

Analysis of Excluded Volume Effect in Theta Solvent Systems of Polymethyl Methacrylate and Polystyrene by Means of a Modified Scaled Temperature Parameter

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The expansion of two different kinds of hydrodynamic size of polymethyl methacrylate (PMMA M_w : $1.56-2.04 \times 10^6$ g/mol) has been measured by dynamic light scattering and viscometry above the Flory Θ temperature of the various solvents such as n-butyl chloride, 3-heptanone, and 4-heptanone. The expansion of PMMA chains was analyzed in terms of universal temperature parameters and also compared with previous results of polystyrene (PS) system. First it was found that simple τ/τ_c parameter no longer had its universality for the expansion behavior of hydrodynamic size in the chemically different linear polymer chains. However after modifying τ/τ_c parameter into $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$, we observed a much better universality for both PMMA and PS systems. Here M_w , R_o , $\tau=[(T-\Theta)/\Theta]$, and $\tau_c=[(\Theta-T_c)/T_c]$ are defined as the weight average molecular weight, the unperturbed end-to-end distance, the reduced temperature and the reduced critical temperature, respectively.

Keywords : Polymethyl methacrylate, Hydrodynamic size, Expansion factor, Universality, Scaled reduced temperature parameter.

Introduction

As the importance of polymer chain expansion above the Flory Θ temperature was widely appreciated for several decades, there were many theoretical or empirical trials¹⁻¹⁴ to describe the excluded volume effect in terms of so-called universal parameter. However, each theory has its own strong points and weak points. For example, in the blob theory,¹²⁻¹⁴ universality is introduced through a reduced blob parameter (N/N_c) for the expansion of the dimension of polymer chain. Here N is the number of monomer units in a polymer chain and N_c is a temperature-dependent cutoff separating the Gaussian and the excluded volume regimes and at the same time also means the number of monomers contained in a temperature blob. For the guaranty of an excellent universality it needs to introduce one adjusting parameter of no physical meaning for each polymer/solvent system.

Recently, in order to solve this problem, Dondos^{15,16} has proposed a universal molecular blob parameter N/N_c , which is identical with the original thermal blob parameter but can be obtained from the empirical relation $N_c = 0.37a^{-7.7}$ from the exponent of the Mark-Houwink equation a , without introducing any adjustable parameter. As this N_c parameter is calculated with the very large absolute value ($|7.7|$) of this exponent, it is too much sensitive to error of the Mark-Houwink exponent a . For example, if we assume that the error for the determination of a is of the order of $\pm 3.3\%$ (say $a = 0.6 \pm 0.02$), the relative error of N_c value becomes approximately $\pm 25\%$.

On the contrary, the τ/τ_c parameter suggested by Park *et al.*¹⁷⁻¹⁹ has more theoretical background and is based on the determinable physical quantities with much less experimental error. In this paper, we try to investigate both its universality

in the various polymethyl methacrylate (PMMA)/solvent systems and its limit for the chemically different polymer systems. Here $\tau=[(T-\Theta)/\Theta]$ and $\tau_c=[(\Theta-T_c)/T_c]$ are defined as the reduced temperature and the reduced critical temperature, respectively.

Theoretical Background

When the polymer solution temperature increases above the Flory Θ temperature, the repulsive intramolecular interaction makes the polymer chain expand. Such expansion is well described by Flory equation of the expansion factor $\alpha = [R(T)/R(\Theta)]$ ^{1,2,5}

$$\alpha^5 - \alpha^3 = 2.846 \times 10^{-24} (v^{3/2}/V_1^{1/2})(M/R_o^2)^{3/2} \psi [(T-\Theta)/\Theta] M^{1/2} \quad (1)$$

where v , V_1 , R_o^2 , and M are the partial specific volume of polymer chain, 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 equation¹ which relates the critical solution temperature, T_c to the molecular weight, M

$$\frac{1}{T_c} = \frac{1}{\Theta} \left(1 + \frac{b}{\sqrt{M}} \right) \quad (2)$$

where $b = (V_1/v)^{1/2} \psi$. Equations of (1) and (2) lead to Eq. (3) and a modified scaled reduced temperature parameter $(M/R_o^2)^{3/2}(\tau/\tau_c)$ appears¹⁷⁻¹⁹ in the following equation.

