monomer reactivity ratios and the compositions in feed. The eight different T_g values are again untractable, however. Without ambiguous assumptions to T_g values related to the respective triad sequences, it is impossible to draw the prediction in the figure. What is worse, such assumptions are not expected to be examined by experiments.

In conclusion, the diad model seems satisfactory to describe the dependence of copolymer T_g on composition and sequence distribution. Both equations of Barton and of Johnston are seen to work for the three systems shown in Figures 2–4 and also for the five others, with an exception, whose T_{gAB} values have been reported.[13] The exception is the system vinylidene chloride/methyl acrylate. For T_{gAB}, 357.5 K has been predicted by the Barton equation,[3] while the experimental value of Hirooka and Kato[13] was 325.7 K, some 22 K lower than the prediction. This significant disagreement and detailed comparison of the Barton equation with the Johnston equation remain for consideration in subsequent papers.

Acknowledgment. We are indebted to Dr. S. Ross-Murphy, Unilever Research Colworth Laboratory, Professor M. Gordon, University of Cambridge, and Professor B. Wunderlich, University of Tennessee, for critical reading of the manuscript and to reviewers for helpful comments.

Registry No. (AN)(BD) (copolymer), 9003-18-3; (AN)(BD) (alternating copolymer), 106974-60-1; (S)(MMA) (copolymer), 25034-86-0; (S)(AN) (copolymer), 9003-54-7.

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Concentration-Dependent Collapse of Polymer Gels in Solution of Incompatible Polymers

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ABSTRACT: The volume change of polystyrene (PS) gels in a semidilute solution of poly(methyl methacrylate) (PMMA)/benzene was measured as a function of PMMA concentration for various PMMA molecular weights and degrees of cross-linking of the gel. In the case of small PMMA compared with the mesh size of the gel, a sharp transition from the swollen state to the collapsed state was observed with increasing PMMA concentration. The transition amplitude increased with decreasing PMMA dimension relative to the mesh size of the gel, and the transition concentration of PMMA increased with decreasing PMMA molecular weight, being independent of the degree of cross-linking. The deswelling behavior was analyzed on the basis of scaling concepts and described by a scaled form in a good approximation.

Introduction

Swelling and deswelling behavior of chemically cross-linked polymer gels is a rather old problem but has become of recent interest again because of newly developed aspects in this field: new approaches of rubber elasticity,[1] a phase transition with critical phenomena in swollen gels discovered by Tanaka,[2] and scaling arguments for semidilute solutions.[3] A swollen polymer gel immersed in the solution of a linear polymer shrinks as the concentration of the linear polymer increases because of reduction in effective solvent quality of the polymer solution.[4-8] Recently, Bastide et al.[9] investigated the volume change of polystyrene gels in toluene with incorporating linear polystyrenes in dilute and semidilute regions and interpreted the shrinking behavior of the gels on the basis of scaling concepts. This paper will deal with the gel deswelling by incorporation of incompatible linear polymers in the solvent. The deswelling behavior has some similarities to the collapse of single polymer chains by changing the solvent quality. In fact, Erman and Flory[10] have recently treated both problems on the same theoretical basis. Concentration-dependent collapse of single chains in the semidilute solution of incompatible polymer was studied theoretically by Tanaka[11] and Nose[12] and experimentally by Lerman,[13] Laemmli,[14] and Ushiki and Tanaka,[15] but no study on gel collapse has been reported to our knowledge.

For this problem, we can consider various cases according to the combination of the mesh size ξ_e of gels in the swollen state, the chain dimension R_g of the incorporated linear polymers, and compatibility of the linear polymers with the gel polymers which is characterized by the χ-parameter for segment interactions between them. (Hereafter, the solvent is considered to be thermodynamically good for the both polymers.) In case of $R_g > \xi_e$, the gel shrinks gradually when the concentration of the linear polymer ϕ_l increases, passing through the overlap concentration ϕ^*, and eventually it changes its volume such that $\phi_g \simeq \phi_l$, where ϕ_g is the volume fraction of polymers in the swollen gel. In this case of $R_g > \xi_e$, the linear polymer cannot interpenetrate into the gel and the equi-

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Table I
Characterization of Polystyrene Gel Samples

sample	irradtn time t, h	irradtn dose D, Mrad	Q_0	M_c[a]	ξ_e,[b] nm	$M_{\xi g}$[b]
G27	20	22.0	73.7	2.72×10^5	19.1	1.10×10^5
G11	25	27.5	42.6	1.09×10^5	12.7	5.55×10^4
G9	30	32.1	37.1	8.67×10^4	11.4	4.66×10^4
G4	50	53.5	23.9	4.21×10^4	8.22	2.70×10^4
G2	100	107.0	14.2	1.78×10^4	5.56	1.41×10^4

[a] Estimated by eq 1 with $\chi_s = 0$. [b] Calculated by eq 2.

