Conformational Transition of the Poly(ethylene oxide) Chain near the Critical Point of the Tetrahydrofuran/Water Mixed Solvent System

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ABSTRACT: Inherent viscosities were measured for poly(ethylene oxide) (PEO) in tetrahydrofuran/water (THF/WT). The measured temperature range covered the range from 35 °C close to the lower critical solution temperature T_c of THF/WT system. It was found that near the critical temperature, the inherent viscosities contract down to about one-third of the value at 35 °C. The overall contraction behavior agrees well with de Gennes' theory, but two observations contradict his prediction. First, the reduced Θ temperature, τ_Θ, at which the unperturbed chain dimension is observed strongly depends on the molecular weight. Second, we observed only the contraction behavior instead of the contraction-and-reswelling on approaching close to the critical point. The expansion factors $\alpha_\eta^3 (=[\eta]/[\eta]_\Theta)$ for the different molecular weight samples fall on one master curve when plotted as a function of $[\log \tau - \log \tau_\Theta]\ M_w^{1/2}$. Here $\tau\ (=(T_c - T)/T_c)$ and M_w are the reduced temperature and the weight-average molecular weight, respectively.

Introduction

About 2 decades ago, de Gennes and his colleague reported that a single polymer chain dissolved in a mixture of solvents having a critical point should contract on approaching close to the critical temperature.[1,2] According to his argument, not only composition fluctuations of the solvent mixture but also the preferential adsorption on the polymer segments play important roles in establishing the chain dimension. It is well-known in the field of critical phenomena that the composition fluctuation can be described by a simple Ornstein−Zernike form.[3] The change of chemical potential of one monomer, W_1 can be thus expressed by the same type equation of $W_1(r_{ij}) = -b/r_{ij} \exp(-r_{ij}/\xi)$ which is always attractive. Here b is a system-dependent constant, ξ stands for the correlation length, and r_{ij} is the distance between the ith and the jth monomers. Even though each solvent is good solvent for the polymer, the monomeric units experience a strong attractive interaction, and the polymer chain eventually collapses near the critical point.[1,2]

In 1986, G. Staikos and A. Dondos first tried to test the above-mentioned idea of de Gennes in the systems polystyrene (PS)/cyclohexane/methanol and poly(ethylene glycol) (PEG)/cyclohexane/methanol.[4] However their final conclusion was that the dimension of the polymer chain was almost constant even near the critical point. When examining their experimental condition thoroughly, we found that they used relatively low molecular weight polymer samples (for example, PS = 7700, PEG = 6000). Such low molecular weight polymer samples are unsuitable for this particular experiment since the factor α [=$R(T)/R(\Theta)$] by which a polymer chain expands beyond its unperturbed dimensions is not significant for chains of relatively low molecular weight.[5−7] Therefore in this paper we reexamined de Gennes' theoretical prediction for some high molecular weight poly(ethylene oxide)s (PEO: 111 000∼633 000) in the mixed solvent tetrahydrofuran/water (THF/WT) system having a lower critical solution temperature. For measurement of the dimension of a PEO polymer chain near the critical point, the light scattering technique cannot be applied due to very large scattering intensity due to the solvent composition fluctuations,[3,8] but closed capillary viscometry could be used as an appropriate tool since shear viscosity has a relatively weak critical anomaly.[9−11]

Theoretical Background[1,2]

When a polymer chain is dissolved in a mixture solvent A/B close to the critical solution temperature T_c, there exists a long range indirect interaction between two monomers of the polymer chain. First, let us consider the ith monomer located at r_i in the mixed solvent A/B with a critical point. The average composition of solvent A is C_A, but it has the local fluctuation $\delta C_A(r_i)$. The chemical potential of one monomer in the chain has the form

$$\epsilon = \epsilon_o + \epsilon_1 \delta C_A(r_i) \tag{1}$$

Here ϵ_o is a composition independent term and ϵ_1 of the composition dependent term has an arbitrary sign. If ϵ_1 is positive, the local fraction of A around r_i will be decreased. The composition fluctuation is linked with the potential fluctuation by the linear response function and the susceptibility, χ:

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

The integral over space of $\delta C_A(r_i)$ is essentially the parameter of preferential solvation λ'

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

where the susceptibility $\chi(r - r_i)$ has a simple Ornstein−Zernike form:

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

When another jth monomer residue is added around the ith monomer residue, the interaction free energy, $W_1(r_{ij})$ is of the form

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$$W_1(r_{ij}) = \epsilon_1 \delta C_A(r_j) = -\epsilon_1^2 \chi(r_i - r_j) = \frac{-b}{r_{ij}} e^{-r_{ij}/\xi} \quad (5)$$

According to de Gennes' theory, this indirect interaction between monomer residues has the following feature: One monomer creates a cloud of preferential solvation which attracts a second monomer. The size of the cloud is on the order of the correlation length ξ of the A/B mixture and is large near the critical point. Thus the interaction W_1 is always attractive and is 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 $W(r_{ij})$ becomes

$$W(r_{jj}) = W_1 + W_2 \cong -\frac{b}{r_{ij}} e^{-r_{ij}/\xi} + k_B T v \delta(r_{ij}) \quad (6)$$

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

$$v_{\text{eff}} = \frac{1}{k_B T} \int W(r_{ij})\, dr_{ij} = v - 4\pi b \xi^2 \quad (7)$$

There is a special correlation length at which this effective excluded volume parameter vanishes ($v_{\text{eff}} = 0$) and the polymer chain has its unperturbed ideal size, i.e., the Θ correlation length, ξ_Θ. Near the critical point the correlation length is related to the reduced temperature τ [$=(T_c - T)/T_c$] by $\xi \sim \tau^{-\nu'}$ where ν' is a critical exponent of $\sim 2/3$. The reduced Θ temperature, τ_Θ, also can be defined as the reduced temperature corresponding to $v_{\text{eff}} = 0$.

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

$$\xi_\Theta \cong \tau_\Theta^{-\nu'} = \left(\frac{T_\Theta - T_c}{T_c}\right)^{-\nu'}$$

We designate T_Θ as the Θ-like temperature in order to avoid confusion with Flory's Θ temperature, Θ.

If a polymer chain is very close to the critical temperature, what happens to the chain conformation? 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 solvation 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. This leads to an unusual dependence of the polymer chain extension on solution temperature very near the critical point.

Experimental Section

Materials. The five poly(ethylene oxide) (PEO) samples used in this study were purchased from Polymer Laboratories. These samples were characterized in methyl acetate solution by laser light scattering, as shown in Table 1. Anhydrous and spectroscopy grade tetrahydrofuran (THF) (Merck) was used without further purification, and water was deionized by a Millipore milli-Q.

Table 1. Characteristics of Poly(ethylene oxide) Samples

$10^{-3}M_w$[a]	M_w/M_n[b]	M_z/M_w[c]
111	1.02	1.21
163	1.10	1.20
254	1.06	1.24
543	1.05	1.28
633	1.10	1.24

[a] Measured by light scattering in methyl acetate solution. [b] Values obtained from the supplier (Polymer Laboratories). [c] Calculated from $M_z/M_w = 1 + 4 \times$ variance; the variance was obtained by dynamic light scattering.

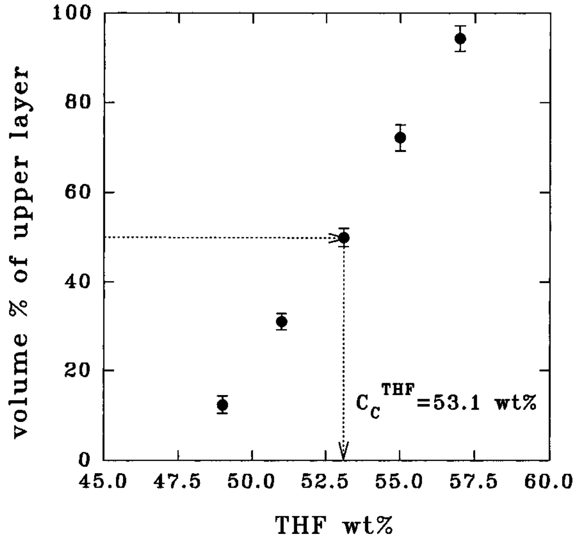

Figure 1. Volume % of the upper layer after phase separation as a function of the weight % of THF in the tetrahydrohuran/water mixture. The critical composition is obtained as 53.1 wt % of THF, for a 1:1 volume ratio of the upper layer and lower layer.

