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Deswelling of Polystyrene Chains Immersed in Poly(methyl methacrylate)/Benzene Solutions near the Θ-Condition

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Introduction

A swollen polymer chain in a good solvent shrinks with incorporation of incompatible polymers into the solution due to reduction in effective solvent quality, and a concentration-dependent collapse of the chain will occur when the concentration of the incorporated polymer becomes high enough.[1-7] The chain swelling and deswelling in polymer matrix solutions must dominantly be controlled by the two-body interaction between chain segments as in the case of ordinary dilute polymer solutions. However, nature of the interaction is very different between these two cases. The deswelling or the collapse of a single chain immersed in an incompatible polymer solution was studied theoretically by Tanaka[1] and Nose[2] and experimentally by Lerman,[3] Laemmli,[4] Kuhn et al.,[5] Lin and Rosen,[6] and Ushiki and Tanaka.[7] Very recently, we have studied such a concentration-dependent collapse of a gel and found that the gel deswells in a way quite similar to a single chain.[8] This paper will deal with the change in chain dimension with increasing concentration of matrix polymers near the Θ-concentration at which the two-body interaction between the guest chains changes from repulsive to attractive.

Here, we consider a single chain of a guest polymer immersed in a semidilute solution of incompatible polymer with a solvent that is thermodynamically good for both polymers, where concentration of the guest polymer is alway dilute. As pointed out in a previous paper,[2,9] the relative size of the guest chain to the chain dimension or the mesh size of the matrix polymer is a very important element in considering guest-chain behaviors, because the renormalized excluded volume in the guest chain may depend on the relative size of the chain or chain segment considered to the screening length of the matrix polymer solution. In Figure 1 is shown a diagram schematically representing three regimes classified according to the situation of a guest chain in the matrix solutions. If the matrix solution is dilute (regions I and I′), the chain dimension is essentially the same as that in a good solvent irrespective of polymeric indexes of the guest chain (N_N) and the matrix chains (N_p). In the semidilute region of the matrix solution, however, the relative chain length N_N to N_p is necessary to be taken into account. The guest chain interacts with the matrix polymers beyond a screening length ξ only, having no essential interactions with the matrix chain within the distance of ξ. In the case of $N_N < N_p$, we may have the region II where the radius R_N of the guest chain is smaller than ξ. In this region, the chain is expanded as in a good solvent since the excluded-volume effect still works within the distance of ξ. On the other hand, in region III, where $R_N > \xi$, the dimension of the whole chain shrinks and would collapse because of the incompatibility of the two polymers, although the chain within a blob of radius ξ is still expanded. Deswelling with increasing concentration is expected to be more rapid in the case of $N_N/N_p > 1$ than in the case of $N_N/N_p < 1$, because the shrinkage starts at $\xi < R_N$ when the deswelling is observed from region I to region III, while it starts around $\xi \cong R_N$ in the case of the deswelling from region II to region III.[2] In our previous paper,[9] it was experimentally shown that the R_g is almost the same as that in good solvent even at Θ condition for the case of $N_N < N_p$, in accordance with the theoretical expectation.

