$

In eq 4 the molecular-weight-dependent exponent of the critical concentration, −0.43, seems to be reasonable compared with the other values of −0.38 and −0.37 in PS[25,26] and PMMA[27] systems, respectively. The corresponding equations of T_C for PS and PMMA systems were reported in details in the refs 22−24. The Θ temperature of PBD/PA is obtained as 31.5 ± 1.2 °C, and such uncertainty of the Θ temperature gives a negligibly small effect to the determination of the unperturbed size (i.e., $\Delta\Theta = \pm 1.2$ °C becomes $\Delta(\tau/\tau_C) \cong \pm 1.2/(31.5 - 24.18) = \pm 0.17$ for 823K PBD and then $\Delta(\alpha_\eta^3)^{1/3} < 1\%$ as shown Figure 2).

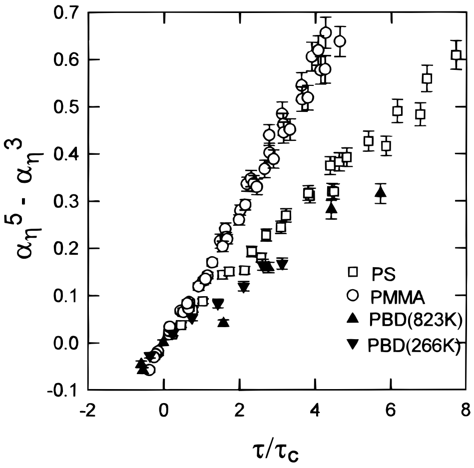

Figure 2. Plots of $\alpha_\eta^5 - \alpha_\eta^3$ versus τ/τ_C in the three different polymer systems incorporating polystyrene (PS), poly(methyl methacrylate) (PMMA), and polybutadiene (PBD).

The scaling constants of the unperturbed radii of the PBD chain were measured at 31.5 °C by means of laser light scattering (Brookhaven Instrument) and obtained as $M_w/R_{G,0}^2 = (5.30 \pm 0.23) \times 10^{16}$ and $M_w/R_{H,0}^2 = (1.19 \pm 0.04) \times 10^{17}$ g mol^{-1}cm^{-2}. The intrinsic viscosity of PBD solutions were measured by means of closed capillary viscometry as a function of increasing solution temperature. The expansion factor of the intrinsic viscosity, α_η^3, is defined as the ratio of the intrinsic viscosity at temperature T, $[\eta]_T$, to that of at the Θ temperature, $[\eta]_\Theta$.

When both the $\alpha_\eta^5 - \alpha_\eta^3$ data of the different molecular weight PBD samples and those of PS and PMMA samples were plotted as a function of τ/τ_C in Figure 2, it was found that each polymer system of chemically different structure formed its own curve. Therefore, the τ/τ_C parameter cannot be the universal parameter for the chemically different polymer systems. Next the τ/τ_C parameter can be modified by simply multiplying by $(M/R_0^2)^{3/2}$. The important thing is that the term of $(M/R_0^2)^{3/2}$ has a strong polymer 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 $R_{G,0}$ at the Θ temperature using the relation of $R_{G,0}^2 = R_0^2/6$. From our measurements and some other references,[22−24] the values of $(M_w/R_0^2)^{3/2}$ for PBD, PS, and PMMA systems are given as $(8.31 \pm 0.12) \times 10^{23}$, $(2.60 \pm 0.2) \times 10^{24}$, 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 3, data points of PS and PMMA systems formed one master curve within experimental error, but the data points of the PBD system were far off from the curve for both PS and PMMA.

