Transition phenomena of polymers in mixed solvents in the vicinity of theta conditions: Effect of preferential adsorption

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Viscosimetric measurements were obtained with the ternary systems polystyrene/dioxane/methanol, polystyrene/benzene/methanol and poly(methyl methacrylate)/dioxane/cyclohexane, changing the solvent mixture composition at constant temperature. The polystyrene and poly(methyl methacrylate) systems exhibit a transition phenomenon with solvent–mixture composition in which the polymer is just above the theta condition. In the case where two theta conditions occur ((θ-intra, θ-inter) the transition point is closely related to the intramolecular theta conditions. Moreover the intramolecular theta conditions vary with the molecular weight in the region of molecular weights where the preferential adsorption also varies. This variation induces a variation of the transition point with molecular weight which obeys a formula analogous to that giving the variation of the preferential adsorption with molecular weight.

(Keywords: polystyrene; poly(methyl methacrylate); ternary systems; polymer solvent–non-solvent; transition phenomenon; intramolecular theta conditions; preferential adsorption)

INTRODUCTION

In two recent communications[1,2] we presented some viscosimetric results showing that a transition phenomenon takes place for polystyrene and poly(methylmethacrylate) near theta conditions. More precisely, a discontinuity in the variation of intrinsic viscosity of the two polymers is observed as the quality of the solvent improves by increasing the temperature. The transition always appears at a temperature a few degrees above the theta temperature.

It is well known that the theta conditions of a polymer are also obtained in a mixture of two liquids (solvent + non-solvent) at constant temperature; it will be interesting to see if the same transition phenomenon occurs near the theta conditions in a solvent mixture.

In this paper the following three ternary systems have been studied: polystyrene/dioxane/methanol, polystyrene/benzene/methanol and poly(methyl methacrylate)/dioxane/cyclohexane. The quality of the solvent is improved by lowering the quantity of non-solvent in the mixture instead of increasing the temperature, which was the case in the two previous communications[1,2].

As is shown, the behaviour of polymers in the binary solvent systems is affected by preferential adsorption phenomena[3–5]. More precisely it has been observed[6] that in a given binary solvent, two different theta conditions occur. For one of these, called the intermolecular theta conditions (θ-inter), the second virial coefficient A_2 is equal to zero and for the other, which is called intramolecular theta conditions (θ-intra), the chains obey Gaussian statistics. Only when there is no preferential adsorption do the two theta conditions coincide.

Our results have shown that even in a solvent mixture, a polymer exhibits a transition phenomenon which is closely related to its theta conditions. This is especially so in systems where preferential adsorption phenomena occur, the transition point being related mainly to the intramolecular theta conditions.

As the preferential adsorption coefficient changes with the molecular weight of the polymer[7,8], the intramolecular theta conditions appear in a number of different analytical compositions of the binary solvent for different fractions of the polymer. Consequently the transition point must be changed with the molecular weight of the polymer. Our results are in good agreement with this assumption and the transition point varies with molecular weight in the same manner as with preferential adsorption.

EXPERIMENTAL

The samples of polystyrene and atactic poly(methylmethacrylate) were prepared by anionic polymerization at the Centre des Recherches sur les Macromolécules in Strasbourg (France) and had very low polydispersity.

All reagents were analytical grade chemicals from Merck and were used as received. All solvent mixtures were prepared by volume and are reported as the volume fraction ϕ_2 of the non-solvent in the solvent mixture.

Viscosity measurements were carried out in a modified Ubbelohde viscometer with applied pressure. The temperature was controlled to ±0.02°C. The efflux time for all solutions was more than 100 s and kinetic energy correction was negligible and was not applied. The reproducibility of the efflux time was better than 0.1 s. The limiting viscosity numbers $[\eta]$ were calculated by means of the Huggins relationship and were expressed in ml g^{-1}. The initial concentration of the polymers in the solutions was lower than 0.8×10^{-2} g/ml.

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RESULTS AND DISCUSSION

Ternary system polystyrene/dioxane/methanol (PS/diox/MeOH)

In this system the theta conditions for the polymer are obtained in a mixture containing 33.5% per volume methanol ($\phi_2=0.335$ volume fraction) at 35°C. In this composition the PS does not show preferential adsorption[9] and for this reason the intermolecular ($A_2=0$) and intramolecular ($B=0$) theta conditions coincide. In other words the analytical composition of the solvent mixture, which exists between the macromolecular coils, is the same with the solvent composition existing in the interior of the coils.