Table II
Characterization of Poly(methyl methacrylate)

sample	M_w	M_w/M_n	R_g, nm[a]
P2	1.83×10^4	1.24	3.73
P7	7.10×10^4	1.14	8.38
P80	8.00×10^5	1.03	35.6
P240	2.40×10^6	1.11	68.5

[a] R_g in benzene calculated by R_g (nm) $= 1.06_4 \times 10^{-2} M_w^{0.597}$.[18]

librium is attained at $\mu_s^g = \mu_s^l$, where μ_s^g and μ_s^l are the chemical potentials of solvent μ_s in the gel and the surrounding polymer solution, respectively, which results in $\phi_g \sim \phi_l$ at higher concentrations since μ_s in the semidilute solution of good solvents is determined by the polymer concentration ϕ only. Note that this behavior does not depend on the compatibility of polymers, i.e., the sign of χ. On the other hand, in case of $R_g < \xi_e$, the deswelling behavior has to depend on χ. When the gel and the linear polymer consist of the same monomers, i.e., $\chi = 0$, or are compatible, $\chi < 0$, then the gel does not deswell so much, because the linear polymers can interpenetrate the gel and behave like a good solvent. An interesting case is the last case where $R_g < \xi_e$ and $\chi > 0$ (incompatible), on which we focus our attention in the present study. In this case, we can expect a sharp transition of the gel from the swollen state to the collapsed state because of incompatibility of the gel and linear polymers, in analogy with the concentration-dependent collapse of a very large single chain in the solution of a small, incompatible linear polymers. The linear polymers may enter the gel by a slight but effective amount. Interaction between polymers of different species in semidilute solution, which may play an important role in the deswelling behavior, is another interesting subject in this study. Very recently, Broseta et al.[16] have proposed a new scaling theory of the blob picture for a polymer/polymer/good solvent ternary system based on the result of a renormalization group theory, suggesting that the critical concentration of phase separation between the two polymers is not comparable to ϕ^* but higher than ϕ^*.

In this work, the volume change of chemically cross-linked polystyrene gels in the semidilute solution of linear poly(methyl methacrylate) (PMMA)/benzene has been measured as a function of PMMA concentration, PMMA molecular weight, and the degree of cross-linking of the gels to investigate the collapse of the gels by increasing the concentration of the surrounding linear polymers. The following section will describe sample preparation, sample characteristics, and the method of volume-change measurements. In the Results and Discussion, sets of data of deswelling behavior in various conditions will be presented, compared with the Flory–Rehner theory,[17] and analyzed on the basis of the new scaling theory.

Experimental Section

Cross-linked polystyrenes were prepared by irradiation of ^{60}Co to the bulk of polystyrene. The linear precursor polystyrene was the Toso Co. product with weight-average molecular weight $\bar{M}_w = 2.89 \times 10^6$ and polydispersity index $\bar{M}_w/\bar{M}_n = 1.09$. Dose rates are shown in Table I. After the irradiation, uncross-linked chains were completely removed by extraction with toluene. The degree of cross-linking was evaluated from the degree of swelling Q_0 in benzene, which is equivalent to the reciprocal of ϕ_{g0}: $Q_0 = \phi_{g0}^{-1}$, where ϕ_{g0} is ϕ_g in the good solvent, benzene. The molecular weight M_c between cross-links calculated by the Flory–Rehner equation[17]

$$Q_0^{5/3} = (1/2 - \chi_s) M_c \rho v / (1 - 2M_c/M) \qquad (1)$$

assuming that the polymer–solvent interaction parameter $\chi_s = 0$,[22] is shown in Table I along with the values of Q. Here, M is the molecular weight of precursor polymers, ρ is the polymer density, and v is the molar volume of solvent.

In Table I are also shown the mesh size ξ_e of the gel in benzene and the corresponding molecular weight $M_{\xi g}$ of PS chains, which were calculated from the relation

$$\xi_e = l \phi_{g0}^{-\nu/(3\nu-1)} = l (M_{\xi g}/M_0)^{\nu} \qquad (2)$$

where l and M_0 are the length and molecular weight of the statistical segment and ν is the exponent of the power law for molecular weight dependence of radius of gyration of polymer chains in good solvents. Here we put $\nu = 0.6$ and $M_0 = 5.1 \times 10^2$ and used $l = 0.76$ nm.[18]

Poly(methyl methacrylate)s were synthesized by radical polymerization and fractionated by molecular weight from their benzene solutions with methanol as a precipitant. In Table II are listed their molecular weights measured by light scattering and the polydispersity indexes M_w/M_n measured by a GPC equipped with a light-scattering apparatus. Estimated radii of gyration are also shown in Table II.

The volume of swollen samples V was determined by measuring the cross section area S of the samples with a cathetometer at 30 °C: the degree of swelling Q ($\equiv \phi_g^{-1}$) was given by $Q = V/V_b = (S/S_b)^{3/2}$, where V_b and S_b are V and S in the dried bulk state, respectively. The three dimensions of the sample species were about 2 mm × 1 mm × 0.2 mm in the bulk state, and it took a few hours to attain the equilibrium volume, so that the sample size was measured after leaving the sample at an experimental condition overnight. Q values for different sample species cross-linked under the same condition agreed with each other within ±10%.