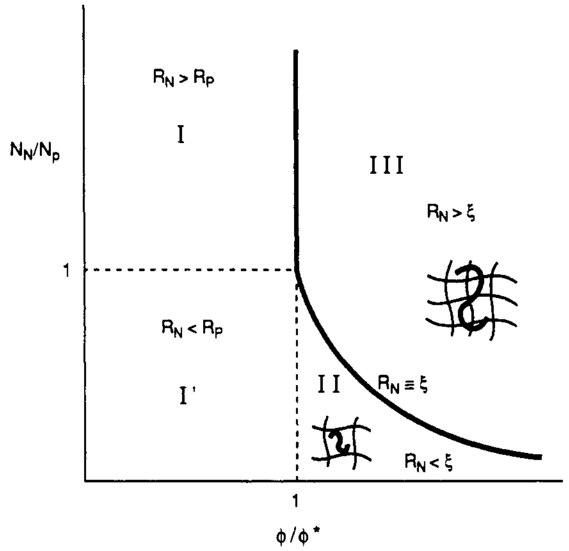

Figure 1. Single guest chain (polymeric index N_N) in the matrix solution of incompatible polymer (N_p). R_N, R_p: radii of gyration. ϕ: concentration of the matrix solution in volume fraction. ϕ^*: overlap concentration ($=N_p^{1-3\nu}$). ξ: screening (or correlation) length. The boundary between regions II and III is determined by $R_N = \xi$, which is given by $N_N/N_p = (\phi/\phi^*)^{1/(1-3\nu)}$. In the simple blob model, contact probability between guest and matrix chains in the semidilute region is assumed to be the same as that between matrix chains, so that the ξ for the guest chain (ξ_N) and the ξ of the matrix semidilute solution (ξ_p) are identical and $\phi_\Theta = \phi^*$. In the new blob model, the contact probability is less than that between the same polymers, so that $\phi_\Theta < \phi^*$ and $\xi_N > \xi_p$. Therefore, ϕ^* should read ϕ_Θ, and ξ means ξ_N in the above picture. More quantitatively, $\phi_\Theta \cong N_p^{(1-3\nu)/(1+a)}$ and $\xi_N = bN_p^{\nu}(\phi/\phi_\Theta)^{\nu(1+a)/(1-3\nu)}$, and the boundary between regions II and III is $N_N/N_p = (\phi/\phi_\Theta)^{(1+a)/(1-3\nu)}$. The symbol ϕ_Θ used above is ϕ_Θ at $N_N > N_p$, being independent of N_N. The concentration ϕ_Θ at $A_2 = 0$ for $N_N/N_p < 1$ may be determined by $g_\Theta \cong N_N$, which gives $\phi_\Theta = g_\Theta^{(3\nu-1)/(1+a)} \cong N_N^{(3\nu-1)/(1+a)}$ for $N_N/N_p < 1$ in the new blob model. This is identical with the boundary between regions II and III given above.

This study aims to investigate the deswelling behavior for the case of $N_N > N_p$. Here, we select the same combination of polymers and solvent as in our previous studies for single chains and gels,[8,9] i.e., polystyrene (PS) as a guest polymer and poly(methyl methacrylate) (PMMA)/benzene as a matrix polymer solution, which is a well-known isorefractive solution. The molecular weight of PS is high enough compared with that of PMMA. The radius of gyration, R_g, and the second virial coefficient, A_2, of PS chains were measured as functions of PMMA concentration for various PMMA molecular weights by light scattering. The results will be compared with theories based on scaling concepts, and similarity and dissimilarity in deswelling behavior between single chains and gels will be discussed as well.

Experimental Section

Sample. Polystyrene was the product of the Toso Co. with a weight-average molecular weight of $M_w = 8.42 \times 10^6$ and a polydispersity index of $M_w/M_n = 1.17$. Poly(methyl methacrylate) (PMMA) prepared by free-radical polymerization was fractionated by molecular weight from its toluene solution with

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Table I
Characterization of PMMA Samples and $R_{g\Theta}$ of PS ($M_w = 8.42 \times 10^6$) in Their Benzene Solutions Relative to R_{g0} in Pure Benzene

sample code	M_w	M_w/M_n	$R_{g\Theta}/R_{g0}$
P22	2.2×10^5	1.17	0.71
P47	4.7×10^5	1.17	0.76
P94	9.4×10^5	1.28	0.77
P193	1.93×10^6	1.04	0.89

methanol as a precipitant. In Table I are listed M_w and M_w/M_n of PMMA samples, which were determined by light scattering in 2-butanone and gel permeation chromatography. Reagent-grade benzene was dehydrated on CaH_2 and purified by fractional distillation.

PMMA+benzene solution with a concentration of 2–10 wt % was filtered repeatedly through a Millipore filter of nominal pore diameter 0.22 μm to remove dust particles. Ternary solutions were prepared by diluting the PMMA+benzene solution thus purified with dust-free PS+benzene dilute solution and benzene in a light-scattering cell. All cells containing solutions of desired concentrations were subsequently flamed sealed under a mild vacuum.