Viscosimetric measurements were carried out at a constant temperature of 35°C for four fractions of polystyrene changing the composition of the solvent mixture by lowering the percentage of methanol. As one can see in *Figure 1*, a sharp discontuinity in the variation of intrinsic viscosity $[\eta]$ with mixed solvent composition ϕ_2 is observed. The lowering of the intrinsic viscosity at the transition point is of the order of 6–9% and is beyond the experimental error.

The transition point appears when the macromolecular coil is just above the Gaussian conformation (very low positive expansion factor) as has already observed when one solvent was used[1,2]. For all the fractions of PS the transition starts at $\phi_2=0.31$ which is the analytical intermolecular and the intramolecular solvent composition. The two compositions are the same in the present case, because, as we have already mentioned, no preferential adsorption takes place.

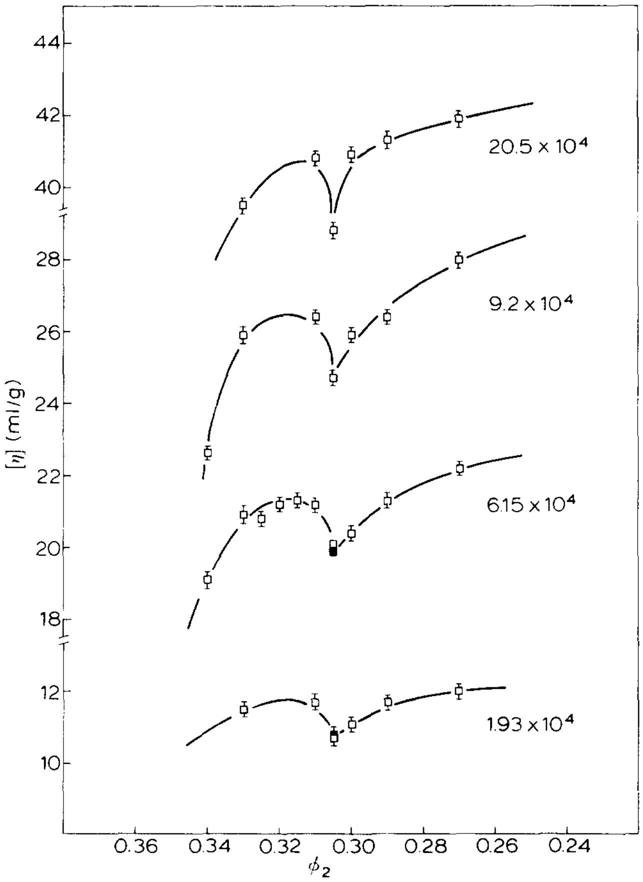

Figure 1 Variation of intrinsic viscosity $[\eta]$ for four fractions of PS with mixed solvent composition ϕ_2 (volume fraction of methanol) in dioxane/methanol system at 35°C

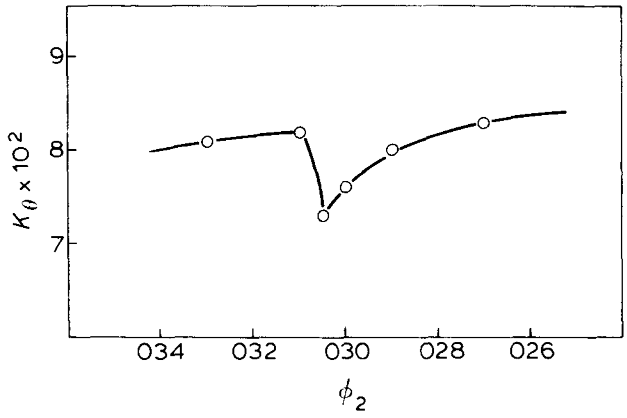

Figure 2 Unperturbed dimension parameter K_θ of PS as a function of solvent mixture composition ϕ_2 in dioxane/methanol system

In the following, using the well known Stockmayer–Fixman–Burchard[10,11] equation

$$[\eta]M^{-1/2}=K_\theta+0.51\Phi_0 BM^{1/2} \qquad (1)$$

where K_θ is related to the unperturbed dimensions

$$K_\theta=\Phi_0(\langle r_0^2\rangle/M)^{3/2} \qquad (2)$$

and B is the long range interaction parameter, we have determined the unperturbed dimensions of PS in different solvent compositions.