Results and Discussion

Profile of Deswelling Curve Q–ϕ_l. Figures 1 and 2 shows double-logarithmic plots of Q against the volume fraction ϕ_l of PMMA as a function of PMMA molecular weight for the gels of G9 and G27, respectively, and Figure 3 shows those for G4, G9, and G27 in the PMMA solutions of P2. For convenience of discussion, let us divide the deswelling curve into three regions, although the boundaries are not so well-defined: the swollen region where the PMMA concentration ϕ_l is low enough to cause no deswelling, the collapsed region where the matrix polymers are rejected from being dissolved more into the gel because of shrinkage of the gel, and the transition region wherein the gel collapses from the swollen to the collapsed state.

In the collapsed region, similarly to the case of $R_g > \xi_e$, the degree of swelling is determined by equalization of the chemical potential of the solvent in the gel to that in the surrounding solution, so that the volume fractions of the polymers in the gel and the solution should be equal to each other irrespective of PMMA molecular weight (M_l)

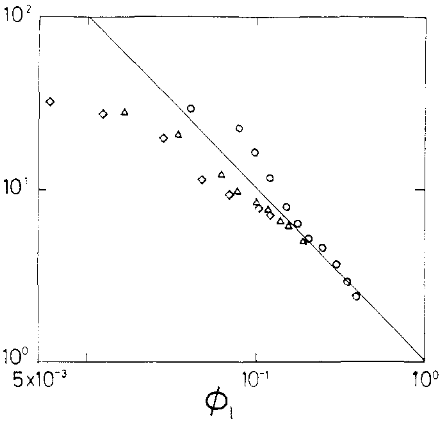

Figure 1. Plots of Q versus the PMMA concentration ϕ_l of the PS gel with $M_c = 8.67 \times 10^4$ for various PMMA molecular weights: (○) $M_l = 1.83 \times 10^4$; (△) $M_l = 7.10 \times 10^4$; (◇) $M_l = 8.00 \times 10^5$.

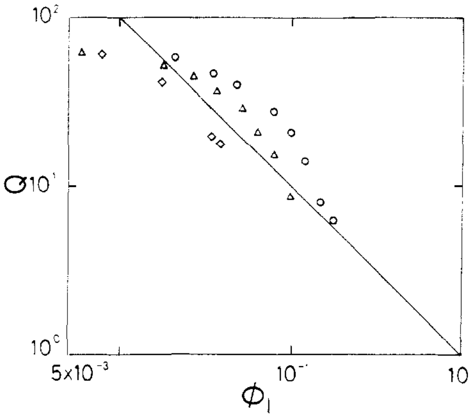

Figure 2. Plots of Q versus the PMMA concentration ϕ_l of the PS gel with $M_c = 2.72 \times 10^5$ for various PMMA molecular weights: (○) $M_l = 1.83 \times 10^4$; (△) $M_l = 7.10 \times 10^4$; (◇) $M_l = 8.00 \times 10^5$.

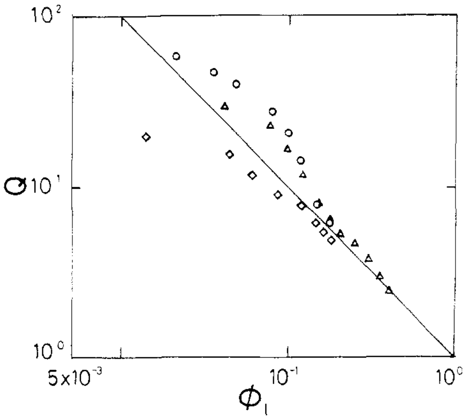

Figure 3. Plots of Q versus ϕ_l of the gels with different M_c's for the PMMA molecular weight $M_l = 1.83 \times 10^4$: (○) $M_c = 2.72 \times 10^5$; (△) $M_c = 8.67 \times 10^4$; (◇) $M_c = 4.21 \times 10^4$.

and M_c in the good-solvent limit, because the cross-linking effect is negligible in the collapsed state and the chemical potential of the solvent is a function of the polymer volume fraction only in both the gel and solution phase. This is actually the case in the present systems as seen in Figures 1–3, where all the deswelling curves merge in the single line $Q^{-1} = \phi_g = \phi_l$, although some do not reach the collapse region deep enough. On the contrary, the Q–ϕ_l behavior in the transition region depends on both of M_l and M_c.

M_l and M_c Dependences of the Collapse Point. Figures 1 and 2 demonstrate that collapse in the higher M_l takes place at the lower concentration of PMMA when M_l is low and that the Q–ϕ_l curve becomes independent of M_l at larger M_l's. On the other hand, Figure 3 shows that at the fixed M_l, the Q–ϕ_l curves merge in the line of $Q = \phi_l^{-1}$ at the same ϕ_l value irrespective of M_c when $M_l < M_c$. Comparison of these figures suggests that the value of M_l relative to M_c, which implies the size R_g of the PMMA chain relative to the mesh size ξ_e of the gel, is important in the collapse behavior. The smaller M_l/M_c (or R_g/ξ_e) gives rise to the sharper collapse. If the ratio R_g/ξ_e is less than about 0.5, a sharp transition was observed.