Static and Dynamic Light Scattering. The scattered light intensity was measured by a commercial light scattering instrument (Brookhaven Model: BI9000AT) operated with the $\lambda_0 = 632.8$ nm line of the He−Ne laser (35 mW). The molecular weights of PEO samples were obtained using a Zimm plot. The polydispersities of M_z/M_w were estimated using the equation of $M_z/M_w = 1 + 4 \times$ variance.[12]

Calibration of Viscometer. As the lower critical solution temperature of the mixed solvent (tetrahydrofuran/water: THF/WT) was higher than the normal boiling temperature of THF,[13] the closed capillary viscometer was designed as described in a previous paper,[14] but, unlike the previous experiment, a single calibrated viscometer was used throughout the entire experiment. In order to calculate the precise kinematic viscosity (=shear viscosity/density) from the flow time t, the viscometer was calibrated with the shear viscosity, η, and the density, d, of pure benzene solvent[15] at various temperatures using the equation $\eta/d = a't + b'/t$, where a' and b' were the instrument constants, respectively. For the shear viscosity−temperature relationship, a Bingham type equation was used:

$$T = 0.32052/\eta + 260.82 - 2633.1\eta \quad \text{(for benzene; units, K and cP)} \quad (9)$$

The average shear rate of our closed capillary viscometer appeared to be approximately in the range of $\sim 800\ \text{s}^{-1}$. The water bath was thermostated using a 5 mK Bayley temperature controller (Model 123).

Critical Composition of the Binary System of THF/WT. To determine the critical composition of the binary system THF/WT, we prepared various binary mixtures and measured the volume fraction of the upper layer after phase separation at the temperature $T = T_c + 0.2$ °C. From Figure 1, we found the critical composition of THF/WT system $C_c^{\text{THF}} = 53.1$ wt %. Hereafter all ternary samples of poly(ethylene oxide) were dissolved in this critical mixture solvent, THF/

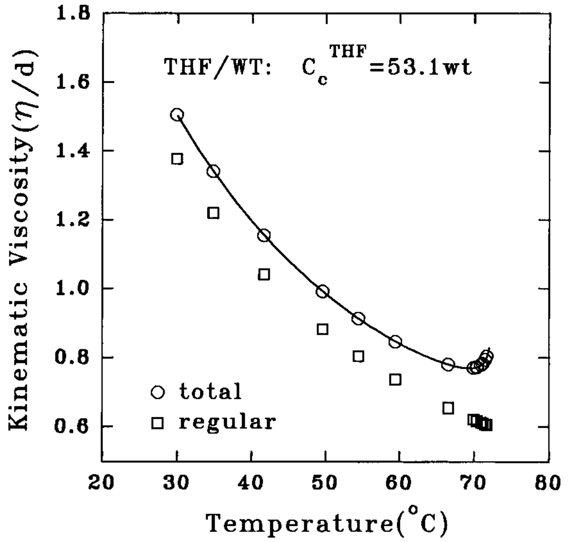

Figure 2. Kinematic viscosity of the binary tetrahydrohuran/water system vs the temperature. The square symbol denotes the noncritical, regular part of the Bingham type equation. The measured kinematic viscosity (circle) is well fitted by eq 9 (solid line) within a relative error of ±0.1%.

WT. C. M. Sorensen[33] reported for the critical composition and temperature of this system 53.7 wt % (22.5 mol %) of THF and 71.85 °C, respectively.

Measurement of T_c. The phase separation temperature was measured by means of a homemade turbidimeter. 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 phase separation temperature was taken as the temperature at which the intensity of the transmitted beam began to decrease abruptly at the slow heating rate of ~2 °C/h.

Results and Discussion

Kinematic Viscosity of THF/WT System. In general, the shear viscosity near the critical point consists of the noncritical, regular temperature-dependent part, η_{reg}, and the singular, critical effect part, η_{cri}. The regular temperature-dependent part of the viscosity is well expressed by the Bingham type equation rather than the Arrhenius equation $\eta = A \exp(B/T)$ because of the wide temperature range of 37 °C (~72–35 °C). The singularity of the viscosity near the critical point can be expressed by a power law of the reduced temperature, $\eta_{\text{cri}} \sim ((T_c - T)/T_c)^{-\nu}$. Finally, the kinematic viscosity of the binary THF/WT system of the critical composition is given as

$$(\eta/d)_{\text{solvent}} = \frac{(287.282 - \mathrm{T}) + \sqrt{(287.282 - \mathrm{T})^2 + 1307.97}}{17.207} \times \left(\frac{T_c - T}{T_c}\right)^{(-0.0427)} \quad \text{(units, cP and cm}^3\text{/g)} \quad (10)$$