In *Figure 2* we present the variation of the K_θ parameter *versus* the solvent mixture ϕ_2 and we have observed an abrupt lowering of the unperturbed dimensions at $\phi_2=0.31$. The K_θ parameter is again rising as the solvent quality improves. These results show that at the transition point the macromolecular chain suddenly becomes more flexible as was the case when one solvent was used[1,2].

Ternary system polystyrene/benzene/methanol (PS/benz/MeOH)

In this system the PS preferentially solvated by benzene and the preferential adsorption coefficient λ' changes with the molecular weight of the PS[7,8].

As has already been reported[6] the polymer exhibits two different theta points at 25°C. One of these is called θ-inter ($A_2=0$) and is obtained at $\phi_2=0.22$ (volume fraction of methanol) and the other is called θ-intra ($B=0$, $\alpha=1$) which is obtained at $\phi_2=0.255$. It is evident that the existence of these two theta points, due to the preferential adsorption, changes the analytical composition in the interior of the coil.

Viscosimetric measurements were performed at 25°C in different solvent mixtures in the neighbourhood of theta conditions. In *Figure 3* we present the variation of intrinsic viscosity $[\eta]$ as a function of the solvent mixture composition ϕ_2 for four fractions of PS. Again transition phenomena have been observed but in this system the transition point depends on the molecular weight of the polymer.

We now call $\phi_2^\ddagger$ the composition at which the transition point occurs (intrinsic viscosity starts to drecrease) and in *Figure 4* we have plotted $\phi_2^\ddagger$ as a function of molecular weight M. As we can see the transition point $\phi_2^\ddagger$ is a

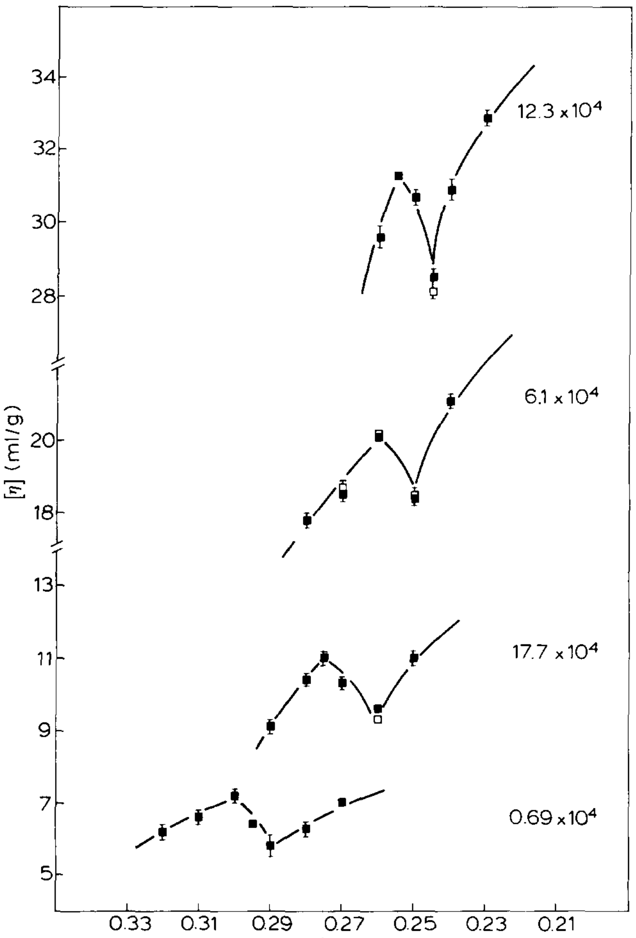

Figure 3 Variation of intrinsic viscosity $[\eta]$ for four fractions of PS with mixed solvent composition ϕ_2 (volume fraction of methanol) in benzene/methanol system at 25°C