To consider the dependence of the transition concentration on the PMMA molecular weight, let us define conventionally the transition concentration ϕ_{lt} as the concentration at which the Q–ϕ_l curve merges with the line $Q = \phi_l^{-1}$, when the transition is sharp. Then we have $\phi_{lt} \simeq 0.089$ and 0.175 for P7 ($M_l = 7.10 \times 10^4$) and P2 ($M_l = 1.83 \times 10^4$), respectively, irrespective of M_c if $M_c > M_l$. The origin of the collapse has to be the change in the two-body interactions between the gel chains from repulsive to attractive with increasing PMMA concentration, so that the transition point may roughly correspond to the Θ-point at which the second virial coefficient of PS dissolved in the PMMA/benzene matrix vanishes. Therefore, it is expected that $\phi_{lt} \simeq \phi_\Theta$, where ϕ_Θ is the PMMA concentration at the Θ-point. According to the mean-field theory

$$\phi_\Theta \sim (2\chi N_l)^{-1} \qquad \text{(mean field)} \tag{3}$$

while the simple blob theory predicts

$$\phi_\Theta \sim (2\chi N_l)^{1-3\nu} \qquad \text{(simple blob)} \tag{4}$$

at the limit of large N_l,[12] where N_l is the polymeric index of the linear polymer PMMA and χ is the interaction parameter between the gel polymer and the linear polymer. Here, we have assumed for simplicity that the solvent is an athermal solvent for both the polymers; i.e., the interaction parameters for the pairs gel polymer–solvent and the linear polymer–solvent are taken as zero. The observed molecular weight dependence can be compared with those predictions by taking the ratio $\phi_{lt}(\text{P2})/\phi_{lt}(\text{P7})$: the observed ratio = 0.175/0.089 = 1.97, while the mean-field and the simple blob theories give 3.88 and 2.96 for the ratio, respectively, assuming $\nu = 0.6$. The observed ratio is less than both of the theoretical values, which implies the observed N_l dependence of ϕ_t is weaker than that predicted. Very recently, Broseta et al.[16] have proposed a new scaling theory for the ternary system on the basis of renormalized group calculation, which predicts

$$\phi_\Theta \sim (2\chi N_l^{1-a})^{1-3\nu} \qquad \text{(new blob)} \tag{5}$$

where a is about 0.22. The term of the exponent a comes from the fact that it is less probable for a segment of other component polymers to be in an adjacent site compared with the segment contact of the same component, giving rise to a weaker N_l dependence of ϕ_Θ than the simple blob theory predicts. Taking the ratio $(1.83/7.10)^{(1-a)(1-3\nu)} \simeq 2.33$, one can find the theory gives a value close to the observed one (1.97); i.e., the deviation from the simple blob picture and the mean-field theory is consistent with the new scaling law. Success of the new blob theory has already been found in the experimental results of the critical solution point and the second virial coefficient of ternary (polymer I/polymer II/good solvent) systems.[19,20] A detailed scaling analysis will be made later.

Comparison with the Flory–Rehner Theory. The free energy of a swollen gel, ΔF, may be given by the sum of the mixing free energy ΔF_{mix} and the elastic free energy ΔF_{el}:

$$\Delta F = \Delta F_{\text{mix}} + \Delta F_{\text{el}} \tag{6}$$

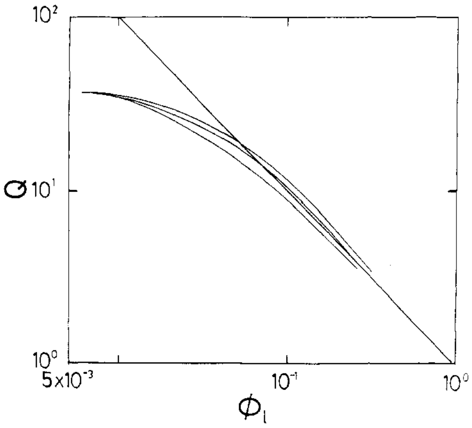

Figure 4. Theoretical curves of Q versus ϕ_l for different M_l's by the Flory–Rehner theory: $M_c = 8.67 \times 10^4$; $\chi_{01} = \chi_{12} = \chi_{20} = 0.1$ (0, solvent; 1, linear polymer; 2, gel polymer); (top) $M_l = 780$, (middle) $M_l = 1170$, (bottom) $M_l = 3900$.

