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Conformational transition of polystyrene chain near the critical point of *N*,*N*-dimethylformamide/cyclohexane mixed solvent system

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Abstract

Inherent viscosities were measured for polystyrene (PS) in *N*,*N*-dimethylformamide (DMF)/cyclohexane (CH) in the temperature range covered from 65°C close to the upper critical solution temperature T_C of the DMF/CH system. It was found that near the critical temperature, the inherent viscosities contracted to about one-third of the value at 65°C. The overall contraction behavior agrees well with de Gennes' theory and some interesting results have been observed. First, in the far off-critical temperature range ($\log\tau > -1.5$), the strong synergetic, co-solvency effect of the mixed solvent was shown by higher values of the inherent viscosity than those measured in any single solvent. Second, the reduced theta temperature, τ_θ, at which the chain dimension was supposed to have the unperturbed, ideal dimension, weakly depends on the molecular weight. Third, although we observed only the contraction behavior instead of contraction-and-reswelling on approaching the critical point, the expansion factors $a_\eta^3(=[\eta]/[\eta]_\theta)$ for the different molecular weight samples fell on one master curve when plotted as a function of $(\log\tau - \log\tau_\theta)M_w^{1/2}$. Here $\tau[=(T-T_C)/T_C]$ and M_w are the reduced temperature and the weight-average molecular weight, respectively.

Keywords: Conformational transition; Mixed solvent with critical point; Preferential solvation.

1. Introduction

In 1976, de Gennes first predicted [1] a very interesting conformational transition of the single polymer chain dissolved in a mixed solvent having a critical point. According to his argument [1], [2], when the chain is close to the critical point of the mixed solvent, the preferential adsorption of the better solvent molecules on polymer segments as well as the composition fluctuation of the solvent mixture play important roles in establishing the chain dimension. In this situation, the change of chemical potential of one monomer due to the composition fluctuation, W_1 can thus be expressed by the Ornstein–Zernike type equation [3] of $W_1(\mathbf{r}_{ij}) = -(b/\mathbf{r}_{ij})\exp(-\mathbf{r}_{ij}/\xi)$. Here b is a system-dependent constant, ξ stands for the correlation length and $\mathbf{r}_{ij}$ is the distance between the ith and the jth monomer. In fact the most important thing in this equation is that this potential is always attractive. Thus even though each solvent is regarded as the good solvent for the polymer, the monomeric units experience a strong attractive interaction near the critical point [1], [2], and the polymer chain eventually collapses.

Ten years later, Staikos and Dondos tried to test de Gennes' idea in the systems of polystyrene (PS, M_w = 7700 g/mol)/cyclohexane/methanol and polyethyleneglycol (PEG, M_w = 6000 g/mol)/cyclohexane/methanol [4]. However, their final conclusion was that the dimension of the polymer chain was almost constant even near the critical point. Recently, upon the basis of the well-known fact [5]–[7] that the length of the polymer chain is one of the most dominant factors in the expansion (or contraction) of the polymer chain near the Flory theta temperature, Park et al. reinvestigated [8] this topic with the high molecular weight poly(ethylene oxide)s in the mixed solvent tetrahydrofuran/water system having a lower critical solution temperature. They found that the inherent viscosity remained almost constant until $\tau[=(T_C - T)/T_C]\sim 10^{-2}$ but contracted to one-third of the initial value in the region of $\tau\sim 10^{-3.5}$.

In this paper we tried to reconfirm de Gennes' theoretical prediction experimentally with some high molecular weight polystyrene samples (PS: 9.4×10^5 g/mol$\sim 3.84\times 10^6$ g/mol) in the mixed solvent *N*,*N*-dimethylformamide/cyclohexane (DMF/CH) system having a upper critical solution temperature. For measurement of the dimension of a PS polymer chain near the critical point, the closed capillary viscometry was also used as an appropriate tool since shear viscosity has a relatively weak critical anomaly [9]–[11].

