velopment Co. supplied us with the block copolymers used in this investigation.

Registry No. (S)(I) (block copolymer), 105729-79-1.

References and Notes

(1) Meier, D. J. In *Block and Graft Copolymers*; Burke, J. J., Weiss, V., Eds.; Syracuse University: Syracuse, NY, 1973; p 105.
(2) Gallot, R. B. *Adv. Polym. Sci.* **1978**, *29*, 85.
(3) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1978**, *11*, 960.
(4) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(5) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *81*, 697.
(6) Hashimoto, T.; Tsukahara, Y.; Kawai, H. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 585.
(7) Hashimoto, T.; Shibayama, M.; Kawai, H.; Watanabe, H.; Kotaka, T. *Macromolecules* **1983**, *16*, 361.
(8) Hashimoto, T.; Kowsaka, K.; Shibayama, M.; Kawai, H. *Macromolecules* **1986**, *19*, 754.
(9) Roe, R. J.; Fishkis, M.; Chang, J. C. *Macromolecules* **1981**, *14*, 1091.
(10) Zin, W. C.; Roe, R. J. *Macromolecules* **1984**, *17*, 183.
(11) Nojima, S.; Roe, R. J. *Macromolecules* **1987**, *20*, 1866.
(12) Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.
(13) Chung, C. I.; Gale, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1149; Chung, C. I.; Lin, M. I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 545.
(14) Gouinlock, E. V.; Porter, R. S. *Polym. Eng. Sci.* **1977**, *17*, 534.
(15) Futamura, S.; Meinecke, E. *Polym. Eng. Sci.* **1977**, *17*, 563.
(16) Widmaier, J. M.; Meyer, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2217.
(17) Bates, F. S. *Macromolecules* **1984**, *17*, 2607.
(18) Han, C. D.; Kim, J. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *22*, 1741.
(19) Han, C. D.; Lem, K. W. *Polym. Eng. Rev.* **1983**, *2*, 135.
(20) Chuang, H. K.; Han, C. D. *J. Appl. Polym. Sci.* **1984**, *29*, 2205.
(21) Han, C. D.; Chuang, H. K. *J. Appl. Polym. Sci.* **1985**, *30*, 2431.
(22) Han, C. D.; Ma, Y. J.; Chu, S. G. *J. Appl. Polym. Sci.* **1986**, *32*, 2478.
(23) Han, C. D.; Jhon, M. S. *J. Appl. Polym. Sci.* **1986**, *32*, 3809.
(24) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1941**, *9*, 341.
(25) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802, 1818.
(26) Reference 23 considered only a special case for $p = 1$ in eq 1 and 2, but eq 4 is for all values of p.
(27) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(28) Helfand, E. *Acc. Chem. Res.* **1975**, *8*, 295.
(29) (a) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 879. (b) *Polym. Eng. Sci.* **1977**, *17*, 535. (c) *Macromolecules* **1980**, *13*, 994.
(30) Meier, D. J. In *Thermoplastic Elastomers*; Legge, N. R., Holden, G., Schroeder, H., Eds.; Hanser: New York, 1987; Chapter 11.
(31) Noolandi, J.; Hong, K. M. *Ferroelectrics* **1980**, *30*, 117. Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 727.
(32) de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1970**, *31*, 235.
(33) Helfand, E.; Wasserman, Z. R. In *Development in Block Copolymers*; Goodman, I., Ed.; Applied Science: New York, 1982; Chapter 4.
(34) Helfand, E.; Sapse, A. M. *J. Chem. Phys.* **1975**, *62*, 1327.
(35) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.
(36) Supplied by Shell Development Co.
(37) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(38) Fredrickson, G. H.; Larson, R. G. *J. Chem. Phys.* **1987**, *86*, 1553.
(39) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1983**, *16*, 1093.
(40) Hashimoto, T.; Tsukahara, Y.; Kawai, H. *Polym. J.* **1983**, *15*, 699.
(41) Keller, A.; Pedemonte, E.; Willmouth, F. M. *Kolloid Z., Z. Polym.* **1970**, *238*, 385.
(42) Dlugosz, J.; Keller, A.; Pedemonte, E. *Kolloid Z., Z. Polym.* **1970**, *242*, 1125.
(43) Pedemonte, E.; Turturro, A.; Bianchi, U.; Devetta, P. *Polymer* **1973**, *14*, 146.
(44) Fetters, L. J.; Meyer, B. H.; McIntire, D. *J. Appl. Polym. Sci.* **1972**, *10*, 2079.
(45) Hashimoto, T.; Nakamura, N.; Shibayama, M.; Izumi, A.; Kawai, H. *J. Macromol. Sci., Phys.* **1980**, *B17*, 389.
(46) Lin, J. L.; Roe, R. J. *Macromolecules* **1987**, *20*, 2168.
(47) Rounds, N. A. "Thermodynamics and Phase Equilibria of Polystyrene-Polydiene Binary Mixtures". Doctoral Dissertation, University of Akron, Akron, OH, 1971.
(48) Richardson, M. J.; Savill, N. G. *Polymer* **1977**, *18*, 3.
(49) Rigby, D.; Roe, R. J. *Macromolecules* **1986**, *19*, 721.
(50) Mori, K.; Hasegawa, H.; Hashimoto, T. *Polym. J.* **1985**, *17*, 799.
(51) This correlation was computed by us, using information on the specific volume for polyisoprene, 1.0953 cm^3/g at 25 °C, as a reference state, and the volume expansion coefficient, $(1/v)(\partial v/\partial T) = 6.70 \times 10^{-4}$ (1/K), given in: *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p V-7.
(52) Fesko, D. G.; Tschoegl, N. W. *J. Polym. Sci., Part C* **1971**, *No. 35*, 51.
(53) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.