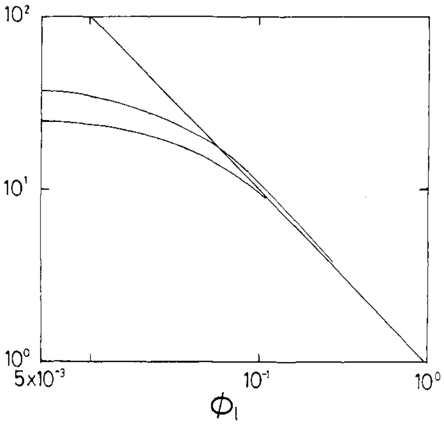

Figure 5. Theoretical curves of Q versus ϕ_l for different M_c's, $M_l = 1170$: $\chi_{01} = \chi_{12} = \chi_{20} = 0.1$ (0, solvent; 1, linear polymer; 2, gel polymer); (top) $M_c = 8.67 \times 10^4$, (bottom) $M_c = 4.21 \times 10^4$.

In the Flory–Rehner theory, ΔF_{mix} is evaluated by the Flory–Huggins theory for polymer solutions, which is a mean-field theory, and ΔF_{el} is given by the classical theory of rubber elasticity by Flory.[17] The equilibrium degree of swelling for given N_l, ϕ_l, and interaction parameters χ_{ij} can be calculated from the above ΔF with the equilibrium condition that each of the chemical potentials of the linear polymer and the solvent is identical in the gel and the surrounding solution. Details of the calculations are shown in the Appendix.

Figures 4 and 5 illustrate theoretical curves for M_l and M_c dependences, corresponding to Figures 1 and 3, respectively, where the polymeric index was calculated by taking the monomer as a segment. The theory can satisfactorily predict qualitative changes in Q–ϕ_l curves with M_l and M_c, but the M_l values chosen are much smaller than the real M_l's and the sharp transition observed for $M_l < M_c$ cannot be reproduced by any choice of parameters. Instead, the profile of the sharp transition is quite similar to that of a single chain in the incompatible polymer solution predicted by Nose's theory[12] based on scaling arguments, as described in the next section.

Scaling Analysis. First, consider the concentration-dependent collapse of *a single chain* in the solution of incompatible polymers by reviewing the scaling arguments made in a previous paper[12] based on a simple blob model. An extension of the thermal and concentration blob models to the ternary system gives an analytical expression of the radius of gyration R_{gs} of the guest chains as a function of N_N (polymeric index of the guest chain), N_p (polymeric index of the matrix chain), ϕ (concentration of the matrix solution), and χ interaction parameter. It has the following scaled form:

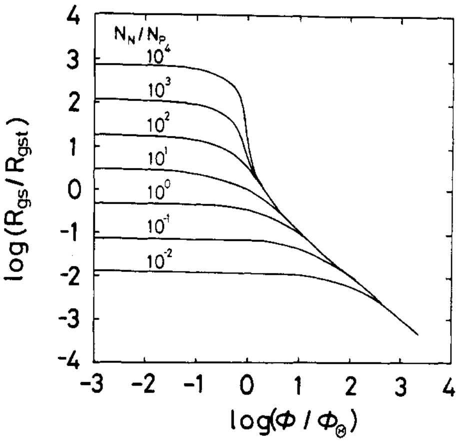

Figure 6. Double-logarithmic plots of the reduced chain dimension R_{gs}/R_{gst} against the reduced concentration ϕ/ϕ_Θ of the matrix polymer as a function of N_N/N_P for a single chain in the solution of incompatible polymers ($\chi = 0.1$) predicted by the simple blob theory.[12]

$$R_{gs} = lN_N^{\nu} f_R(\phi/\phi^*, N_N/N_P, \chi) \tag{7}$$

Here, $\phi^* = N_P^{1-3\nu}$ and $f_R = 1$ when $\phi/\phi^* \to 0$. If $\phi/\phi^* \gg 1$ with $|\chi| > (N_N^{-1}\phi^{1/(1-3\nu)})^{1/2}$ and $N_P^{-1}\phi^{1/(1-3\nu)}$, where the chain is in the collapsed state, one has

$$R_{gs} = lN_N^{\nu}(N_N/N_P)^{(3\nu-1)}\chi^{-1/3}(\phi/\phi^*)^{-1/3} \tag{8}$$

Therefore, eq 7 can be rewritten in the alternative form

$$R_{gs} = R_{gst} f_R'(\phi/\phi_\Theta, N_N/N_P, \chi) \tag{9}$$

with

$$R_{gst} = lN_N^{\nu}(N_N/N_P)^{(3\nu-1)}\chi^{-(2-3\nu)/3}(2+\chi)^{-(1-3\nu)/3} \tag{10}$$

where ϕ_Θ is the concentration ϕ of linear chains at the Θ-point, which is given as $\phi_\Theta = \phi^*[\chi(2+\chi)]^{1-3\nu} = [\chi(2+\chi)N_P]^{1-3\nu} \simeq (2\chi N_P)^{1-3\nu}$ (assuming $\chi < 1$) (eq 4), and R_{gst} represents the hypothetical R_{gs} at $\phi = \phi_\Theta$ in the collapsed state. In the collapsed state, f_R' is given as $f_R' = (\phi/\phi_\Theta)^{-1/3}$, while in the swollen state, i.e., if $\phi \ll \phi^*$, $R_{gs} = lN_N^{\nu}$, and then $f_R' = lN_N^{\nu}/R_{gst}$. Figure 6 shows the R_{gs}/R_{gst} – ϕ/ϕ_Θ relation for $\chi = 0.1$ as a function of N_N/N_P (obtained from Figure 3 of ref 12).