Here we suggest a new modified scaled reduced temperature parameter $(N/R_0^2)^{3/2}(\tau/\tau_C)$ by substituting the number of repeating units N for the molecular weight M_w in the $(M_w/R_0^2)^{3/2}(\tau/\tau_C)$ parameter while considering the number of repeating units N as a more realistic term for the chain length. To do this, we multiply by the conversion factor $(1/M_0)^{3/2}$, where M_0 is the molecular weight of the repeating unit. We should

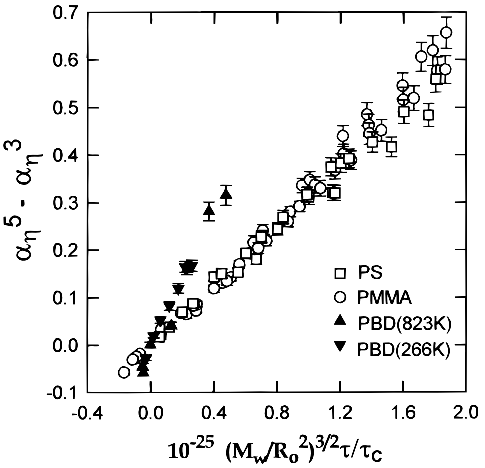

Figure 3. Plots of $\alpha_\eta^5 - \alpha_\eta^3$ as a function of $(M_w/R_0^2)^{3/2}(\tau/\tau_C)$ in the three different polymer systems incorporating polystyrene (PS), poly(methyl methacrylate) (PMMA), and polybutadiene (PBD).

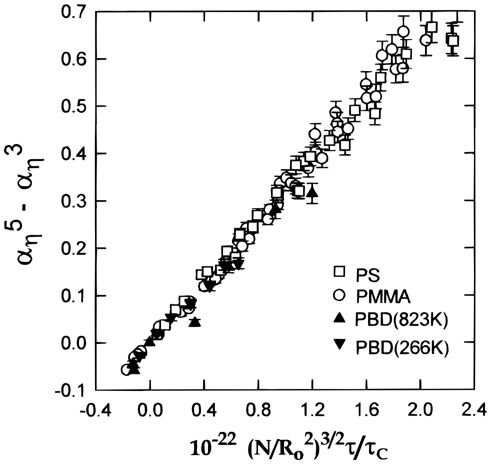

Figure 4. Plots of $\alpha_\eta^5 - \alpha_\eta^3$ as a function of $(N/R_0^2)^{3/2}(\tau/\tau_C)$ in the three different polymer systems incorporating polystyrene (PS), poly(methyl methacrylate) (PMMA), and polybutadiene (PBD).

note that the conversion factors of PS and PMMA have almost the same values but are very different from that of PBD. In Figure 4 all our experimental data are replotted as a function of $(N/R_0^2)^{3/2}(\tau/\tau_C)$. Surprisingly, all data points of the PBD, PS, and PMMA systems fall on one master curve. At first glance one might think that the number of statistical segments N_S should be used for universal description. In reality, the universality has been revealed by N but not by N_S. Why does it happen? At this moment we think the term N/R_0^2 itself can reflect more *system-dependent* chain characters such as chain flexibility while N_S/R_0^2 will be a *system-independent* scaling constant.

In conclusion, several points should be noticed: (1) $(N/R_0^2)^{3/2}(\tau/\tau_C)$ seems to have much wider universal character than $(M_w/R_0^2)^{3/2}(\tau/\tau_C)$ for describing the expansion of linear flexible polymer chains such as PBD, PS, and PMMA. (2) In temperature blob theory N/N_C is a universal parameter for description of the excluded-volume effect. N_C is well-known[12-14] to scale as $N_C \sim \tau^{-2}$. When linking this blob parameter N/N_C and our universal parameter, we can obtain the relation of $N/N_C \cong (N/R_0^2)^3(\tau/\tau_C)^2$. One strong advantage of our parameter is that all characteristic information such as Flory Θ temperature (as the temperature of $A_2 = 0$), the critical solution temperature, and the scaling constant of the unperturbed chain dimension can be obtained sufficiently from just one molecular weight polymer sample. (3) To confirm our observation, soon or later we will examine the universality of this modified parameter for linear polymer systems with repeating units of much higher molecular weight than PS and PMMA.

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