Comparative Study on the Mean-Field and Scaling Theories of Temperature–Concentration Dependence of Slightly Cross-Linked Gel Systems

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ABSTRACT: The temperature dependence of the concentration of loosely cross-linked polymer networks swollen to equilibrium in poor solvent has been studied. An attempt is made to compare the prediction of different theories with experimental results. It is shown that the classical James–Guth network theory gives almost the same result as the modern thermal blob theory. Both theories predict universal dependence if scaled concentration and scaled temperature are used. This dependence excludes the possibility of first-order phase transition in gels below the Θ point. The Flory–Hermans–Wall–Kuhn theory predicts a collapse phenomenon, which has not been observed in our experiments. The results exhibited by poly(vinyl acetate) networks of different cross-linking densities swollen in isopropyl alcohol are diametrically opposed to those predicted on the basis of the Flory–Hermans–Wall–Kuhn theory, while the agreement with the James–Guth and thermal blob theories is quite satisfactory.

Introduction

Considerable attention has been paid recently to the theoretical and experimental investigation of the influence of solvent power on the network properties.[1-13] It is predicted that under certain conditions, the swollen polymer networks undergo a first-order, coil–globula like phase transition marked by a sharp collapse of the gel.[1-7]

Despite the theoretical works, the predicted sharp transition, called collapse, has not yet been observed experimentally, at least for neutral gels. Although poly-

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acrylamide gels were found to have a sudden change in the swelling degree within a narrow range of polymer–solvent interaction, the observed collapse was due to either electrostatic interactions or formation of heterogeneous structures.[6] These two effects were not considered in the theories.

The main purpose of the present paper is to investigate the temperature dependence of the equilibrium concentration of chemically cross-linked neutral gels below and above the Θ temperature. Three basically different approaches are discussed: two from the classical network theories, the James–Guth (JG) approach with the Flory–Hermans–Wall treatment, and the remaining one, which corresponds to the scaling theory. Other models like the constrained junction fluctuation, slip-link, and tube models will be discussed in a forthcoming paper.

Dependence of the Equilibrium Concentration on the Temperature As Given by the James–Guth Theory

The condition of swelling equilibrium with pure diluent can be generally written as

$$A\nu^* q_0^{-2/3}\bar{V}\phi^{1/3} + \ln(1-\phi) + \phi + \chi\phi^2 - B\nu^*\bar{V}\phi = 0 \quad (1)$$

where ν^* is the amount (expressed in moles) of elastically active network chains per unit dry polymer volume, ϕ is the volume fraction of the polymer in the gel, $\bar{V}$ is the partial molar volume of the diluent, χ is the Huggins interaction parameter, and q_0 stands for the isotropic deformation factor through which the system remembers those sets of states at which the cross-links were introduced. A and B are constants, the molecular meaning of them is not understood.