Light-Scattering Measurements. The angular dependence of the integrated intensity of scattered light was measured by a specially designed photometer with a He–Ne laser at 30 °C. Details have been described elsewhere.[9,12] To check the isorefractivity of PMMA and benzene, the angular dependence of the intensity of scattered light was measured for matrix solutions of PMMA+benzene. A higher concentration solution gave enhanced low-angle scattering, which decayed very slowly with a lapse of time. For example, it took about 50 days for the intensity of scattered light from a 15 wt % solution of P22 at an angle of 30° to reduce from 50 times to 10 times the intensity of pure benzene at 30 °C. The enhanced low-angle scattering is considered to be the one usually observed in the semidilute polymer solution with a rather high concentration.[13] The range of PMMA concentration was limited by the excess scattering. The excess intensity at low angles was kept at less than 20% of the intensity of benzene at low angles, which was negligible compared with the intensity scattered from PS solutions, and the highest concentration we reached was about 7 wt % for P22 and 3 wt % for P193. Values of R_g and A_2 were obtained by Zimm plots. Details of data analysis have been described elsewhere.[9]

Results and Discussion

Second Virial Coefficient and Θ-Concentration. As the concentration ϕ of PMMA in the matrix solution increases, the second virial coefficient, A_2, decreases from a positive value of A_{20} in good solvent to negative values, vanishing at a certain concentration, which is here called the Θ-concentration ϕ_Θ. In the present case, polymerization index N_N of the guest polymer (PS) is much larger than that of the matrix polymer (PMMA) N_p, so that the Θ-concentration ϕ_Θ must be a unique quantity independent of M_w of PS; in other words, the present value of ϕ_Θ may be regarded as ϕ_Θ for an infinitely large M_w of PS.

The molecular weight dependence of ϕ_Θ is shown in Figure 2 as log ϕ_Θ–log N_p plots, along with the ϕ_Θ for $N_p = 1.09 \times 10^4$, which was determined as the critical concentration of a PS/PMMA/benzene system at the limit of infinitely large N_N ($N_N \to \infty$).[10] Here, N_p = (M_w of PMMA)/100(molecular weight of PMMA monomer). The ϕ_Θ for $N_p = 1.09 \times 10^4$ agrees reasonably well with the value interpolated from the present data of ϕ_Θ. The double-logarithmic plots of ϕ_Θ vs N_p show a slightly steeper slope at larger N_p. If it was forced to fit to a straight line by least-squares fitting, we obtained the exponent $\alpha = 0.59$ for the power law of $\phi_\Theta \propto N_p^{-\alpha}$. For this exponent α, the mean-field theory predicts that $\alpha = 1$, the simple blob model[2] $\alpha = 3\nu - 1 \cong 0.76$, and the new blob model by Broseta et al.[11] $\alpha = (3\nu - 1)/(1 + a) = 0.63$, where we put $\nu = 0.588$ and $a = 0.22$ (see the caption for Figure 1). The exponent α obtained here is less than those predicted by the mean-field and the simple blob theory and is in better agreement with the prediction of the new blob theory, although the experimental data are not well expressed by a simple power law. In an asymmetric ternary solution PS/PMMA/benzene, the molecular weight (N_N) dependence of the critical concentration for $N_N > N_p$ = constant was weaker than those predicted by the mean-field and the simple blob theories but stronger than that of the new blob theory.[10] The present result seems consistent with this finding. Kuhn et al.[5] made light-scattering studies for the same system but with different combinations of N_N and N_p and found that the Θ-concentration ϕ_Θ decreases with increasing molecular weight N_p of the matrix polymers as $\phi_\Theta \propto 1/[\eta]$, with $[\eta]$ being the intrinsic viscosity of the matrix polymer. This result suggests that $\alpha \cong 3\nu - 1$ in accordance with the simple blob model, since $[\eta] \propto N_p^{3\nu-1}$ approximately. In view of the differences in N_N and N_p used, their result is compatible with the present result.