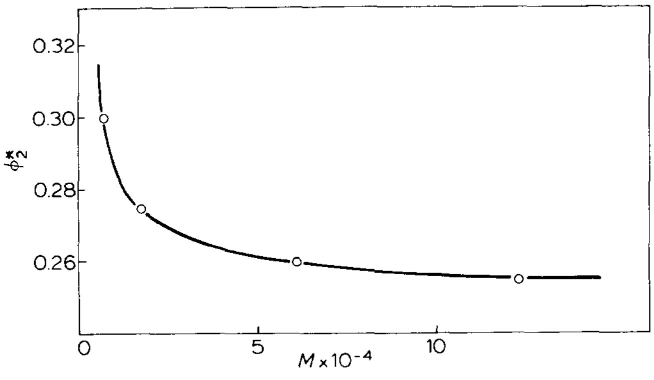

Figure 4 Transition point ϕ_2^* (volume fractions of methanol) as a function of the molecular weight of PS in benzene/methanol system

decreasing monotonic function of M and obeys the following empirical equation:

$$\phi_2^* = \phi_{2\infty}^* + AM^{-1/2} \qquad (3)$$

where ϕ_{2_∞} is the asymptotic limit for high molecular weights and A a constant.

Substituting $M^{1/2}$ from equation (4)

$$[\eta] = K_\theta M^{1/2} \alpha^3 \qquad (4)$$

where $[\eta]$ is the intrinsic viscosity in ϕ_2^* composition, we obtain

$$\phi_2^* = \phi_{2\infty}^* + AK_\theta \alpha^3 [\eta]^{-1} \qquad (5)$$

And knowing that the expansion factor lies near unity, because we are in the vicinity of the theta point, the above relation finally becomes:

$$\phi_2^* = \phi_{2\infty}^* + A'[\eta]^{-1} \qquad (6)$$

where A' is a constant.

Here we have to point out that the K_θ parameter at the transition point (at ϕ_2^*) is the same for all the molecular weight samples because in the interior of the coil the solvent composition (intramolecular composition) must be the same. For this reason the expansion factor is also the same as we shall see later.

Evidently a plot of $\phi_2^*[\eta]$ as a function of $[\eta]$ should give a straight line according to the above relation and as we can see in *Figure 5* this is the case.

The linear relationship between the transition point ϕ_2^* and the inverse of the intrinsic viscosity suggests a correlation between ϕ_2^* and the preferential adsorption coefficient λ'. This coefficient represents the excess volume of the good solvent which has been adsorbed per unit mass of the polymer and is linear in relation to the average segment density of the coil p which is proportional to the inverse of the intrinsic viscosity[12–14] according to Flory's well known equation

$$[\eta] = \Phi 6^{3/2} \frac{(\langle R^2 \rangle)^{3/2}}{M} = \Phi 6^{3/2} \frac{1}{p} \qquad (7)$$

If the transition point is closely related to the intramolecular theta conditions, which must be established with different analytical compositions of the solvent mixture because of the preferential adsorption, then it must be also related to the preferential adsorption coefficient. As we can see in *Figure 6* the above hypothesis is verified.

The question now is, if the transition point appears above the intramolecular theta conditions, which is the point where the chain is assumed to obey random-flight statistics, then the expansion factor reaches unity and the B parameter of the Stockmayer–Fixman–Burchard equation vanishes.

For this system all these conditions are obtained with $\phi_2 = 0.255$. However, in the region of low molecular weights ($M < 160000$) the expansion factor is greater than unity[7] because the preferential adsorption increases the quality of the binary solvent in the interior of the macromolecular coil in the range where the equation (8) is valid.