The "front factor", A, includes the possible corrections due to elastically ineffective chain ends, loops, and entanglements. It is often taken as unity if instead of the network chains, the elastically active chains are regarded.[2]

The value of the coefficient B is also controversial. According to Flory and Wall $B = 2/f$ where f is the functionality of the cross-links. On the basis of the James–Guth theory $B = 0$, while Kuhn and Hermans write $B = 1$.

There are different experimental results available from the literature concerning the value of B. Van der Kraats et al.[15] and Froelich et al.[16] found that $B = 0.5$, Pennings and Prins[17] and Rijke[18] obtained $B = 1$, and Horkay et al.[19,20] concluded that $B = 0$.

It is obvious that the swelling behavior of a gel predicted by eq 1 is greatly affected by the value of B. In this paper we are going to discuss what can be said about the temperature dependence of equilibrium concentration of different networks.

According to the JG theory the equilibrium condition for free swelling is given by

$$A\nu^* q_0^{-2/3}\bar{V}\phi^{1/3} + \ln(1-\phi) + \phi + \chi\phi^2 = 0 \quad (2)$$

Since we focus on highly swollen (loosely cross-linked) networks, it is more straightforward to use the virial form of eq 2. In this approach the logarithmic term is substituted by its third-order series and generalized in order to take into account not only the binary but also the ternary monomer interactions:

$$a\phi^{1/3} - u\phi^2 - w\phi^3 = 0 \quad (3)$$

where $a = A\nu^* q_0^{-2/3}\bar{V}$ and u and w are dimensionless second and third virial coefficients of monomer interactions. In the literature u is usually identified as $u = {}^1/_2 - \chi$. The third virial coefficient, w, is supposed to be temperature independent and dominated by chain flexibility. In eq 3 the only quantity that depends on the temperature is u, as long as the difference in heat expansion between the dry network and the solvent can be neglected. In our analysis we neglect the possible temperature dependence of the products $\nu^*\bar{V}q_0^{-2/3}$ and $\nu^*\bar{V}$.

Near the critical solution temperatures and consequently near the Θ temperature, the second virial coefficient has been predicted to be linearly proportional with the reduced temperature,[4,14,21] τ, defined as $\tau = (T - \Theta)/T$

$$u = (d/\Theta)\tau \quad (4)$$

At Θ condition eq 3 can be written as follows:

$$a\phi_\Theta^{1/3} = w\phi_\Theta^{3} \quad (5)$$

where the Θ subscript refers to the Θ state. Combinations of eq 3–5 results in

$$\phi^{1/3} - c\tau\phi_\Theta^{-8/3}\phi^2 - \phi_\Theta^{-8/3}\phi^3 = 0 \quad (6)$$

where

$$c = d/w\Theta$$

One can see that the equilibrium concentration, or swelling degree ($q = \phi^{-1}$), depends on the reduced temperature, the cross-linking density which is taken into consideration via ϕ_Θ, and the numerical factor c, which includes the effects of chain stiffness and interaction between the network polymer and the swelling agent.

For network homologues swollen in the same liquid c is constant and consequently the equilibrium concentration of the gels are determined by the τ and ϕ_Θ values. At first sight one may think that ϕ is a two-variable, implicit function of τ and ϕ_Θ. However, eq 6 has simple scaling properties with respect to the reduced temperature, and as a result of this, the number of variables can be decreased. Introducing scaled temperature, $\tilde{T}$, and scaled concentration, $\tilde{\phi}$ (or swelling degree $\tilde{q}$) defined as

$$\tilde{T} = \tau/\phi_\Theta \qquad \tilde{\phi} = \phi/\phi_\Theta \qquad \tilde{q} = |\tilde{\phi}|^{-1} \quad (7)$$

one can see that τ is eliminated from eq 6 and the equilibrium concentration can be given by a single-variable function:

$$\tilde{\phi} = f(\tilde{T}) \quad \text{or} \quad \phi = \phi_\Theta f|\tau/\phi_\Theta| \quad (8)$$