The deswelling behavior of the single chain illustrated in Figure 6 is very similar to that of the gel observed here (Figures 1–3), if one replaces R_{gs}^3/N_N by ϕ_g^{-1} and N_N by $(\xi_e/l)^{1/\nu}$. However, they are not exactly the same: the gel is not a simple sum of isolated single chains with the dimension being ξ_e but consists of many subchains connected by chemical cross-links and entanglements. As a consequence, the elastic free energy has to arise from the cross-linking and the two macroscopic phases coexist in the (gel + solution) system, while in the single-chain case there exist no two macroscopic phases. The later difference results in, for example, a difference in χ-dependence of the volume *at the collapsed state*: in the case of the gel, ϕ_g does not depend on χ and is almost identical with ϕ_l irrespective of the χ value as already mentioned, whereas in case of the single chain the chain dimension may depend on the χ value as suggested by eq 8. Note that, in our simple blob model, the matrix linear chain was assumed to freely interpenetrate the coil of the guest chain.

Although there have to exist some differences between these two cases, we can still expect a strong similarity, so that we presume the following translations from the single-chain problem to the gel problem to approximately describe the volume change of the gel with increasing concentration of the matrix polymers. That is, presuming that the behavior of a chain between cross-linking points corresponds to that of a single-chain, then we may replace R_{gs}/R_{gst} and N_N/N_p by $(\phi_{gt}/\phi_g)^{1/3}$ and $(\xi_e/R_{gm})^{1/\nu}$, respectively, where ϕ_{gt} is ϕ_g at $\phi_l = \phi_\Theta$ in the collapsed state and R_{gm} is R_g of the matrix polymer. Namely, eq 9 is transformed to $(\phi_g/\phi_\Theta)^{-1} = f_g(\phi_l/\phi_\Theta, \xi_e/R_{gm}, \chi)$, where we used $\phi_{gt} = \phi_{lt} = \phi_\Theta$. Furthermore, the χ-independence of the volume of the collapsed state mentioned above is assumed, and this assumption demands that the function f_g should be reduced to $f_g(\phi_l/\phi_\Theta, \xi_e/\xi_{m\Theta})$, where $\xi_{m\Theta}$ is the ξ of the matrix at $\phi_l = \phi_\Theta$. Since $\xi_e/\xi_{m\Theta} = (\phi_{g0}/\phi_\Theta)^{\nu/(1-3\nu)}$, we can finally write the simple scaled form:

$$(\phi_g/\phi_\Theta)^{-1} = f_g(\phi_l/\phi_\Theta, \phi_{g0}/\phi_\Theta) \qquad (11)$$

where ϕ_{g0} denotes ϕ_g at infinite dilution $\phi_l \rightarrow 0$. The quantity ϕ_{g0} is a parameter that characterizes the network structure, related to ξ_e by eq 2, while the quantity ϕ_Θ is determined by the size of the matrix polymer N_l and the χ parameter by eq 4 or 5. Now, the gel volume ϕ_g^{-1}, which must be generally given as a function of ξ_e, N_l, ϕ_l, and χ, that is, $\phi_g^{-1} = F(\xi_e, N_l, \phi_l, \chi)$, has been written in the scaled form of eq 11. The formula of the f_g function has to be very similar to that of f'_R illustrated in Figure 6. If the gel is in the swollen state, i.e., if $\phi_{g0}/\phi_\Theta < 1$ and $\phi_l/\phi_\Theta < 1$ or if $\phi_{g0}/\phi_\Theta > 1$ and $\phi_l/\phi_{g0} < 1$, one has $\phi_g = \phi_{g0}$, therefore

$$f_g = (\phi_{g0}/\phi_\Theta)^{-1} \quad \text{(swollen state)} \qquad (12)$$

while in the collapsed state, i.e., if $\phi_{g0}/\phi_\Theta < 1$ and $\phi_l/\phi_\Theta > 1$ or if $\phi_{g0}/\phi_\Theta > 1$ and $\phi_l/\phi_{g0} > 1$, one has $\phi_g = \phi_l$, that is

$$f_g = (\phi_l/\phi_\Theta)^{-1} \quad \text{(collapsed state)} \qquad (13)$$

When $\phi_{g0}/\phi_\Theta > 1$, the crossover from the swollen to the collapsed state takes place at $\phi_l \sim \phi_{g0}$, exhibiting no sharp change in ϕ_g with ϕ_l, i.e., f_g changes gradually having no gap between f_g values of eq 12 and 13 at $\phi_l = \phi_\Theta$. On the other hand, when $\phi_{g0}/\phi_\Theta < 1$, the crossover occurs at $\phi_l \sim \phi_\Theta$ with a rapid change in ϕ_g with ϕ_l, i.e., f_g shows a sharp transition, and in fact, the f_g values given by eq 12 and 13 have a gap at the crossover $\phi_l \sim \phi_\Theta$. The ratio of the volume in the swollen state to that in the collapsed state at $\phi_l \sim \phi_\Theta$ can represent the transition amplitude, which is given by