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2. Theoretical background [1], [2]

When a single polymer chain is dissolved in a solvent mixture A/B and is approaching the critical solution temperature T_C, there exists a long range indirect interaction between the two monomers of the polymer chain. First, let us consider the ith monomer located at $\mathbf{r}_i$ in the solvent mixture A/B with a critical point. The average composition of solvent A is C_A but it has the local fluctuation $\delta C_A(\mathbf{r}_i)$. The chemical potential of one monomer of the chain ϵ is of the form

$$\epsilon = \epsilon_0 + \epsilon_1 \delta C_A(\mathbf{r}_i) \tag{1}$$

Here ϵ_0 is a composition independent part and ϵ_1 of the composition dependent term has an arbitrary sign. If ϵ_1 is positive, the local fraction of solvent A around $\mathbf{r}_i$ will be decreased since the composition fluctuation is linked to the potential fluctuation by the linear response and the susceptibility, χ:

$$\delta C_A(\mathbf{r}_i) = -\chi(\mathbf{r} - \mathbf{r}_i)\epsilon_1 \tag{2}$$

The integral over space of $\delta C_A(\mathbf{r}_i)$ is essentially the parameter of preferential solvation λ':

$$\lambda' \cong \epsilon_1 \int \chi(\mathbf{r} - \mathbf{r}_i)\,\mathrm{d}\mathbf{r} = \epsilon_1 \bar{\chi} \tag{3}$$

where the susceptibility $\chi(\mathbf{r} - \mathbf{r}_i)$ has a simple Ornstein–Zernike form:

$$\chi(\mathbf{r}) = \frac{\bar{\chi}}{4\pi\xi^2}\frac{1}{\mathbf{r}}e^{-\mathbf{r}/\xi} \tag{4}$$

On adding another jth monomer residue around the ith monomer residue, the interaction free energy, $W_1(\mathbf{r}_{ij})$ is of the form:

$$W_1(\mathbf{r}_{ij}) = \epsilon_1 \delta C_A(\mathbf{r}_j) = -\epsilon_1^2 \chi(\mathbf{r}_i - \mathbf{r}_j) = -\frac{-b}{\mathbf{r}_{ij}}e^{-\mathbf{r}_{ij}/\xi} \tag{5}$$

where b means $\frac{\bar{\chi}\epsilon_1^2}{4\pi\xi^2}$ but the value of $\frac{\bar{\chi}}{\xi^2}$ is finite and essentially independent of both T and C_A near the critical point. According to de Gennes' theory [1], this indirect interaction between monomer residues has the following feature. One monomer creates a cloud of preferential solvation which attracts a second monomer. As the size of the cloud is the order of the correlation length ξ of the A/B mixture and becomes larger near the critical point, the interaction W_1 is always attractive and a screened Coulomb type force.

The most interesting prediction concerns the behavior of a polymer chain in the mixed solvent when both A and B are good solvents for the polymer chain. In this particular case, in addition to W_1, we have also short range forces W_2, characterized by the excluded volume parameter v. If v has a positive and fixed value in the critical region of interest, the total monomer–monomer interaction $W(\mathbf{r}_{ij})$ becomes

$$W(\mathbf{r}_{ij}) = W_1 + W_2 \cong -\frac{b}{\mathbf{r}_{ij}}e^{-\mathbf{r}_{ij}/\xi} + k_B T v \delta(\mathbf{r}_{ij}) \tag{6}$$

The effective excluded volume parameter V_{eff} can be obtained by means of the space integration of this total interaction energy

$$v_{\mathrm{eff}} = \frac{1}{k_B T}\int W(\mathbf{r}_{ij})\,\mathrm{d}\mathbf{r}_{ij} = v - 4\pi b \xi^2 \tag{7}$$

There is a special correlation length at which this effective excluded volume parameter vanishes ($V_{\mathrm{eff}} = 0$) and the polymer chain has its unperturbed ideal size, i.e., the theta correlation length, ξ_θ. Near the critical point the correlation length is related to the reduced temperature $\tau[= (T - T_C)/T_C]$ by $\xi \sim \tau^{-\upsilon}$ where υ is a critical exponent of ~2/3. The reduced theta temperature, τ_θ also can be defined as the reduced temperature corresponding to $V_{\mathrm{eff}} = 0$.

$$\xi_\theta = \left(\frac{v}{4\pi b}\right)^{1/2} \tag{8}$$

$$\xi_\theta \cong \tau_\theta^{-\upsilon} = \left(\frac{T_\theta - T_C}{T_C}\right)^{-\upsilon}$$

We designate T_θ as the theta-like temperature in order to avoid confusion with Flory's theta temperature, θ. When a single polymer chain is very close to the critical temperature, according to Brochard and de Gennes [2] the chain first collapses to the compact size due to strong attractive interaction and then the increase of the monomer density inside the chain leads to additional sorption by the preferentially selective solvent. Under this condition, the shift of solvent composition suppresses severely the critical feature. Thus the polymer chain tends to return to a swollen conformation. And this leads to an unusual dependence of the polymer chain extension on solution temperature very near the critical point.