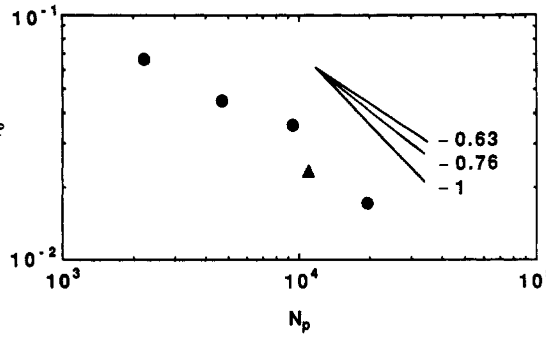

Figure 2. Molecular weight dependence of the Θ-concentration ϕ_Θ for PMMA/benzene solution against PS ($M_w = 8.42 \times 10^6$) at 30 °C. ●: present work. ▲: estimated from the critical solution temperature.[8] ϕ_Θ: in volume fraction. N_p: polymeric indexes of PMMA.

Radius of Gyration at Θ. In Table I are listed the ratios of the radius of gyration $R_{g\Theta}$ at the Θ-concentration to R_{g0} at $\phi = 0$ for various molecular weights (M_p) of PMMA. The radius of gyration $R_{g\Theta}$ is about 10–30% smaller than R_{g0} in benzene and decreases with decreasing M_p, while, in the previous case of $N_N < N_p$, $R_{g\Theta}$ is almost equal to R_{g0} in benzene. It can also be pointed out that, even in the present case of $N_N > N_p$, $R_{g\Theta}$ of the PS chain in the PMMA solution is much larger than that in a pure Θ-solvent, e.g., $R_{g\Theta}/R_{g0} = 0.54$ in the Θ-solvent cyclohexane at 34.5 °C.[14] At $\phi = \phi_\Theta$, i.e., at $A_2 = 0$, the interactions between two PS single chains vanish apparently, and at the same time those between the blobs vanish as well in the case of $N_N > N_p$. However, there must remain excluded-volume effects within the blob, which give rise to the larger $R_{g\Theta}$ in the matrix solution of an incompatible polymer compared with $R_{g\Theta}$ in the usual Θ-solvents. Therefore, $R_{g\Theta}$ may be expressed by R_g of a Gaussian chain consisting of N_N/g_Θ blobs, with g_Θ being the number of monomers in each blob at ϕ_Θ

$$R_{g\Theta} = b g_\Theta^{\nu} (N_N/g_\Theta)^{1/2} \qquad N_N > N_p \tag{1}$$

where b is the statistical segment length. In the simple blod model,[2] $\phi_\Theta \cong N_p^{1-3\nu}$ and $g \cong \phi^{1/(1-3\nu)}$, so that $g_\Theta \cong \phi_\Theta^{1/(1-3\nu)} \cong N_p$. In the new blob model,[11] $\phi_\Theta \cong N_p^{(1-3\nu)/(1+a)}$ and $g \cong \phi^{(1+a)/(1-3\nu)}$ because of less easiness of contact between PS and PMMA chains, so that one may expect $g_\Theta \cong N_p$ again. (Also see the caption of Figure 1.) Therefore, g_Θ can be put as $g_\Theta \cong N_p$, independent of the model. Eventually one may obtain from eq 1 with R_{g0} =

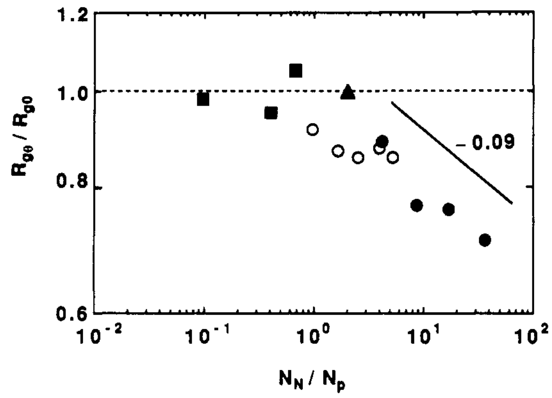

Figure 3. Degree of shrinkage of PS chains at ϕ_Θ against the relative polymeric index of PS to the matrix PMMA. ●: present work. ■: previous work[9] [PS ($M_w = 1.21 \times 10^6$, 5.2×10^6, and 8.4×10^6) in PMMA ($M_w = 1.21 \times 10^7$)]. ▲: Kuwamoto et al.[15] (PS, $M_w = 8.42 \times 10^6$; PMMA, $M_w = 4.06 \times 10^6$ at $\phi_\Theta = 0.1$ [extrapolated value from Figure 1]). ○: Lin and Rosen[6] (PS, $M_w = 1.6 \times 10^5$–8.6×10^5; PMMA, $M_w = 1.6 \times 10^5$ in toluene at 20 °C.