Here the critical exponent ν of −0.0427 is in good agreement with the theoretical value[9–11] of −0.04. In Figure 2, the total kinematic viscosity of the mixed solvent and the regular part are plotted against solution temperature. The difference of two values denoted by circles and squares is the critical effect. It should be noted that dynamic renormalization group correction-to-scaling of the viscosity was not taken into account,[16] since this correction did not improve the present fitting level of ±0.1%, as shown in Figure 3. As our experimental error of the viscosity is also on the order of ±0.1%, an application of the high-order correction is meaningless without establishing higher accuracy in the viscosity measurement.

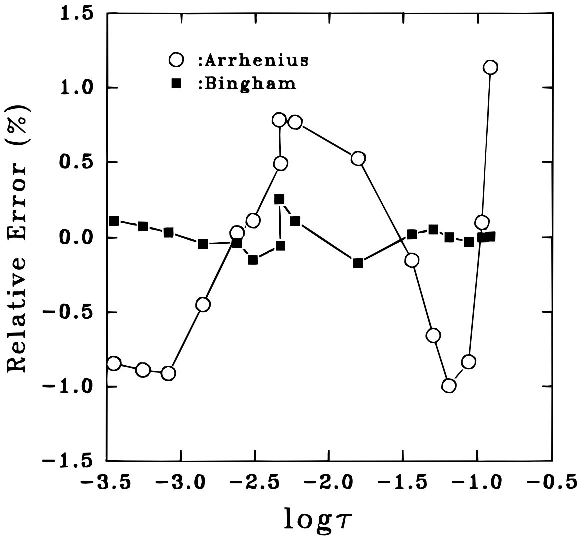

Figure 3. Relative error vs the logarithmic reduced temperature (log τ) in the tetrahydrofuran/water system. The 4–5 times better regression result is obtained when a Bingham type equation is used for the noncritical, regular part rather than the Arrhenius equation.

On addition of a very small amount of polymer (e.g. C_p = 0.05 wt %) into this binary solvent system having 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 verified experimentally by observing the volume ratio of the two layers after phase separation of the ternary polymer solution. The real experimental results show that the volume ratio of phase separation is not exactly a 1:1 ratio but is 0.88:1. This means that there is some shift of the critical composition. However, if this shift produces a negligible effect on the the critical exponent of the viscosity, ν, we can still handle this problem. To check this point, we intentionally prepared another binary mixture solvent with an off-critical composition of 50.4 wt % THF and observed the volume ratio of ~0.25:1 after phase separation. For this off-critical mixture solvent, the value of ν is 0.0384, where the deviation of 0.0043 (=0.0427 − 0.0384) is less than expected in spite of this unsymmetrical separation. Thus we conclude that in our ternary system, small deviations (e.g. on the order of 10%) from the volume ratio of 1:1 have almost no influence on ν.

Investigation of Solvent Quality in Binary and Ternary Systems of PEO. In order to interpret correctly the preferential solvation effect near the critical point, we need to know the relative solvation of PEO by the two solvents. Mark–Houwink relations for the binary systems of PEO/THF and PEO/water are given in eqs 11 and 12. THF appears to be a little better solvent for PEO than water at 72 °C.

$$[\eta] = 8.50 \times 10^{-2} M_w^{\ 0.60} \quad \text{(for PEO/THF at 72 °C; unit, mL/g)} \quad (11)$$

$$[\eta] = 7.68 \times 10^{-2} M_w^{\ 0.58} \quad \text{(for PEO/water at 72 °C; unit, mL/g)} \quad (12)$$

It is worth noting that water becomes a poorer solvent at increasing temperatures, while THF solvent becomes