$$\lambda' = \lambda'_\infty + AM^{-1/2} \qquad (8)$$

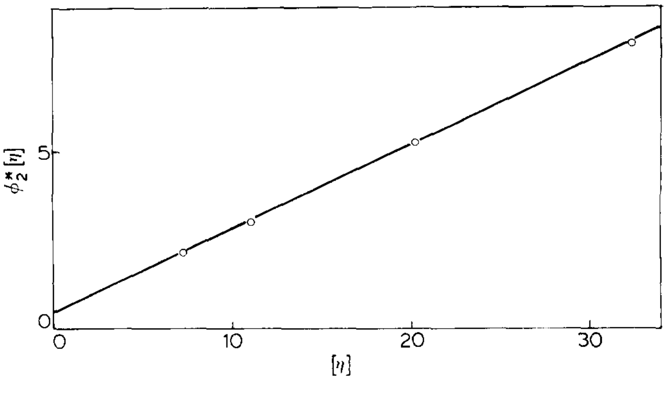

Figure 5 Application of equation (6) for the ternary system PS/benz/MeOH

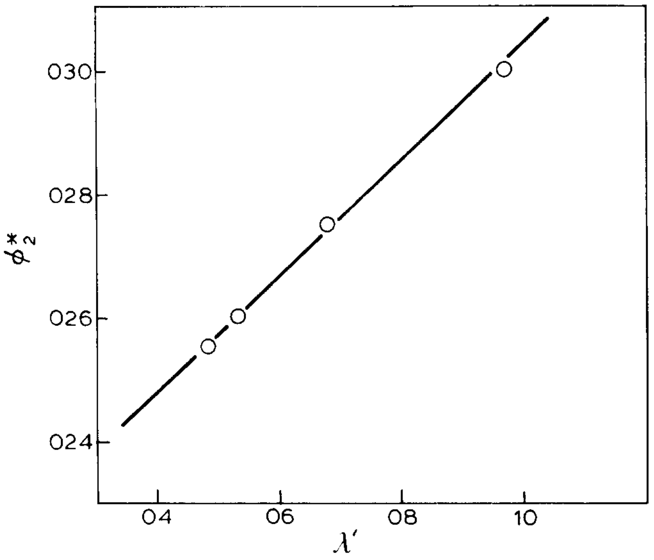

Figure 6 Transition point ϕ_2^* (volume fraction of methanol) as a function of the preferential adsorption coefficient λ' for the ternary system PS/benz/MeOH. The value of λ' has been taken from refs. 7 and 8

Moreover the expansion factor increases as the molecular weight decreases or the preferential adsorption coefficient increases. Evidently the intramolecular theta point varies with the molecular weight in the region where the preferential adsorption also varies.

We might conclude now that the variation of the transition point is induced from the variation of the intramolecular theta point and always lies above it. Calculating the expansion factor in the transition point

$$\alpha_\eta^3 = \frac{[\eta]}{[\eta]_\theta} = \frac{[\eta]}{K_\theta M^{1/2}} \tag{9}$$

(using $K_\theta = 0.079$ cm^3 g$^{-3/2}$ mol$^{1/2}$, value at $\phi_2 = 0.255$) the expansion factor is always higher than unity.

Ternary system poly(methyl methacrylate)/dioxane/cyclohexane (PMMA/diox/CH)

Viscosimetric measurements were carried out in the system PMMA/diox/CH in the vicinity of theta conditions[9] at 25°C. Transition phenomena have also been observed (*Figure 7*). The preferential adsorption phenomena in this system[6,9] are less pronounced but sufficient to alter the transition point with the molecular weight, in the same manner as in the system PS/benz/MeOH.

More precisely the variation of the transition point ϕ_2^* with intrinsic viscosity $[\eta]$ obeys equation (6) (*Figure 8*) showing, as we have already mentioned, that the transition point is closely related to intramolecular theta conditions.

CONCLUSIONS

A large number of macromolecules exhibit transition phenomena which can be separated into two groups: helix–coil transitions[15–17] and conformational transitions[18–29]. We believe that we have now a new type of polymer transition which presents the following characteristics:

(i) This transition is closely related to the theta conditions of the polymer either if these conditions are obtained in a pure solvent or in a mixed solvent.

(ii) This transition is independent of temperature but always appears at a temperature some degrees above the theta temperature[1,2].

Evidently the transition point, as we have already mentioned, always appears when the macromolecular coil exhibits a very low expansion factor. More precisely the expansion factor of the coil at the transition point for all