bN_N^ν

$$R_{g\Theta}/R_{g0} = (N_N/N_p)^\beta \tag{2}$$

with

$$\beta = 1/2 - \nu \cong -0.09 \qquad N_N > N_p \tag{3}$$

On the other hand, if $N_N < N_p$, then $g_\Theta \cong N_N$ (see Figure 1); thus, excluded-volume effects still remain within almost whole chains so that $R_{g\Theta} \cong R_{g0}$ or $\beta = 0$ in eq 2. Experimental results of $R_{g\Theta}/R_{g0}$ including those of previous works were plotted against N_N/N_p in a double-logarithmic scale in Figure 3. Values of N_N were give by N_N = (M_w of PS)/104. One can find a very good agreement with the above theoretical prediction. Namely, degrees of deswelling at ϕ_Θ, $R_{g\Theta}/R_{g0}$, for various combinations of N_N and N_p are well described by a universal function of the relative chain length N_N/N_p, and the slope $\beta \cong 0$ for $N_N/N_p < 1$ and $\beta \cong -0.1$ for $N_N/N_p > 1$.

Deswelling Behavior in Comparison with the Gel Collapse. In our previous paper on the collapse of PS gels immersed in PMMA/benzene solutions, we made a scaling argument on the gel collapse on the analogy of a single-chain behavior and presented the scaling formula as an approximate expression[8]

$$(\phi_g/\phi_\Theta)^{-1} = f_g(\phi/\phi_\Theta, \phi_{g0}/\phi_\Theta) \tag{4}$$

with

$$f_g = (\phi_{g0}/\phi_\Theta)^{-1} \quad \text{for swollen state} \tag{5}$$

and

$$f_g = (\phi/\phi_\Theta)^{-1} \quad \text{for collapsed state} \tag{6}$$

where ϕ_g is the volume fraction of the network polymer in the gel and ϕ_{g0} is ϕ_g in a good solvent. It should be noted that, here and hereafter, the symbol ϕ_Θ is the concentration ϕ at $A_2 = 0$ for $N_N > N_p$, being independent of N_N but a function of N_p only. These equations were deduced from a scaling expression for the single-chain deswelling based on the simple blob model[8]