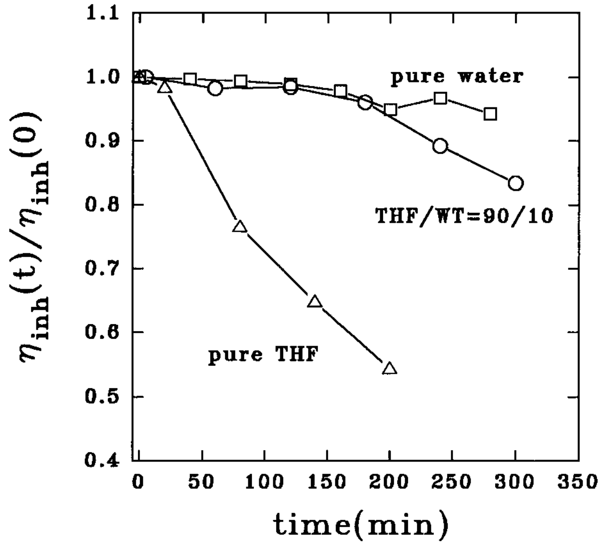

Figure 4. Rate of degradation of poly(ethylene oxide) dissolved in various THF/WT mixtures at 70 °C. The molecular weight and concentration of the samples are $M_w = 633$K and $C_p = 5 \times 10^{-4}$g/g of polymer, respectively. Presence of more than 10 wt % water greatly reduces the degradation.

a better solvent. In the mixed solvent at 35 °C the relation shown in eq 13 was obtained. The exponent 0.60 indicates that this medium is somewhat better than a Θ solvent.

$$[\eta] = 1.19 \times 10^{-1} M_w^{0.60} \quad \text{(for PEO/THF/WT; unit, mL/g)} \tag{13}$$

Degradation of PEO. Since PEO degrades easily at elevated temperatures, we investigated this degradation around 70 °C in various THF/WT mixtures. As shown Figure 4, the rate of degradation of PEO (M_w = 633 K) is very fast in pure THF, while in solvents containing more than 10 wt % of water, the degradation is greatly retarded. Since the polymer solutions in the viscometer are used for no longer than 200 min, we are sure that the decrease of the inherent viscosity results from a contraction of the polymer extension and not from polymer degradation.

Inherent Viscosity in the PEO/THF/WT Ternary System. For calculation of the viscosity of mixture solvent near the critical point, the important quantities will be the critical temperature, T_c, and the critical exponent of viscosity, ν. Prior to final interpretation it is necessary to know how the errors in T_c or ν affect those of the inherent viscosity. As shown in Figures 5 and 6, the error in the critical temperature causes a sudden increase of error in the inherent viscosity only near the critical temperature (i.e. in the range $\tau < 10^{-3}$: $\tau = (T - T_c)/T_c$), but 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.

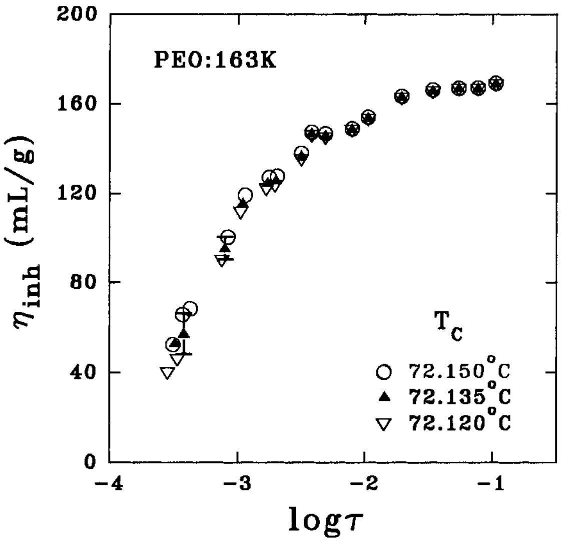

Figure 5. Effect of the error of the critical temperature on the inherent viscosity of poly(ethylene oxide) (M_w = 163K) for various log τ.