A similar scaling form serves to describe the swelling degree–temperature dependence via the scaled temperature:

$$\tilde{q} = f_q(\tilde{T}) \quad \text{or} \quad q = \phi_\Theta^{-1} f_q|\tau/\phi_\Theta| \quad (9)$$

The respective $f(\tilde{T})$ or $f_q(\tilde{T})$ functions can only be given in implicit form:

$$|\tilde{\phi}|^{-5/3} - \tilde{\phi} = c\tilde{T} \quad (10.a)$$

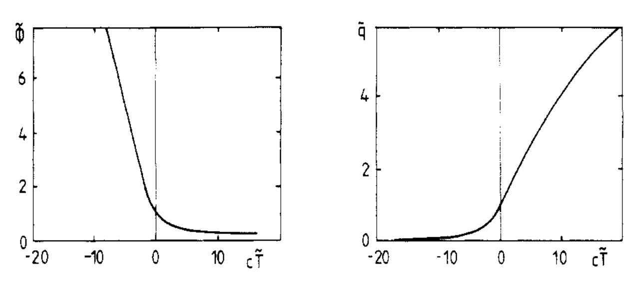
$$|\tilde{q}|^{5/3} - |\tilde{q}|^{-1} = c\tilde{T} \quad (10.b)$$

The dependence of $\tilde{\phi}$ and $\tilde{q}$ on $\tilde{T}$ as given by eq 10.a and 10.b is shown in Figure 1. The monotonically changing character of these curves shows that no phase transition can occur, at least as far as the JG theory is considered.

Equations 10.a and 10.b deserve some attention. They predict that in case of network homologues (c = constant) the $\tilde{\phi}$–$\tilde{T}$ curve is independent of structural details like ν^* and q_0.

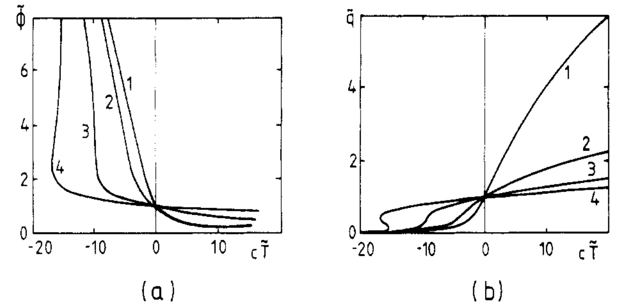
Dependence of the Equilibrium Concentration on the Temperature As Given by the Flory–Hermans–Wall–Kuhn (FHWK) Theory

In this case eq 3 must be completed by the term which takes into consideration the effect of cross-linking on the



(a) (b)

Figure 1. Dependence of the scaled concentration (a) and the swelling degree (b) on the scaled temperature. The latter is multiplied by the constant c.



(a) (b)

Figure 2. Scaled concentration (a) and swelling degree (b) as a function of $c\tilde T$ at different $b/w\phi_\Theta^2$ values. $b/w\phi_\Theta^2 = 0$ (1), 10 (2), 40 (3), and 80 (4).

thermodynamical properties of swollen gels. Let $b = B\nu^*\tilde V$; then one can write the equilibrium condition in the following way:

$$a\phi^{1/3} - u\phi^2 - w\phi^3 - b\phi = 0 \quad (11)$$

At Θ condition eq 11 yields

$$a\phi_\Theta^{1/3} - w\phi_\Theta^3 - b\phi_\Theta = 0 \quad (12)$$

Combination of eq 4, 11, and 12 gives for the $\tilde\phi$–$\tilde T$ and $\tilde q$–$\tilde T$ dependence

$$(\tilde\phi)^{-5/3} - \tilde\phi + \frac{b}{w\phi_\Theta^{2}}|(\tilde\phi)^{-5/3} - (\tilde\phi)^{-1}| = C\tilde T \quad (13.a)$$

$$(\tilde q)^{5/3} - (\tilde q)^{-1} + \frac{b}{w\phi_\Theta^{2}}|(\tilde q)^{5/3} - \tilde q| = C\tilde T \quad (13.b)$$

Now it is obvious that universal dependence of $\tilde\phi$ and $\tilde q$ on $\tilde T$ for homologous networks is no longer expected. The shape of the $\tilde\phi$–$\tilde T$ as well as the $\tilde q$–$\tilde T$ curve is very sensitive to the value of $b/w\phi_\Theta^2$. Figure 2 shows this sensitivity. It can also be seen that above a certain value of $b/w\phi_\Theta^2$ the monotonic character of the $\tilde\phi$–$\tilde T$ or $\tilde q$–$\tilde T$ curve disappears. This indicates a first-order transition marked by a sudden change in the swelling degree or concentration.