3. Experimental

3.1. Materials

The three polystyrene (PS) samples used in this study were purchased from Pressure Chemical and Toyo Soda. These samples were characterized in benzene solution by laser light scattering, as shown in Table 1. Anhydrous and spectroscopy grade *N*,*N*-dimethylformamide (DMF) (Aldrich) and cyclohexane (Junsei, Japan) were used without further purification.

3.2. Static and dynamic light scattering

The scattered light intensity was measured by a commercial light scattering instrument (Brookhaven Model: B19000AT) operated with the $\lambda_O = 632.8$ nm line of He–Ne laser (35 mW).

3.3. Calibration of viscometer

As the upper critical solution temperature of mixed solvent (*N*,*N*-dimethylformamide/cyclohexane:DMF/CH) was

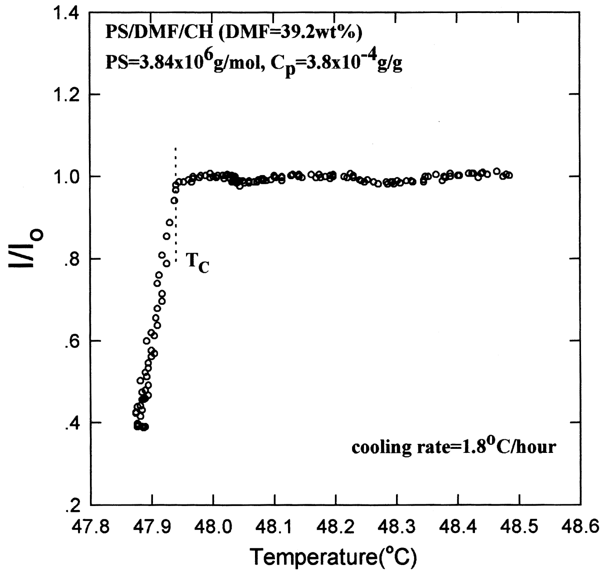

Fig. 1. Plot of the relative transmitted intensity I/Io versus the solution temperature. The point where the intensity begins to decrease abruptly is assumed as a new shifted critical solution temperature of DMF/CH system since a small amount of PS is added.

about 320.18 K (= 47.03°C) and the measurement starting temperature of ~65°C is near the normal boiling temperature (83°C) of CH, the closed capillary viscometer was used; the detailed design and calibration of this viscometer are described elsewhere [8], [13]. The water bath was thermostatted by Bayley temperature controller (model 123) within ± 5 mK.

3.4. Critical composition of the binary system of DMF/CH

We prepared various binary mixtures and measured the volume fraction after phase separation at the temperature $T = T_C - 0.5$°C, where T_C means the critical solution temperature. By interpolating the composition value corresponding to the separated volume ratio of 1:1, we found that the critical composition of DMF/CH system was $C_c^{DMF} = 39.2$ wt%. Hereafter, all ternary samples of polystyrene were dissolved in this critical mixed solvent of DMF/CH.

3.5. Measurement of T_c

As a He–Ne laser beam passed through the liquid reservoir of the viscometer, both the viscosity and the turbidity could be simultaneously measured. The temperature at which the intensity of the transmitted beam began to decrease abruptly at the slow cooling rate of ~1.8°C/h as shown Fig. 1 was regarded as the phase separation temperature.

4. Results and discussion

4.1. Density of DMF/CH system

The modern theory of critical phenomena predicts that, for the mixed solvent of critical composition in the one-phase region, the leading terms in the representation of the density as a function of temperature have the form [14]:

$$d = R_1 + R_2\tau + R_3\tau^{(1-\beta)} + \ldots \qquad (9)$$

where d is the density of the critical binary system; the reduced temperature, τ, is defined as $(T - T_C)/T_C$; R_1, R_2, and R_3 are constants which depend on the particular mixture system; and β is a universal critical exponent which is known to have the value of 0.11 by renormalization group theory. The density measurement of this DMF/CH system using the home-made dilatometer shows that this system has the almost no critical singularity (i.e., $R_3 \ll R_2$) and its density in the temperature range of 47–65°C can be expressed as:

$$d = 0.85739 - 1.0332 \times 10^{-3}t$$
$$\text{(DMF/CH units: g/mL, °C)} \qquad (10)$$

Recently, Gruner and Greer also reported a similar result of no critical anomaly for the density of the PS/diethylmalonate system of the critical composition [14].