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

In this experiment we investigated the expansion of the

hydrodynamic size of PMMA polymer chains by means of viscometry and dynamic light scattering as increasing polymer solution temperature. The expansion factor of intrinsic viscosity α_η^3 is defined as the ratio of the intrinsic viscosity, $[\eta]_T$ at a given temperature T , to $[\eta]_\Theta$ at the Θ temperature. The expansion factor α_H of the effective hydrodynamic radius R_H is also defined by the same manner.

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

$$\alpha_H = R_H(T)/R_H(\Theta) \quad (5)$$

In this particular case, the intrinsic viscosity of polymer chains at each solution temperature can be estimated from a single inherent viscosity η_{inh} by correcting the finite concentration term of $k\eta_{inh}^2C$ in the following Kraemer equation.^{18,20}

$$\ln(\eta-\eta_0)/C \equiv \eta_{inh} = [\eta](1-k[\eta]C) \equiv [\eta]-k\eta_{inh}^2C \quad (6)$$

Experimental Section

Materials. PMMA polymer samples used in this study were purchased from Pressure Chemical Co. and the characteristics of these polymers were listed in Table 1. The solvents such as n-butyl chloride (BC, Merck), 3-heptanone (3HP, Aldrich) and 4-heptanone (4HP, Aldrich) were used without any further purification.

Light scattering. The scattered intensity was measured by a commercial 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 laser (Spectra Physics Model 127). The values of M_z/M_w were estimated approximately by assuming the relation of variance $\sim (M_z/M_w - 1)/4$ which was accepted to be valid in the condition of $M_w/M_n < 1.25$.²¹ The excess Rayleigh ratio, R_{VV} (cm^{-1}) was obtained from absolute excess scattered intensity, using vertically polarized incident and vertically polarized scattered light. In a dilute solution of concentration C (unit: g/cm^3) and at a finite scattering angle it has an approximate form.²²

$$\frac{KC}{R_{VV}} = \frac{1}{M_w P(q)} + 2A_2 C \quad (7)$$

where K is equal to $4\pi^2 n^2 (\text{dn}/\text{dC})^2 / (N_A \lambda_0^4)$ with n , N_A , λ_0 and dn/dC being, respectively, the refractive index of solvent, the Avogadro's number, the wavelength of incident light in vacuo, and the specific refractive index increment. In dynamic light scattering, the z-average characteristic line-

width, $\langle \Gamma \rangle$ and the variance were determined by the second order cumulant method. The effective hydrodynamic radius R_H was calculated from the z-average translational diffusion constant, D_0 using the Stokes-Einstein equation²³

$$D_0 = (\langle \Gamma \rangle / q^2)_{C=0, q=0} = k_B T / 6\pi\eta_0 R_H \quad (8)$$

where k_B and η_0 being the Boltzmann constant and the solvent viscosity, respectively.

Viscometer: As the measuring temperature range was close to the boiling temperature of BC solvent, the closed Ubbelohde type viscometer of the Greek letter Δ shape were used. In this particular viscometer, the polymer solution in the reservoir part of viscometer can be easily transferred to the upper chamber through the side tubing by simply rotating the viscometer mounted on the brass plate.²⁴ In order to measure the accurate shear viscosity, we tried to calibrate the viscometer using the equation of $\eta/d = at - b/t$ with the standard benzene solvent. Its density d and the shear viscosity η at the various temperature were well known in the literature. As far as the instrument constants a and b were determined, the kinematic viscosity, η/d was calculated from the flow time, t without any introduction of the kinetic effect.