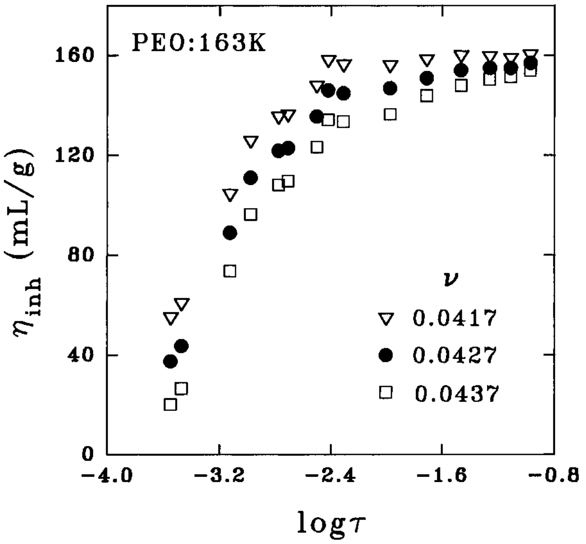

Figure 6. Effect of the error of the critical exponent of viscosity on the inherent viscosity of poly(ethylene oxide) (M_w = 163K) for various log τ.

When all inherent viscosity data are plotted against the logarithmic reduced temperature in Figure 7, the inherent viscosities remain almost constant in the range $\tau > 10^{-2}$ and the dimension of the polymer chain starts to decrease abruptly below $\tau < 10^{-2.5}$. As far as we know, this is the first experimental evidence for de Gennes' theoretical prediction. As a matter of fact, we are more interested in the relative variation of the expansion factor α_η^3 ($=[\eta]/[\eta]_\Theta$) than the absolute value of the inherent viscosity of each PEO sample. For calculation of the expansion factor α_η^3, we should know the values of the intrinsic viscosity not only at a given solution temperature but also at the Θ condition. First, since the concentration was very low, the inherent viscosity can be approximated as the intrinsic viscosity $[\eta]$ within a 2.6% error (this is the overestimated maximum error: $k_K[\eta]C_p \approx 0.15 \times 350 \times 5 \times 10^{-4} = 0.026$; k_K = Kraemer coefficient). Next, to estimate the intrinsic viscosity $[\eta]_\Theta$ at the Θ condition, the value of the prefactor K_Θ in Mark–Houwink equation, $[\eta]_\Theta = K_\Theta M^{1/2}$, should be known. When our additional intrinsic viscosity data measured in pure water at 72 °C are plotted by the Stockmayer–Fixman equation,[17] $[\eta]/M^{1/2} = K_\Theta + B'M^{1/2}$, the prefactor K_Θ has been obtained as 0.180 from the y-axis intercept of Figure 8. This value, $K_\Theta = 0.180$, is a little larger than the literature values of 0.13–0.17.[18] At this moment we think that this discrepancy may come from solvent-dependency[19,20] and/or temperature-dependency[21,22] of the unperturbed dimension. Now the reduced Θ temperature τ_Θ corre-

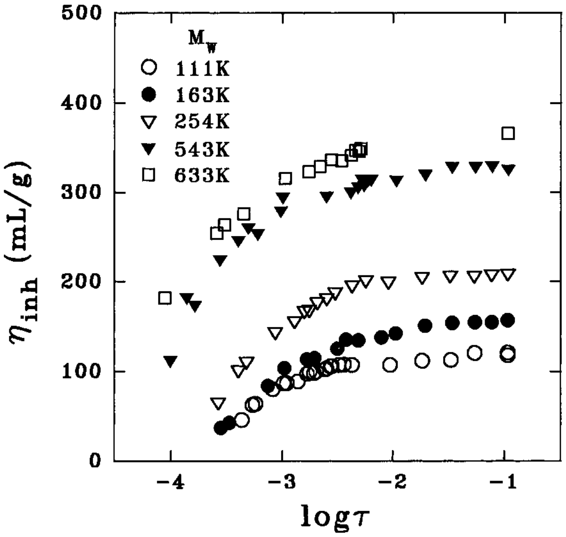

Figure 7. The Inherent viscosity of various molecular weight poly(ethylene oxide) samples as a function of log τ.