Figure 3 shows a predicted collapse phenomenon to occur below the Θ temperature. The higher the value of $b/w\phi_\Theta^2$ is, the lower the transition temperature and the bigger the difference in the swelling degree.

It is difficult to express exactly how the structural parameters which characterize the network make their influence felt on the $\tilde\phi$–$\tilde T$ or $\tilde q$–$\tilde T$ dependence or on the transition temperature. The reason of this difficulty comes from eq 12, which says that the $\phi_\Theta(\nu^*,q_0,w)$ relation cannot be given in explicit form. Numerical investigation of eq 12 gives that the value of $b/w\phi_\Theta^2$ increases with ν^* and q_0. This means that according to the FHWK theory, to achieve collapse one needs high value of ν^* and q_0 and low value of w. It is worth mentioning that the results obtained in this section are in agreement with those obtained by Dušek and Prins[1,2] as well as Khoklov[4] on the basis of different arguments.

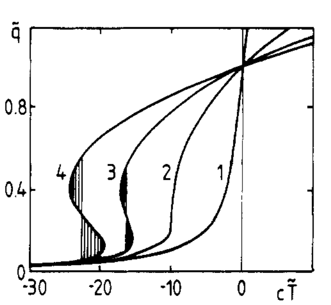


Figure 3. Scaled swelling degree versus the scaled temperature. The numbers denote different values of $b/w\phi_\Theta^2$. $b/w\phi_\Theta^2 = 0$ (1), 40 (2), 80 (3), and 120 (4).

Dependence of the Equilibrium Concentration on the Temperature As Given by the Scaling Theory

Polymer gels in swelling equilibrium with a pure diluent can be considered as a set of closely packed coils kept together by cross-links. de Gennes has postulated that the equilibrium polymer concentration of a swollen network can be expressed in terms of the overlap concentration, ϕ^*, of a polymer having the same molecular mass as the network chains:[21]

$$\phi = k(f)\phi^* \quad (14)$$

where $k(f)$ is a constant of unity depending only on the functionality, f, of the cross-links. Equation 14 is often called the c^* theorem and has also been derived from the classical Flory theory by Brochard[22] and from the scaling theory by Candau et al.[23] It is essentially a generalization of the Flory–Rehner equation.[14]

It must be emphasized that the c^* theorem is only valid if the swollen network is in equilibrium with pure diluent; that is, the chemical potential of the pure swelling agent inside and outside the gel is the same. This situation can be realized at different temperatures and therefore we can use eq 14 with the assumption that c^* depends on temperature.

The overlap concentration divides the dilute polymer solution regime from the semidilute one, and can be expressed as follows:

$$\phi^* = (\text{const})N/R^3 \quad (15)$$

where N is the degree of polymerization and R is the radius of gyration.

The most important statement of the c^* theorem is that at swelling equilibrium with pure diluent ($a_1 = 1$) the end-to-end distance (or the radius of gyration) of the network chain of the gel scales with N, like the end-to-end distance of a free macromolecule of the same molecular mass, in the same solvent. This statement was supported by small-angle neutron scattering experiments of Beltzung et al.[24]

On the basis of the c^* theorem (eq 14), one can determine the temperature dependence of the equilibrium concentration of a gel if the temperature dependence of the end-to-end distance is known. With this known, one can establish the temperature dependence of ϕ^*. This was first done by Daoud and Jannink,[27] who have shown that

$$\phi^*(N,\tau) = (\text{const})N^{1-3\nu}|\tau|^{3(1-2\nu)} \quad (16)$$

where the excluded-volume exponent, ν, takes the value $^3/_5$, $^1/_2$, and $^1/_3$ for T greater than, equal to, or less than Θ, respectively. At a good solvent condition ($\tau \gg N^{-1/2}$) eq 16 predicts $\phi^* \propto N^{-4/5}|\tau|^{-3/5}$, while in the poor solvent regime ($\tau \ll -N^{-1/2}$) ϕ^* is independent of the molecular mass and $\phi^* \propto -\tau$.