Results and Discussion

Determination of Θ temperature in PMMA/solvent systems: In order to investigate the universality of expansion behavior of PMMA chain using τ/τ_C parameter, the critical solution temperature T_C and Flory Θ temperature for each system are required. Actually lots of experimental results for the expansion behavior of PMMA chains had been already reported in the literatures but most of them could not be used in this particular study due to the lack of detailed description of the critical solution temperature T_C of the corresponding system. Thus prior to our main experiment we should determine the precise Θ temperature and Schultz-Flory relation between T_C and M_w for each PMMA/solvent system. First, the cloud point T_{CP} was measured by means of home-made automatic turbidimeter. Next the critical solution temperature T_C is assumed to be identical with the cloud temperature at the critical concentration, which was estimated from the empirical relation of $\phi_C = 6.80 M^{-0.37}$ reported in literature.²⁵ Here even if the estimated critical concentration was somewhat (say 5%) off the true critical concentration, it was well known that the measured cloud temperature T_{CP} is deviated from the true critical temperature by only about ± 10 m°C due to the flatness of the coexistence curve near the critical point.¹⁷ As shown in Figure 1, the Θ temperature of each system was obtained from the y-axis intercept at the infinite limit of the PMMA molecular weight. The relations of T_C and M_w are given as:

$$1/T_C = 3.233 \times 10^{-3} (1 + 0.1242 M_w^{-1/2}) \text{ (PMMA/3HP)} \quad (9)$$

$$1/T_C = 3.173 \times 10^{-3} (1 + 0.1201 M_w^{-1/2}) \text{ (PMMA/4HP)} \quad (10)$$

$$1/T_C = 3.175 \times 10^{-3} (1 + 0.0855 M_w^{-1/2}) \text{ (PMMA/BC)} \quad (11)$$

Table 1. Characteristics of polymethyl methacrylate samples

M_w (10^3 g/mol)	M_w/M_n	$R_{G,0}^a$ (nm)	$R_{H,0}^a$ (nm)	Maker
326	1.10			Pressure Chemical Co.
890	1.04			Pressure Chemical Co.
1560	1.09	30.7	24.1	Pressure Chemical Co.
2040	1.08	35.5	28.0	Pressure Chemical Co.

^a these values are measured at the Θ temperature (41.8 °C) of PMMA/n-butyl chloride system.

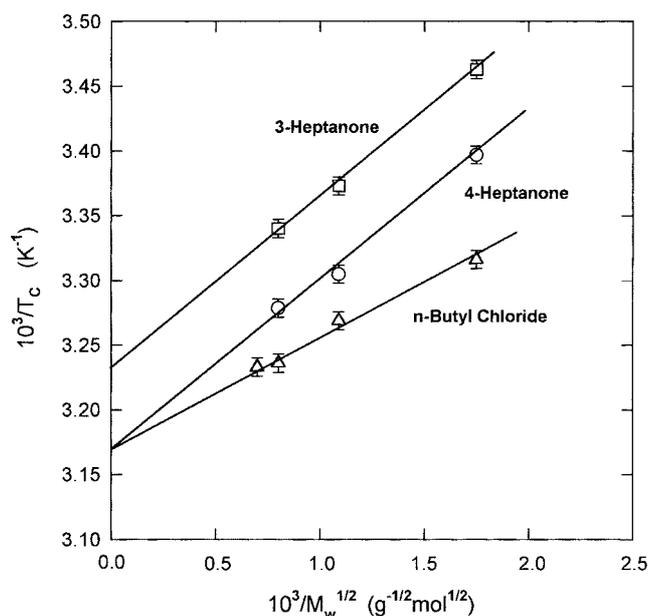


Figure 1. Molecular weight dependence of the critical solution temperature T_c in the three different Θ solvent systems of PMMA.