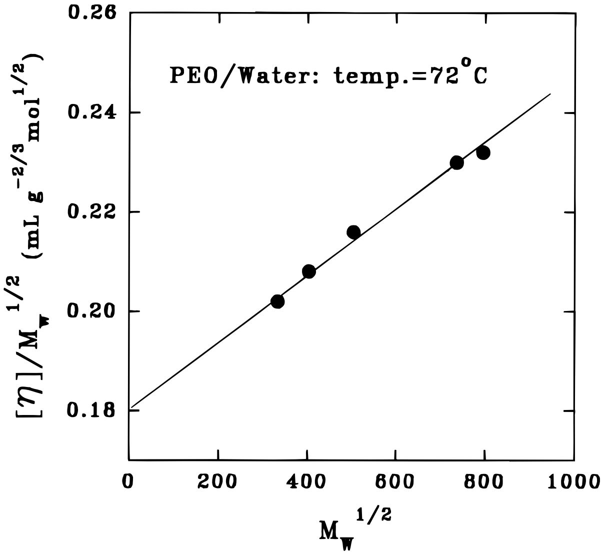

Figure 8. Plot of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ for the binary poly(ethylene oxide)/water system at 72 °C. The y-axis intercept gives a prefactor K_Θ value of 0.180 in the Mark–Houwink equation.

sponding to $[\eta]_\Theta$ can be determined from Figure 7. The reduced Θ temperature τ_Θ only for M_w = 633K PEO sample has been estimated by an extrapolation method because the measured smallest value of η_{inh} is larger than the calculated $[\eta]_\Theta$ even close to the critical point. Figure 9 is a log–log plot of the reduced Θ temperature vs the molecular weight. It is interesting that the reduced Θ temperature τ_Θ depends strongly on the molecular weight of the sample with an exponent value of −1.52. Thus, the high molecular weight PEO shows the ideal state rather nearer the critical point. This is quite contrary to de Gennes' prediction[1] that the reduced Θ temperature will be independent of the number of segments of the polymer chain. As a matter of fact, in his theory he assumed that the presence of polymer chains had no influence on the critical behavior of solvent mixtures. However this would be valid only for extremely low polymer concentrations, perhaps much lower than our experimental values of ~0.05 wt %. In this regard, it may be possible that the presence of polymer chains in the concentrations used in this work influences the critical behavior of solvents and this effect. Thus our finite concentration will be one of the major factors causing the strong molecular weight dependency of the reduced Θ temperature.

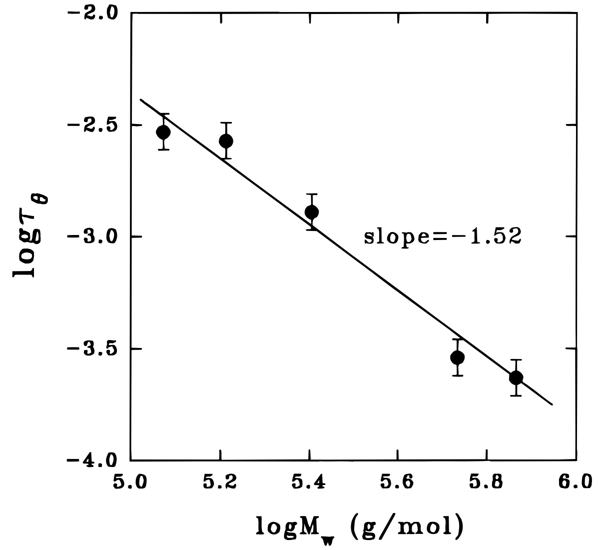

Figure 9. Log–log plot of the reduced Θ temperature τ_Θ vs the weight-average molecular weight M_w.

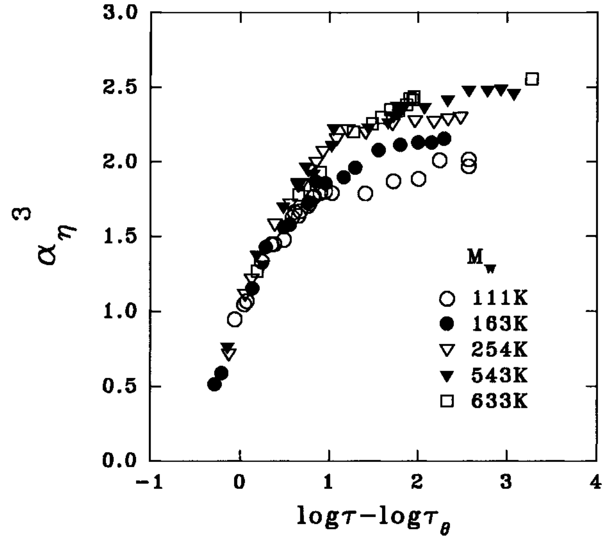

Figure 10. Plots of the expansion factors α_η^3 vs log τ −log τ_Θ in the ternary poly(ethylene oxide)/tetrahydrofuran/water system.