4.2. Kinematic viscosity of the DMF/CH system

In general, the shear viscosity near the critical point consists of the non-critical, regular temperature-dependent part η_{cri}. The regular temperature-dependent part of viscosity is well expressed by the Arrhenius equation $\eta = A\exp(B/T)$. The singularity of viscosity near the critical point can be expressed by a power law of the reduced temperature, $\eta_{cri} \approx \tau^{\phi}$. Finally, the kinematic viscosity of the binary DMF/CH system of the critical

Table 1
Characteristics of polystyrene samples

10^{-6} M_w^a (g/mol)	M_w/M_n^b	M_z/M_w^c	Manufacturer
0.94	1.06	1.08	Pressure Chemical
1.45	1.12	1.10	Pressure Chemical
3.84	1.04	1.06	Toyo Soda

[a] Measured by light scattering in benzene solution.
[b] Values obtained from the manufacturer.
[c] Calculated from $M_z/M_w = 1 + 4$*variance [12].

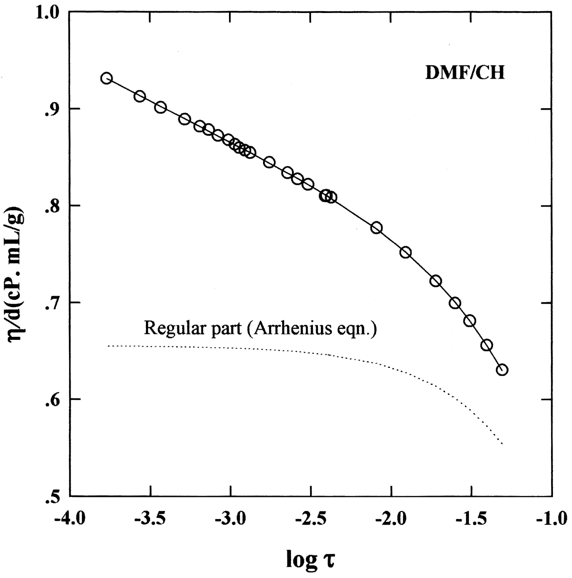

Fig. 2. Kinematic viscosity of the binary dimethylformamide/cyclohexane system versus the logarithmic reduced temperature. The dotted line denotes the non-critical, regular part of the Arrhenius type equation. The measured kinematic viscosity (circle) is well fitted by eq. 11 (solid line).

composition is given as

$$(\eta/d)_{\text{solvent}} = 1.1241 \times 10^{-2} \exp[1234.6/T] \times \left(\frac{T - T_{\text{C}}}{T_{\text{C}}}\right)^{(-0.0406)} \quad \text{(units; cP. mL/g)} \tag{11}$$

The critical exponent ϕ of -0.0406 ± 0.0010 is in good agreement with the theoretical value [9]–[11] of -0.04. In Fig. 2, the total kinematic viscosity of the mixed solvent and the regular part are plotted against the reduced temperature. As our experimental error of the viscosity is also of the order of $\pm 0.15\%$ as shown in Fig. 3, an application of the high order correction is meaningless without establishing higher accuracy in the viscosity measurement [8]. In this experiment it was assumed that on adding a very small amount of polymer (say $C_{\text{p}} \cong 0.04$ wt%) into this binary solvent system of the critical composition, only the critical temperature T_{C} should change but there should be no significant shift of the critical composition. This assumption can be acceptable[1] by observing that the volume ratio of the lower layer to the upper layer becomes approximately ~0.7:1.0 after phase separation of ternary polymer solution at $T \cong T_{\text{C}} - 0.5$°C.

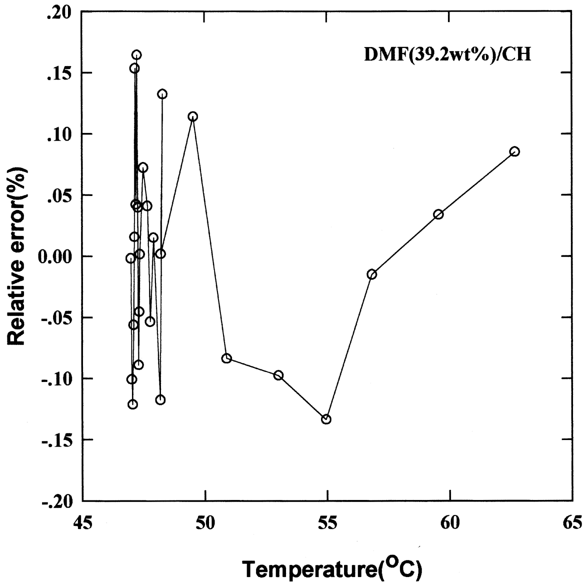

Fig. 3. Relative error in the viscosity measurement versus the temperature in the dimethylformamide/cyclohexane system.