Intrinsic viscosity: The inherent viscosities of PMMA samples were measured as a function of the solution temperature at several different concentrations. As shown in Figure 2, the quality of solvents become gradually better as increasing temperature. In the case of PMMA/4HP system, the inherent viscosities of the two different concentrations seem to be crossed around 70 °C due to the zero value of the Kraemer coefficient, k at this temperature range. From several concentration data, we can calculate the Kraemer coefficient, k as well as the intrinsic viscosity $[\eta]$ at the various temperature. According to our previous results, all

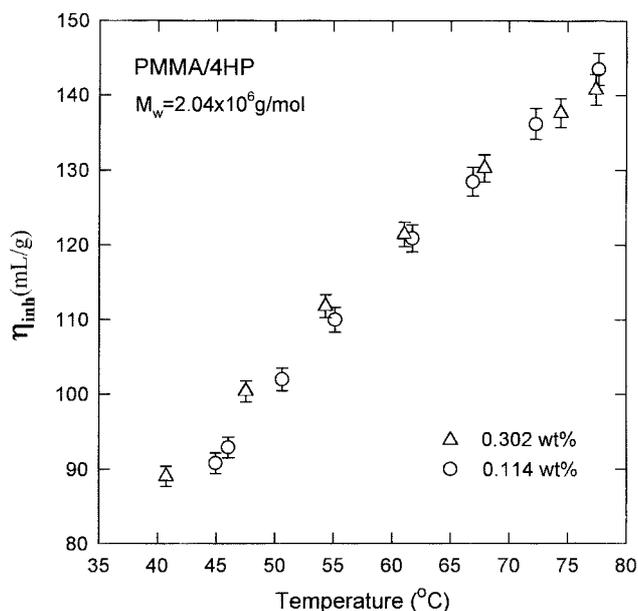


Figure 2. Temperature dependence of the inherent viscosity η_{inh} at the two different concentration of PMMA/4-heptanone system.

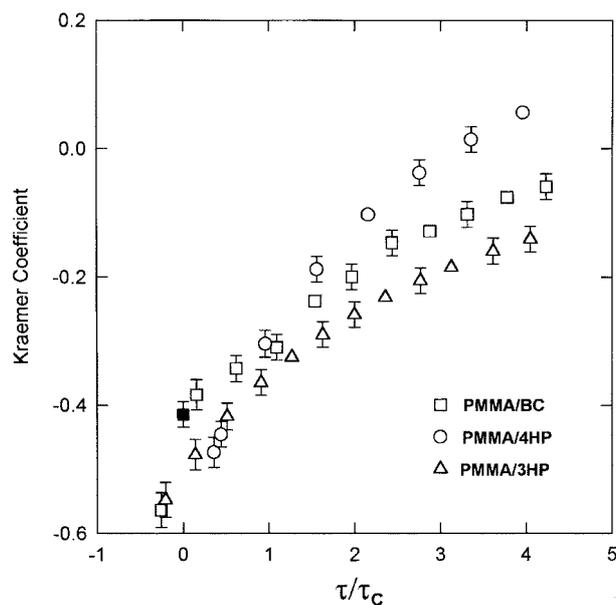


Figure 3. Plots of the Kraemer coefficient versus τ/τ_c parameter. Filled square: PMMA of $M_w = 2.04 \times 10^6$ g/mol at Θ temperature of *n*-butyl chloride, hollow square: PMMA ($M_w = 1.56 \times 10^6$ g/mol) in *n*-butyl chloride, circle: PMMA ($M_w = 2.06 \times 10^6$ g/mol) in 3-heptanone, diamond: PMMA ($M_w = 2.06 \times 10^6$ g/mol) in 4-heptanone.

excluded volume-related physical quantities such as the expansion factor and Kraemer coefficient k can be expressed by a universal function of τ/τ_c for the different solution temperature of the same polymer/solvent system. For example, the function of Kraemer coefficient, $k(\tau/\tau_c)$, obtained from the PMMA (1.54×10^6 g/mol)/BC system, can be also applied for any molecular weight PMMA/BC system. To test this assumption, we measured the k value for PMMA of $M_w = 2.04 \times 10^6$ g/mol at one temperature. This datum was plotted as the filled square symbol in the same Figure 3. As expected, this point fell down on the same curve of $M_w = 1.54 \times 10^6$ g/mol. With help of this curve of k , hereafter, the intrinsic viscosity can be approximated from the inherent viscosity measured at a single concentration using Eq. (6). As the error of $\Delta k = \pm 0.02$ in this estimation corresponds to the relative error of 0.5% ($\Delta k \eta_{inh} C \cong 0.02 \times 120 \text{ mL/g} \times 0.002 \text{ g/mL} = 0.0048$) in the value of $[\eta]$, such process is acceptable as an approximation method of $[\eta]$.