Instead of the logarithmic reduced temperature, the shifted logarithmic reduced temperature is used in Figure 10 so that the unperturbed, ideal state becomes zero on the new x-axis scale. As shown in Figure 10, the high molecular weight PEO have expanded more rapidly than the low molecular weight one, being farther off the critical temperature. This expansion behavior shows a trend similar to those for binary polymer/solvent systems near Flory's Θ temperature. According to Flory's equation[5] for the expansion factor $\alpha = [R(T)/R(\Theta)]$

$$\alpha^5 - \alpha^3 = 2C_m\,\psi[(T - \Theta)/\Theta]M^{1/2} \qquad (14)$$

the solvent quality is not simply a function of the temperature distance from the Θ temperature but is governed through the term $[(T - \Theta)/\Theta]M^{1/2}$. 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 we try to go one step

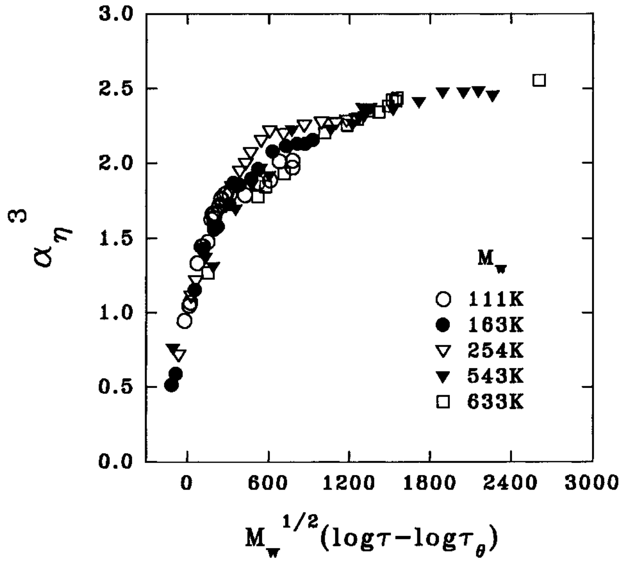

Figure 11. Plots of the expansion factors α_η^3 vs (log τ − log τ_Θ)$M_w^{1/2}$ in the ternary poly(ethylene oxide)/tetrahydrofuran/water system.

further by assuming that there exist analogous correspondences not only between the Flory Θ temperature Θ, in the usual binary polymer solution and the logarithmic reduced Θ temperature log τ_Θ in our ternary system but also between the solution temperature T and the logarithmic reduced temperature log τ. Expansion factors in this ternary system are a function of [log τ − log τ_Θ]$M^{1/2}$. In a plot of α_η^3 vs [log τ − log τ_Θ]$M_w^{1/2}$ (Figure 11), we found surprisingly that all our expansion factor data fall on one master curve within an experimental error of ±10%.

However, the reswelling behavior of polymer dimension mentioned in the Theoretical Background section was not observed close to the critical temperature, although de Gennes predicted that after a very compact size was attained, the strong adsorption of a preferentially selective solvent should reswell the chain.[2] At present, two plausible ways can be considered to reach the reswollen state. One is to find another pair of good solvents with a big difference in the preferential adsorption power. But in fact it seems impossible to find such a solvent mixture for PEO. Another way is to amplify the effect of preferential adsorption by approaching as close to the critical point as possible. It would be difficult to obtain the reliable inherent viscosity data in the range of $\tau < 10^{-4}$, especially at very dilute polymer concentrations.

Conclusions

The inherent viscosities of high molecular weight PEO polymer samples were investigated in the mixed solvent THF/WT system using a closed capillary viscometer. It was found that the inherent viscosity remains almost constant until $\tau = 10^{-2}$ but contracts to about one-third on approaching the lower critical solution temperature. The overall contraction behavior agrees well with de Gennes' theory, but in detail two experimental observations are not clearly understood. First we do not know why the reduced Θ temperature of the unperturbed chain dimension has a strong molecular weight dependence. Second, we observe only a contraction of the polymer chain on approaching close to the critical point while this collapsed chain is theoretically predicted to reswell from the compact size. All data of expansion factors for the different molecular weight samples fall on a master curve when α_η^3 is plotted against [log τ − log τ_Θ]$M_w^{1/2}$.

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