4.3. Investigation of solvent quality in single solvent system of PS

To interpret correctly the preferential solvation effect near the critical point, we need to know the relative solvation of PS by the two solvents. The Mark–Houwink relation for each binary system of PS/DMF and PS/CH is given as Eq. (12) or Eq. (13). It is worth noting that the solvent quality of CH increases with increasing temperature, and above 53°C it becomes a better solvent for PS than DMF, while DMF solvent keeps almost the same quality for the wide range of solution temperature as shown Fig. 4.

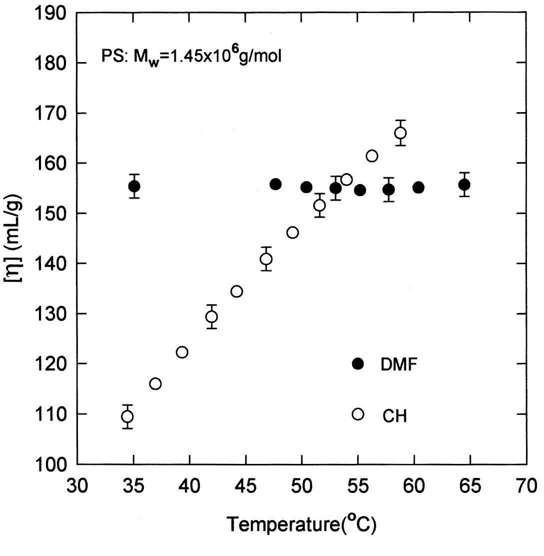

Fig. 4. Plots of the intrinsic viscosity for PS of $M_{\text{w}} = 1.45 \times 10^{6}$ g/mol in two different single solvents (dimethylformamide and cyclohexane) as a function of temperature. While its value keeps almost constant in DMF, there is a strong temperature dependence in CH which is a kind of theta solvent ($\theta = 35$°C) of PS.

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[1] For the binary THF/WT mixed solvent of an off-critical composition phase-separated into the volume ratio of 0.25:1, the change of the shear viscosity exponent ν is reported as $\Delta\nu = 0.0043$ in Ref. [8]. Thus for the phase separation of the volume ratio of ~0.7:1, the estimated $\Delta\nu$ will be approximately 0.0015 which corresponds to the order of the standard deviation.

$$[\eta] = 3.12 \times 10^{-2}\, M_w^{0.60} \quad \text{(for PS/DMF at the range of } 35 - 65^\circ\text{C : unit mL/g)} \tag{12}$$

$$[\eta] = 3.36 \times 10^{-2}\, M_w^{0.589} \quad \text{(for PS/CH at } 47.5^\circ\text{C : unit mL/g)} \tag{13}$$

4.4. Inherent viscosity in PS/DMF/CH system

For the correct interpretation of this system, it is necessary to know how the errors in the critical exponent of viscosity ϕ are propagated into the calculation of inherent viscosity. As shown in Fig. 5, the effect of the critical exponent error appears to be introduced into the inherent viscosity in a slowly increasing manner over the entire range of temperature. However, the smaller the value of the critical exponent, the higher is the inherent viscosity obtained. When all inherent viscosity data are plotted against the logarithmic reduced temperature in Fig. 6, the dimension of the polymer chain decreases abruptly below $\log\tau \leq -2.0$ as predicted by de Gennes and the inherent viscosities of three different PS samples seem to be scaled as $\eta_{\text{inh}} \sim \tau^{0.062 \pm 0.002}$ in the range of $\log\tau \geq -1.5$. Here this finite, non-zero exponent of 0.062 indicates that even in the far off-critical temperature range the polymer chain still expands with increasing temperature. Such result can be also explained qualitatively by de Gennes theory. If the b value of Eq. (7) can be assumed to have a relatively large value in the mixed solvent system with the strong co-solvency effect, small change of the correlation length leads to the large variation of the effective excluded volume parameter V_{eff}. This eventually causes the temperature dependence of the polymer chain dimension even at the far off-critical temperature range. Actually we can confirm the strong synergetic, co-solvency character of this system with experimental observations of $\eta_{\text{inh}} = 260$ mL/g in the mixed solvent, 170 mL/g in CH, and 155 mL/g in DMF for a PS sample of $M_w = 1.45 \times 10^6$ g/mol at 65°C.