In Figure 4 the expansion factors of intrinsic viscosity α_η^3 of the three different solvent systems such as PMMA/BC, PMMA/4HP and PMMA/3HP were plotted against the $(T-\Theta)$ parameter. This parameter did not show any universality even for the different molecular weight of the same solvent system, for example PMMA/BC. Here we should note that apparent overlapping of PMMA/3HP and PMMA/4HP occurred by chance mainly due to almost the same slope of two systems in the plot of $1/T_c$ vs $M_w^{-1/2}$ in Figure 1.

$\tau M_w^{1/2}$ parameter: In Figure 5, the $\tau M_w^{1/2}$ parameter was used instead of the $(T-\Theta)$ parameter for the abscissa. All data of the different molecular weight PMMA in the same

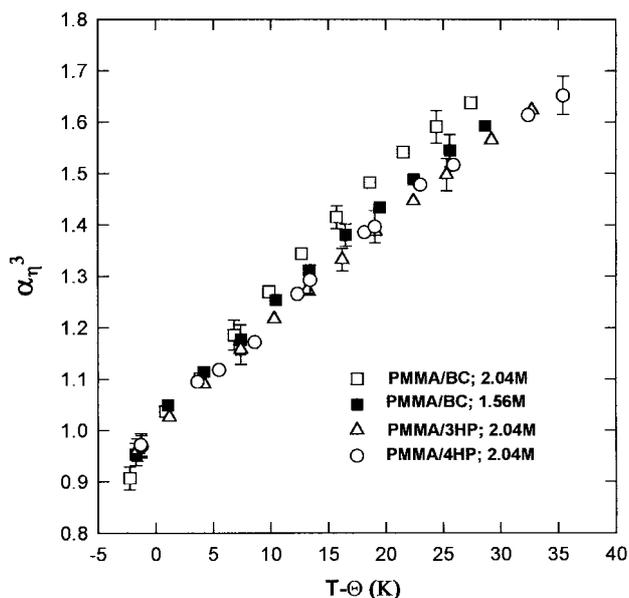


Figure 4. Plots of the expansion factor α_{η}^3 versus $T-\Theta$ at the various solvent systems of PMMA.

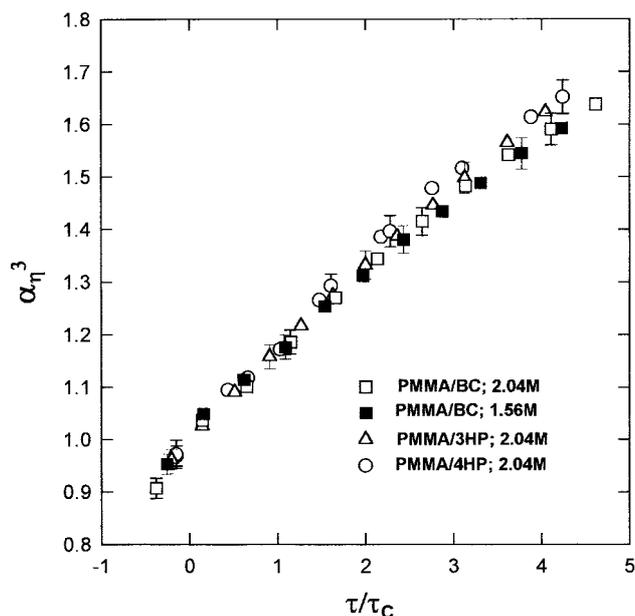


Figure 6. Plots of the expansion factor α_{η}^3 versus τ/τ_c at the various solvent systems of PMMA.