$$A_t \equiv \phi_g(\text{collapsed})/\phi_g(\text{swollen}) = (\phi_{g0}/\phi_\Theta)^{-1} \qquad (14)$$

which makes sense when $\phi_{g0}/\phi_\Theta < 1$, otherwise there exists no sharp transition. Equation 4 or 5 gives

$$A_t \simeq (2\chi)^{1-3\nu}(N_{\xi g}/N_l)^{3\nu-1} \qquad (15)$$

for the simple blob model or

$$A_t \simeq (2\chi)^{1-3\nu}(N_{\xi g}/N_l^{1-a})^{3\nu-1} \qquad (16)$$

for the new blob model, where $N_{\xi g} = M_{\xi g}/M_0$ (see eq 2). The criterion for the sharp transition is given by $A_t > 1$. Namely, the sharp transition is expected if

$$N_l/N_{\xi g} < (2\chi)^{-1}, \quad \text{i.e.,} \quad R_g/\xi_e < (2\chi)^{-1/\nu} \quad \text{(simple blob)} \qquad (17)$$

or if

$$N_l^{1-a}/N_{\xi g} < (2\chi)^{-1}, \quad \text{i.e.,} \quad R_g N_l^{-a}/\xi_e < (2\chi)^{-1/\nu} \quad \text{(new blob)} \qquad (18)$$

For a family of systems with the same combination of the same polymer species, i.e., in case of χ = constant, the scaling factor ϕ_Θ in eq 11 can be replaced by the overlap concentration ϕ^* or $N_l^{1-3\nu}$ of the matrix polymer in the simple blob model and by $\phi^* N_l^{a(3\nu-1)}$ or $N_l^{(1-a)(1-3\nu)}$ in the new blob model. Figures 7 and 8 show the $(\phi_g/N_l^{1-3\nu})^{-1}$ versus $\phi_l/N_l^{1-3\nu}$ plot and the $(\phi_g/N_l^{(1-a)(1-3\nu)})^{-1}$ versus $\phi_l/N_l^{(1-a)(1-3\nu)}$ plot, respectively. Here, we put $a = 0.22$, $\nu = 0.6$, and $N_l = M_w$/(molecular weight of a monomer unit). The scaled ϕ^* and ϕ_Θ values indicated by arrows with $\tilde{\phi}^*$ and $\tilde{\phi}_\Theta$ in the figures were calculated by $\phi^* = M_w/\rho N_A R_g^3$ with the values of M_w and R_g in Table II (ρ, density of PMMA 1.21 g cm^{-3};[21] N_A, Avogadro's number) and by the experimental value of ϕ_Θ for the PMMA of $M_w = 1.09 \times 10^6$ obtained previously.[21] In Figure 7, the scaled curves of the gels in the lower molecular weight PMMA P2 (○, ●, ■) and those of the gels in the higher molecular weight P7 (△, □) cross each other in the transition region, and the curves for P2 merge into the solid line at a lower scaled value of ϕ_l than those for P7, whereas, in Figure 8 they merge into the line of $\phi_g = \phi_l$ in a right manner without crossing. The scaled relation based on the new blob model (Figure 8) works better than that based on the simple blob (Figure 7). The experimental finding mentioned before, that the sharp transition was observed when $R_g/\xi_e < \sim 0.5$,

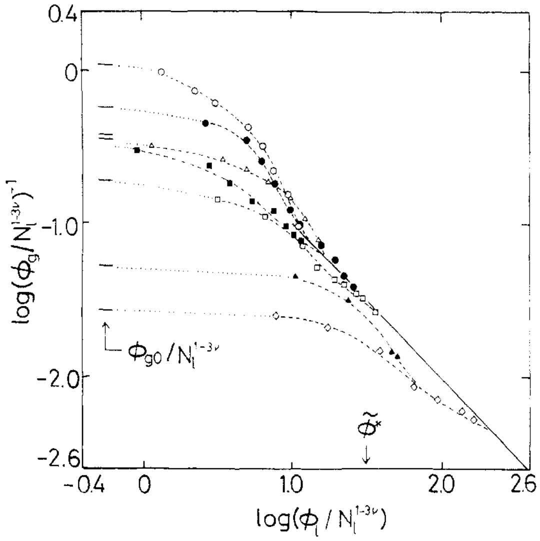

Figure 7. ϕ_g^{-1}–ϕ_l relations scaled on the basis of the simple blob theory: G27 in P2 (○), P7 (△), and P80 (▲); G9 in P2 (●), P7 (□), and P80 (◇); G4 in P2 (■). $\tilde{\phi}^* = \phi^*/N_l^{1-3\nu}$ (see text). The dashed lines are guides to the eye only. The solid line represents the relation $\phi_g = \phi_l$.