Actually, we are more interested in the relative variation of the expansion factor a_η^3 ($= [\eta]/[\eta]_\theta$) rather than the absolute value of the inherent viscosity of each PS sample. For calculation of the expansion factor a_η^3, we should know the values of the intrinsic viscosity not only at a given solution temperature but also at the theta condition. First, since the concentration was very low, the inherent viscosity can be approximated as the intrinsic viscosity $[\eta]$ within a 4% error (this is corresponding to the maximum error for the worst case: $k_K[\eta]C_p \cdot\simeq 0.15 * 600 * 4 \times 10^{-4} = 0.036$, where k_K is the Kraemer coefficient). Next the intrinsic viscosity $[\eta]_\theta$ can be easily estimated using the well-established relationship [15] $[\eta]_\theta = 8.46 \times 10^{-2}\, M_w^{0.5}$ for the theta condition of PS/CH. Now the reduced theta temperature τ_θ corresponding to $[\eta]_\theta$ can be determined from Fig. 7 by the interpolation method. Fig. 8 is a log–log plot of the reduced theta temperature versus the molecular weight. It is interesting that the molecular dependence of the reduced theta temperature τ_θ appears to be very weak with the exponent value of -0.17 compared with the large value of -1.52 shown in the system of poly(ethylene oxide)/tetrahydrofuran/water (PEO/THF/WT) [8]. However, this weak dependence is in qualitative agreement with de Gennes' prediction [1] that the reduced theta temperature will be independent of the number of segments of the polymer chain. Although in his theory he assumed that this would be valid only for extremely low polymer concentration, in reality our experimental

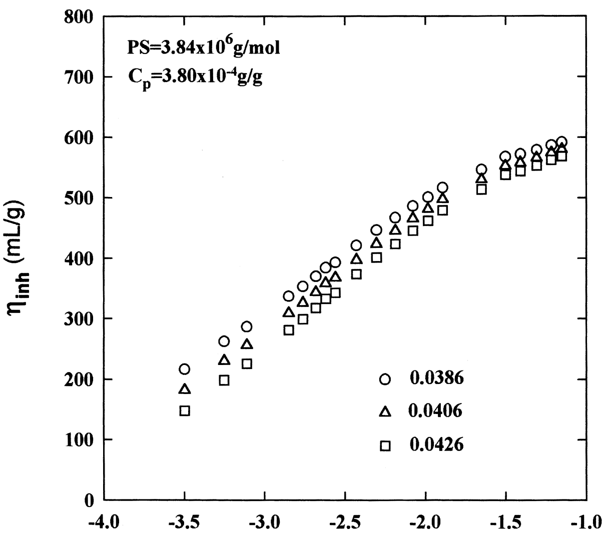

Fig. 5. Effect of the error of the critical exponent of viscosity on the inherent viscosity of polystyrene ($M_w = 3.84 \times 10^6$ g/mol) for various $\log\tau$.

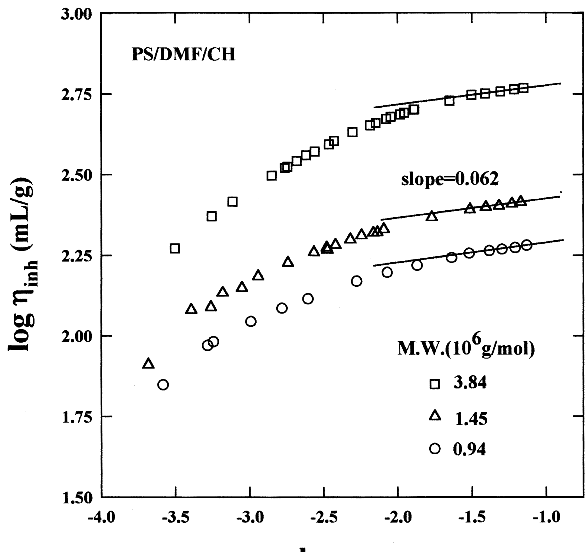

Fig. 6. The inherent viscosity of various molecular weight polystyrene samples as a function of $\log\tau$.