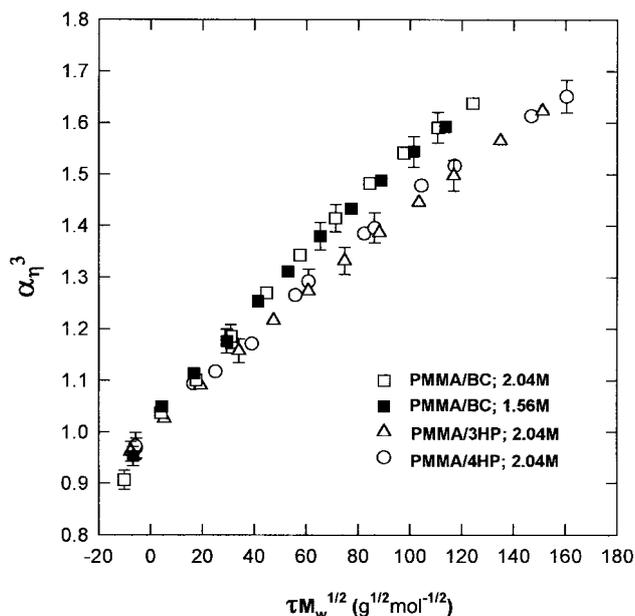


Figure 5. Plots of the expansion factor α_{η}^3 versus $\tau M_w^{1/2}$ at the various solvent systems of PMMA.

solvent system fell on one curve but the different solvent data of PMMA did not overlapped one another. As observed in polystyrene system,^{17,18} we found again that $\tau M_w^{1/2}$ parameter was not able to be a universal parameter for the different solvent system of a given polymer.

τ/τ_c parameter: When the data of α_{η}^3 were plotted as a function of the τ/τ_c parameter in Figure 6, all data points from the different Θ solvents of PMMA fell on one master curve. Similar experimental results had already been observed from three different solvent systems (cyclohexane, trans-decalin, cyclopentane) of PS.^{17,18} Therefore we conclude that the τ/τ_c parameter had the universality at least in different

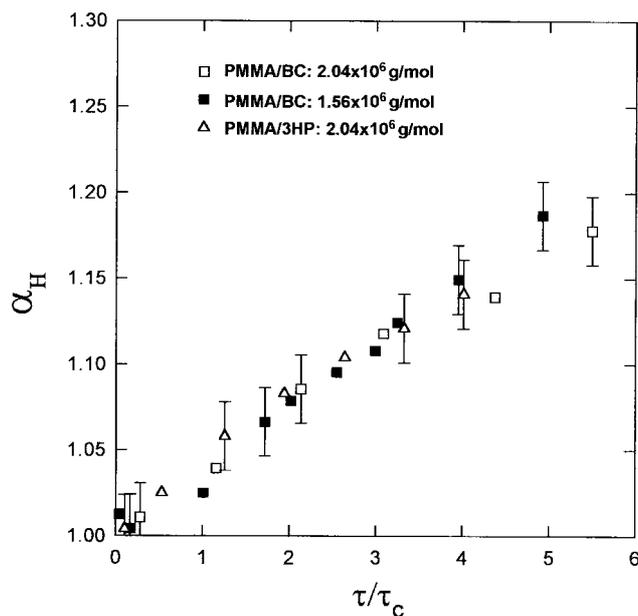


Figure 7. Plots of the expansion factor α_H versus τ/τ_c at the various solvent systems of PMMA.

theta solvents of a given polymer (PMMA or PS).

In Figure 7, we also tried to plot the expansion factor α_H of the effective hydrodynamic radius R_H measured by means of dynamic light scattering. The figures showed that τ/τ_c parameter had the universality for the different kind of expansion factors, α_H and α_{η}^3 , for two different Θ solvents of PMMA. Next step is to check whether this τ/τ_c parameter still works for the chemically different polymer species. All data of expansion factors of PS reported in previous papers^{17,18} and all PMMA data of this study were plotted in the same figure but as shown in Figure 8, the universality of