$$R_g^3 = R_{g0}^3 f_R(\phi/\phi_\Theta, N_N/N_p, \chi) \tag{7}$$

with

$$f_R = 1 \quad \text{for swollen state} \tag{8}$$

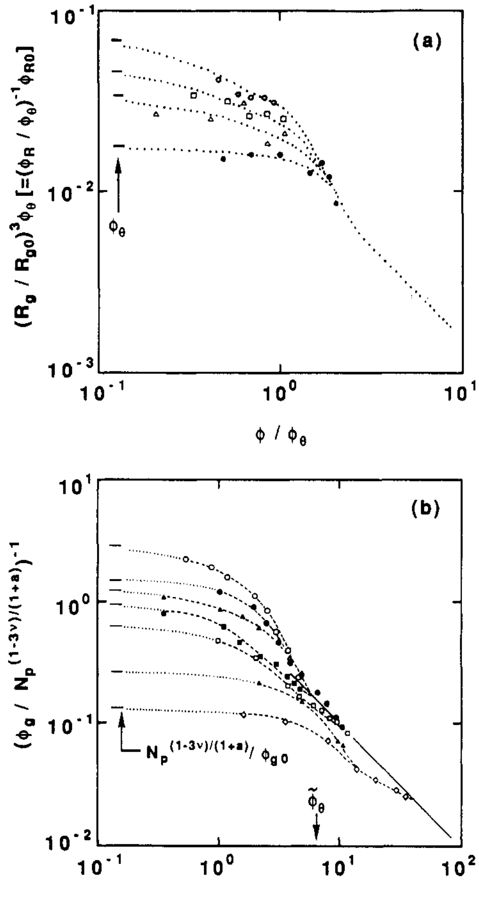

Figure 4. Deswelling behaviors of the single chain and the gel presented by scaled relations of the degree of swelling against the concentration of matrix solution. (a) Single chain: ○, P22; □, P47; △, P94; ●, P193. (Dotted lines are those qualitatively expected from eqs 10–12.) (b) Gel. See ref 8. $\phi_{g0} \sim N_\xi^{1-3\nu}$ (eq 2 in ref 8), with N_ξ being the polymeric index of a subchain between the cross-linking points, so that larger values of $N_p^{(1-3\nu)/(1+a)}/\phi_{g0}$ imply smaller N_p relative to N_ξ.

and

$$f_R \cong (\phi/\phi_\Theta)^{-1}(N_N/N_p)^{(1-3\nu)}\chi^{-1} \quad \text{for collapsed state} \tag{9}$$

Here, χ is the Flory interaction parameter between the guest polymer and the matrix polymer, and it is assumed that $0 < \chi < 1$. The analogy is essentially based on the assumption that a subchain between cross-linking points corresponds to a single chain; i.e., N_N corresponds to the polymeric index N_ξ of the subchain having the size of the correlation length ξ. Rewriting eqs 7–9 in the forms of eqs 4–6, one has

$$(\phi_R/\phi_\Theta)^{-1} = f_R(\phi/\phi_\Theta, N_N/N_p, \chi) \tag{10}$$

with

$$f_R = (\phi_{R0}/\phi_\Theta)^{-1} \quad \text{for swollen state} \tag{11}$$

and

$$f_R = (\phi_R/\phi_\Theta)^{-1}\chi^{-1} \quad \text{for collapsed state} \tag{12}$$

where

$$\phi_R \equiv b^3 N_N/R_g^3 \tag{13}$$

and $\phi_{R0} = b^3 N_N/R_{g0}^3$.

In Figure 4a is plotted log $\{(R_g/R_{g0})^3\phi_\Theta\}$ vs log (ϕ/ϕ_Θ) according to eq 10, where it is noted that $(R_g/R_{g0})^3\phi_\Theta = (\phi_R/\phi_\Theta)^{-1}\phi_{R0} \propto (\phi_R/\phi_\Theta)^{-1}$ for N_N = constant as in the present case. Similar plots for the gels based on eq 4, i.e., double-logarithmic plots of $(\phi_g/N_p^{(1-3\nu)/(1+a)})^{-1}$ vs $\phi/N_p^{(1-3\nu)/(1+a)}$, are illustrated in Figure 4b for comparison, where $N_p^{(1-3\nu)/(1+a)}$ was used instead of ϕ_Θ due to lack of data and the value of scaled $\tilde{\phi}_\Theta$ is indicated.[16] As expected, deswelling behavior of the single chain looks quite similar to that of the gel. The PS chain would shrink more rapidly if the PMMA chain is shorter for $N_N > N_p$, just as the gel shrinks more sharply if N_p is smaller.

A difference between the single chain and the gel, however, can be pointed out: the gel almost reaches the collapsed region at ϕ_Θ, while the single chain does not shrink so much, so that the plots of $(\phi_R/\phi_\Theta)^{-1}$ for different N_p do not merge into a single (straight) line of collapsed state at ϕ_Θ as yet. The deswelling behavior near the crossover from swollen to collapsed regions may be so delicate that the difference between the gel and the single chain shows up pronouncedly. An important difference between the single chain and the gel, which may give the dissimilar behavior, is that, in the gel problem, the osmotic pressure in two phases, the gel phase and the surrounding solution, may play an important role, while, in the single-chain problem, the guest chain directly interacts with the surrounding chains since there are no discrete two phases.

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(16) In ref 8, the correction term a was involved in the form of $N_p^{(1-a)(1-3\nu)}$, which makes almost no difference from the present form $N_p^{(1-3\nu)/(1+a)}$. However, more correctly, the present form should be used.[11]

Registry No. PS, 9003-53-6; PMMA, 9011-14-7; benzene, 71-43-2.