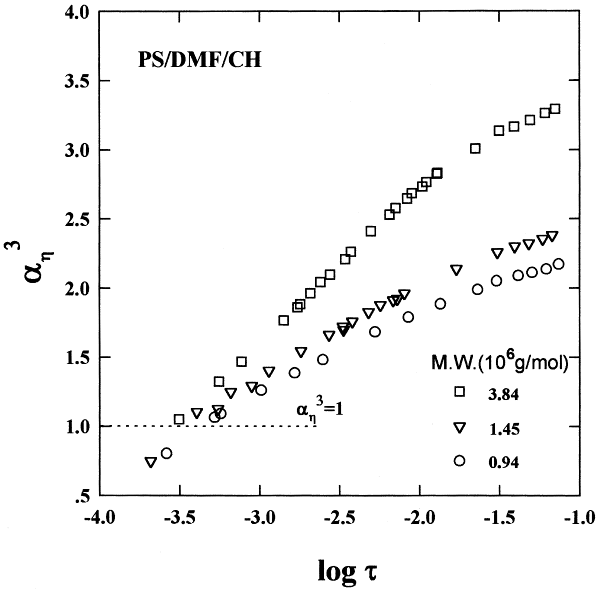

Fig. 7. Plots of the expansion factors a_η^3 versus logτ in the polystyrene/dimethylformamide/cyclohexane system.

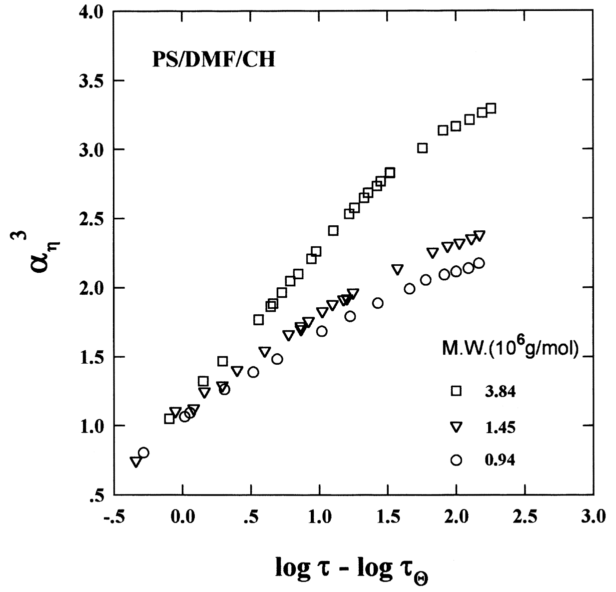

Fig. 9. Plots of the expansion factors a_η^3 versus logτ − logτ_θ in the polystyrene/dimethylformamide/cyclohexane system.

condition of C_p~0.04 wt% seems to be high enough to influence the critical behavior of the mixed solvent system and to show the chemical system dependence.

Instead of the logarithmic reduced temperature, the shifted logarithmic reduced temperature is used in Fig. 9 so that the unperturbed, ideal state becomes zero on the new *x*-axis scale. As shown in Fig. 9, the high molecular weight PS expanded more rapidly than the low molecular weight one, being farther off the critical temperature. As mentioned in the introduction, our assumption that the molecular weight of the polymer sample is one of the most important factors in this particular experiment appears to be correct. A similar trend of expansion behavior has already been observed near Flory's theta temperatures of the various binary PS/solvent systems such as polystyrene/cyclohexane, polystyrene/trans-decalin and so on [6], [7]. According to Flory's equation, $a^5 - a^3 = 2C_m\psi[(T-\theta)/\theta]M^{1/2}$ for the expansion factor $a = [R(T)/R(\theta)]$, solvent quality is not simply a function of the temperature distance from the theta temperature but is governed through the term of $[(T-\theta)/\theta]M^{1/2}$. It has been already experimentally established [6], [7] that expansion factors for some polymer samples with different molecular weights fall on one master curve when plotted against $[(T-\theta)/\theta]M^{1/2}$. Here