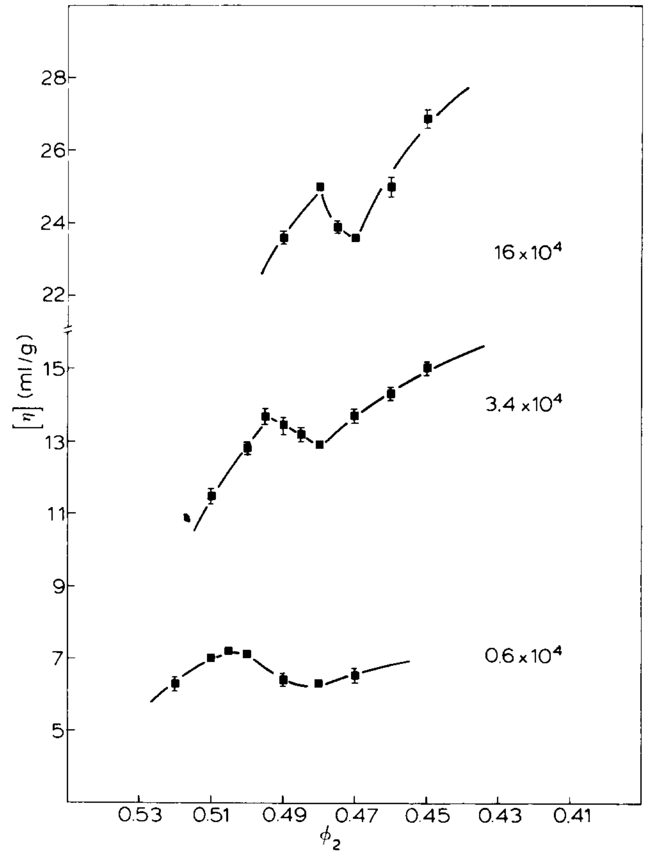

Figure 7 Variation of intrinsic viscosity $[\eta]$ for three fractions of PMMA with mixed solvent composition ϕ_2 (volume fraction of cyclohexane) in dioxane/cyclohexane binary solvent at 25°C

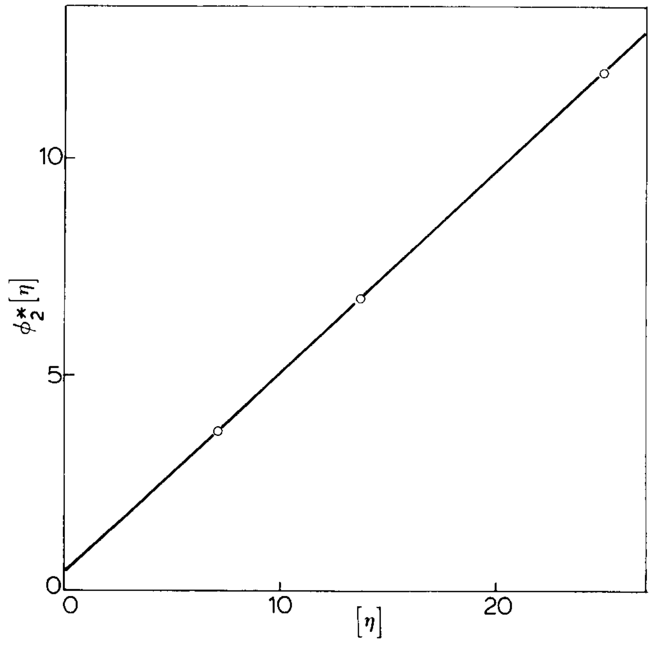

Figure 8 Application of equation (6) for the ternary system PMMA/diox/CH

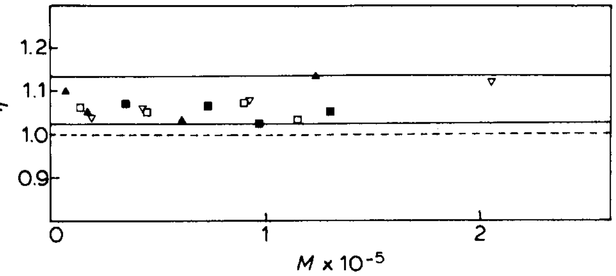

Figure 9 Expansion of α_η^3 at the transition point, as a function of the molecular weight in the following systems: (▲) PS/benz/MeOH at 25°C; (▽) PS/diox/MeOH at 35°C; (■) PS/CH, from ref. 1; (□) PMMA/MeCN, from ref. 2

the systems studied here as well as in our previous papers[1,2], is independent of the molecular weight and lies in a narrow range of values near unity ($1.025 \leqslant \alpha_\eta^3 \leqslant 1.13$) (*Figure 9*).

(iii) This transition appears at the same temperature or at the same composition for all the fractions of a given polymer in the range of molecular weights in which the theta conditions do not change.

(iv) This transition depends on molecular weight of the polymer only when we have a variation of the intramolecular theta conditions with molecular weight or a variation of the theta conditions in a pure solvent in the very low molecular weight range[2].

In the case where the preferential adsorption varies with the molecular weight of the polymer (equation (8)), the intramolecular theta conditions also vary with the molecular weight. Our results show, firstly, that the transition phenomenon is related to these intramolecular theta conditions and secondly that the variation with molecular weight obeys equation (6) which is equivalent to equation (8) giving the variation of the preferential adsorption with the molecular weight.

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