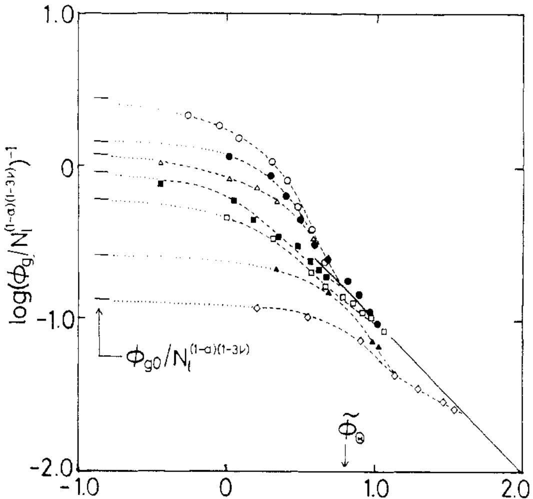

Figure 8. ϕ_g^{-1}–ϕ_l relations scaled on the basis of the new blob theory. $\tilde{\phi}_\Theta = \phi_\Theta/N_l^{(1-a)(1-3\nu)}$ (see text). Symbols are the same as in Figure 7. The dashed lines are guides to the eye only. The solid line represents the relation $\phi_g = \phi_l$.

seems to be consistent with eq 17. However, looking into the details of the experimental results, we can see that eq 18 is a better criterion than eq 17: a sharp transition was found for P7 ($M_l = 7.10 \times 10^4$)/G27 ($M_{\xi g} = 1.10 \times 10^5$), whereas no sharp transition was found for P2 ($M_l = 1.83 \times 10^4$)/G4 ($M_{\xi g} = 2.70 \times 10^4$), although both cases have almost the same value of $M_l/M_{\xi g}$, i.e., the larger M_l can exhibit the sharp transition at the larger $M_l/M_{\xi g}$ ratio, which may imply that the correction of the N_l^{-a} term in eq 18 is necessary. The scaled relation of eq 11 with eq 5, 12, and 13 describes the experimental ϕ_g–ϕ_l relation to a good approximation: namely, it can well describe the concentration-dependent collapse behavior, the location (concentration of the matrix polymer), and the amplitude of the transition in terms of N_l and $N_{\xi g}$. One can see a good similarity between Figures 6 and 8.

In the present analysis the situation was much simplified. For a more precise description of the ϕ_g–ϕ_l relation, especially in the crossover region, it is necessary to improve the expression of the free energy of networks which has to depend on the condition of cross-linking, and the simple scaling will probably be broken in a refined description.

Appendix

In the Flory–Rehner-type theory, the chemical potentials $\Delta\mu$ of solvent and linear polymer in the present system are given as

$$\Delta\mu_0'/RT = \ln \phi_0' + (1 - N_l^{-1})\phi_1' + (1 - \phi_0')\phi_1'\chi_{01} \quad \text{(A-1)}$$

$$\begin{aligned}\Delta\mu_0''/RT = \ln \phi_0'' + (1 - N_l^{-1})\phi_1'' + \phi_2'' + \\ (1 - \phi_0'')\phi_1''\chi_{01} + \\ \chi_{02}(1 - \phi_0'')\phi_2'' - \phi_1''\phi_2\chi_{12} + N_c^{-1}(\phi_2''^{1/3} - \phi_2''/2)\end{aligned} \quad \text{(A-2)}$$

$$\Delta\mu_1'/RT = \ln \phi_1'' + (1 - N_l)\phi_0' + N_l(1 - \phi_1')\phi_0'\chi_{01} \quad \text{(A-3)}$$

$$\begin{aligned}\Delta\mu_1''/RT = \ln \phi_1'' + (1 - N_l)\phi_0'' + \phi_2'' + \\ N_l(1 - \phi_1'')\phi_0''\chi_{01} + N_l\chi_{02}(1 - \phi_1'')\phi_2'' + \\ N_l(1 - \phi_1'')\phi_2''\chi_{12} + N_lN_c^{-1}(\phi_2''^{1/3} - \phi_2''/2)\end{aligned} \quad \text{(A-4)}$$

with

$$\phi_0' + \phi_1' = 1; \qquad \phi_0'' + \phi_1'' + \phi_2'' = 1$$

where the subscripts 0, 1, and 2 denote solvent, linear polymer, and gel, respectively, N_c is the polymeric index of network chains between cross-links, and the prime and the double prime denote the solution and gel phases, respectively. Hence, $\phi_1' = \phi_l$ and $\phi_2'' = \phi_g$ in the text. The last terms in eq A-2 and A-4 come from the elastic free energy ΔF_{el}. Putting $\Delta\mu_0' = \Delta\mu_0''$ and $\Delta\mu_1' = \Delta\mu_1''$, we calculate the equilibrium degree of swelling Q $(=\phi_2''^{-1})$ for given sets of N_l, N_c, and χ_{ij} $(i, j = 0, 1, 2)$ from eq A-1–A-4.

Registry No. PS, 9003-53-6; PMMA, 9011-14-7.

References and Notes

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