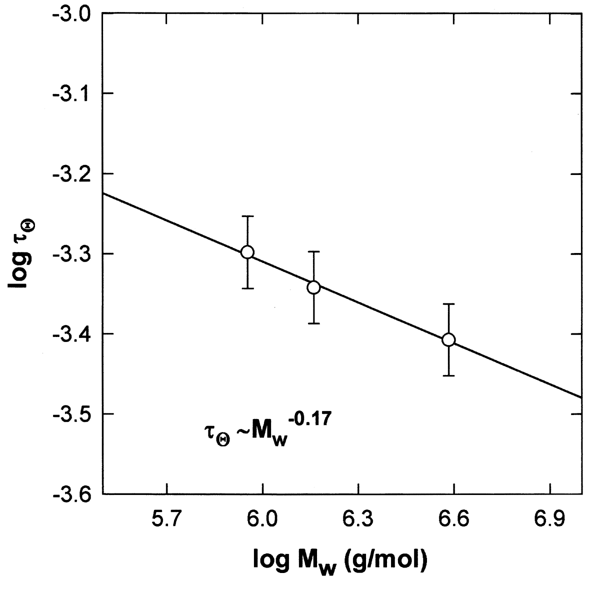

Fig. 8. Log–log plot of the reduced theta temperature τ_θ versus the molecular weight M_w.

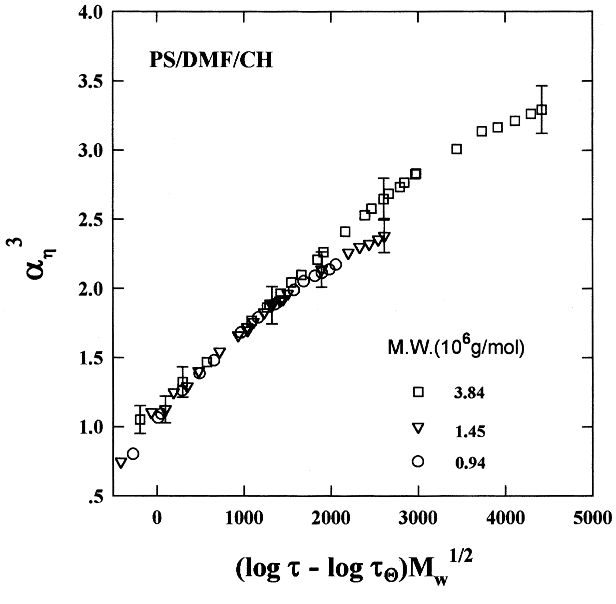

Fig. 10. Plots of the expansion factors a_η^3 versus (logτ − logτ_θ)$M_w^{1/2}$ in the polystyrene/dimethylformamide/cyclohexane system.

we may assume that there exist analogous correspondences not only between Flory theta temperature θ in the usual binary polymer solution and the logarithmic reduced theta temperature $\log\tau_\theta$ in our ternary system but also between the solution temperature T and the logarithmic reduced temperature $\log\tau$. If such an assumption is correct, expansion factors in this particular system can be expressed as a function of $[\log\tau - \log\tau_\theta]M^{1/2}$. In a plot of a_η^3 versus $[\log\tau - \log\tau_\theta]M_\mathrm{w}^{1/2}$ (Fig. 10), we found again that, within an experimental error of ± 8%, all our expansion factor data fall on the one master curve, as observed in the PEO/THF/WT system. Even in this PS/DMF/CH system, however, polymer reswelling was not observed near the critical point, although de Gennes predicted that after attaining a very compact size, the strong adsorption of preferentially selective solvent should reswell the chain [2].

5. Conclusions

The inherent viscosities of high molecular weight PS polymer samples were investigated in the mixed solvent DMF/CH system using a closed capillary viscometer. It was found that the inherent viscosity scales as $\eta_\mathrm{inh} \sim \tau^{0.062}$ in the far off-critical temperature (i.e., $\log\tau \geq -1.5$) but on approaching the upper critical solution temperature it contracts to about one-third, approximately corresponding to the order of dimension of the unperturbed chain. The overall contraction behavior agrees well with de Gennes' theory, but in detail two experimental observations are not clearly understood. First, in this system, the molecular weight dependence of the reduced theta temperature τ_θ is very weak compared with that in the PEO/THF/WT system but this weak trend is in qualitative agreement with the theoretical prediction. Second, we observe only a contraction of the polymer chain on approaching the critical point, while this collapsed chain is theoretically predicted to reswell from the compact size. However, all data of expansion factors for the different weight samples fall on a master curve when a_η^3 is plotted against $(\log\tau - \log\tau_\theta)M_\mathrm{w}^{1/2}$.

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