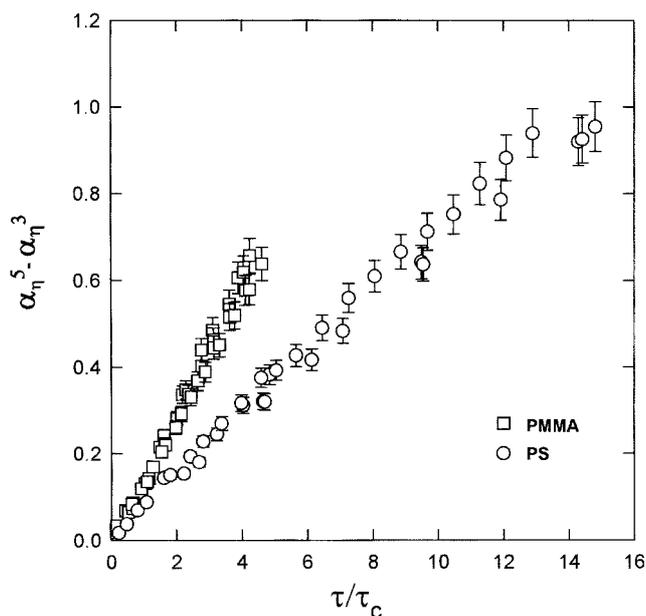


Figure 8. Plots of $\alpha_{\eta}^5 - \alpha_{\eta}^3$ versus τ/τ_c parameter in the two different polymer systems of PMMA and PS.

τ/τ_c parameter was broken down for the chemically different polymers.

$(M_w/R_o^2)^{3/2}(\tau/\tau_c)$ parameter: In order to solve this problem, when coming back to Eq. (1), we can find that the expansion factor does not only depends on τ/τ_c but $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$. Although the scaling constant of M_w/R_o^2 has the weak dependence on the various theta solvents in the same polymer system, there is significant difference between the polymers of chemically different structure. To add the system-dependent term of (M_w/R_o^2) to τ/τ_c , we need

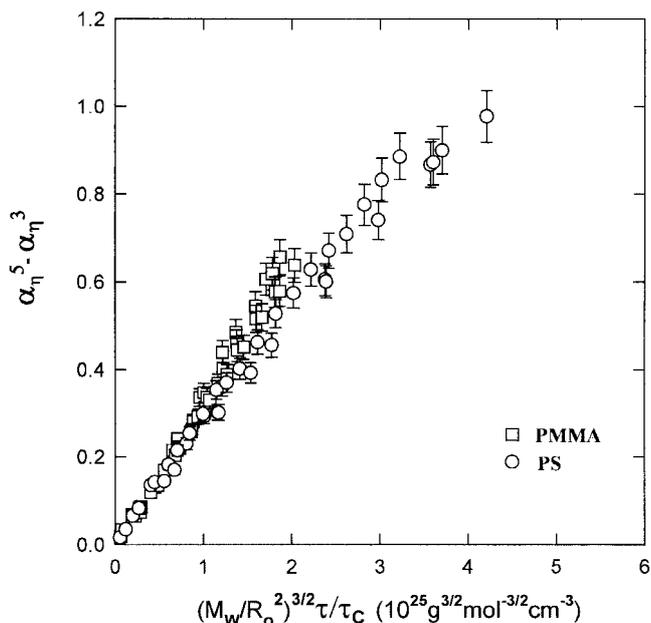


Figure 9. Plots of $\alpha_{\eta}^5 - \alpha_{\eta}^3$ versus $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$ parameter in the two different polymer systems of PMMA and PS. All data points obtained from two polymers of the chemically different structure fell on a master curve.

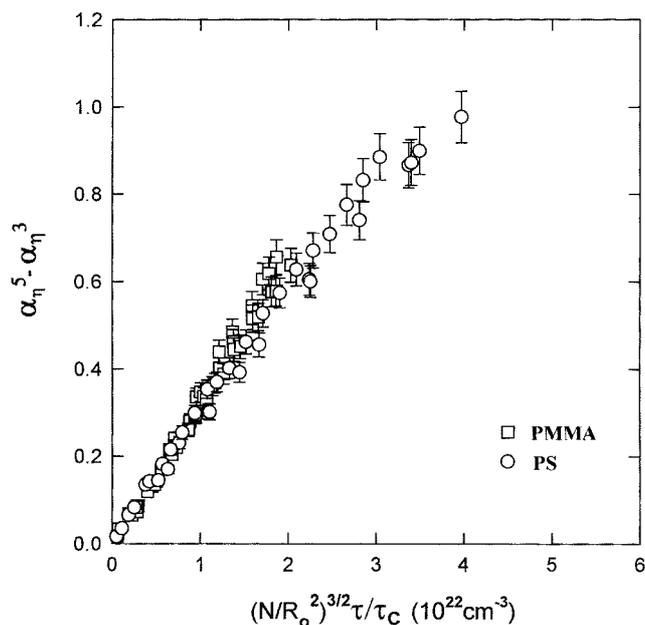


Figure 10. Plots of $\alpha_{\eta}^5 - \alpha_{\eta}^3$ versus $(N/R_o^2)^{3/2}(\tau/\tau_c)$ parameter in the two different polymer systems of PMMA and PS. This parameter has shown a little better universality than $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$ parameter because the PS monomer has a little larger molecular weight by 4% than PMMA.

the unperturbed end-to-end distance R_o , which can be easily calculated from the unperturbed radius of gyration $R_{G,o}$ measured by static light scattering at the Θ temperature using the relation of $R_o^2 = 6R_{G,o}^2$. These scaling constants of $(2.50 \pm 0.2) \times 10^{24} \text{ g}^{3/2} \text{ mol}^{-3/2} \text{ cm}^{-3}$ for PS and $(4.40 \pm 0.2) \times 10^{24}$ for PMMA were obtained from the literatures¹⁷⁻¹⁹ and this study. All data of $\alpha_{\eta}^5 - \alpha_{\eta}^3$ for PS and PMMA systems were replotted in Figure 9 as a function of $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$, all data points fell on one master curve as expected in the theoretical background section. The master curve can be expressed as:

$$\alpha_{\eta}^5 - \alpha_{\eta}^3 = 2.74 \times 10^{-26} (M_w/R_o^2)^{3/2} (\tau/\tau_c) \quad \text{for both PS and PMMA} \quad (12)$$

Based upon our experimental results, $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$ parameter seems to be a true universal scaling parameter for the expansion behavior of linear homopolymer chains with chemically different structure (at least for PS and PMMA). In addition, we would like to comment that $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$ parameter can be replaced with $(N/R_o^2)^{3/2}(\tau/\tau_c)$ parameter with a somewhat better universality as shown Figure 10. It is because the larger M_o value of PS monomer (PS : $M_o = 104 \text{ g/mol}$) than that of PMMA monomer (PMMA : $M_o = 100 \text{ g/mol}$) makes the slope of PS data a little steeper in this plot. Here N and M_o stand for the number of monomer unit and the molecular weight of monomer unit in a polymer chain, respectively.

Conclusion

1. In a given Θ solvent system of PMMA, the expansion

factors of different molecular weight samples can be scaled with the $\tau M_w^{1/2}$ parameter. However for the different Θ solvents, this $\tau M_w^{1/2}$ parameter does not work.

2. For the various Θ solvent systems of a given polymer (for example; PS or PMMA in our study), τ/τ_c parameter has shown universality for the expansion behavior of two different kinds of hydrodynamic size measured by viscometry and dynamic light scattering. But the limit of this parameter has been observed in the chemically different polymer systems such as PS and PMMA.

3. After transforming τ/τ_c parameter into $(M_w/R_o^2)^{3/2}(\tau/\tau_c)$ or $(N/R_o^2)^{3/2}(\tau/\tau_c)$, we have observed a better universality for the expansion of hydrodynamic sizes of both PS and PMMA polymers.

4. In the future we will try to apply this parameter to very flexible linear polymers (*e.g.* polydimethyl siloxane) or more rigid and the branched polymers to investigate the limit of the universality of this parameter.

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