Since $\phi^*(N,\tau)$ is a generalized homogeneous function of variables N and τ, it is convenient to write

$$\phi^*(\lambda N, \lambda^{-1/2}\tau) = \lambda^{-1/2}\phi^*(N,\tau) \tag{17}$$

where we relabeled the variables such that $N \rightarrow \lambda N$ and $\tau \rightarrow \lambda^{-1/2}\tau$.

If we want to compare the results of different theories, then we must have the same quantities for the sake of comparison. That is, instead of ϕ (or ϕ^*) the scaled concentration $\tilde{\phi}$, or instead of τ, the scaled temperature $\tilde{T}$ is needed. ϕ_Θ can enter into the problem through N, since according to eq 15 $\phi_\Theta \propto N^{-1/2}$. To obtain $\tilde{\phi}$ and $\tilde{T}$ from ϕ or τ, one has to substitute $\tau/\phi_\Theta \propto \tau N^{1/2}$ instead of τ and $\phi^*/\phi_\Theta \propto \phi^* N^{1/2}$ instead of ϕ^* in eq 17.

This can be done easily if we choose $\lambda = N^{-1}$. Now the function $\phi^*(1,\tau N^{1/2})$ appearing on the left-hand side of eq 17 is formally a function of two variables, but the first variable is fixed at unity. Hence we can denote it by a function of a single varaible, defined as $f_s(\tilde{T}) = \phi^*(1,\tau N^{1/2})$. Since the left-hand side of eq 17 is proportional with ϕ, one gets for the temperature dependence of the equilibrium concentration

$$\phi = (\text{const})f_s(\tilde{T}) \tag{18}$$

where

$$f_s(\tilde{T}) = (\text{const})(\tilde{T})^{3(1-2\nu)} \tag{19}$$

It must be emphasized that eq 18 and 19 are valid only in the asymptotic limits. To reach these limits the product $N|\tau|^2$ must be high. However, to prepare polymer networks having long chains is rather difficult. The typical values of N in gels are from 50 to 1000. Consequently achieving the limit below the Θ temperature is almost hopeless due to spinodal decomposition. For a better description one has to investigate the crossover regimes, which separate both the good-solvent and the poor-solvent regimes from the Θ regime.[21]

The blob theory[28,29] permits the calculation of chain dimensions in the crossover regimes. It is assumed that a polymer chain is a succession of blobs made of N monomers. The excluded-volume effects become important only when the intersegmental distances are taken over the number of segments exceeding N_τ. In other works, the chains have Gaussian statistics inside the blobs and excluded-volume or globular statistics outside the blobs. N_τ is the temperature dependent cutoff, separating the Gaussian and the excluded-volume regimes, and can be expressed by the reduced temperature as follows:

$$N_\tau = (\text{const})|\tau|^{-2} \tag{20}$$

Several authors[28,29] have calculated the temperature dependence of the chain dimensions. It was found that the static expansion factor, α, is a function of one variable N_τ/N.

The expansion factor can be expressed by the scaled concentration or swelling degree as follows:

$$\alpha = R^3/R_\Theta{}^3 = \phi_\Theta/\phi = \tilde{q} = (\tilde{\phi})^{-1} \tag{21}$$

At this stage the following remark should be made. Equation 21 implies the assumption that the chain dimension of the gel in the Θ state is unperturbed. Since the same holds for the dry network, this means that at least two different mechanisms are supposed to occur during swelling. When the concentration decreases from $\phi = 1$ to $\phi = \phi_\Theta < 1$, desinterspersion is thought to be effective. Then up until the equilibrium concentration is attained, the swelling is followed by the affine deformation of the network chains. These two processes together may result in the loss of affineness reported by Bastide et al.[25]

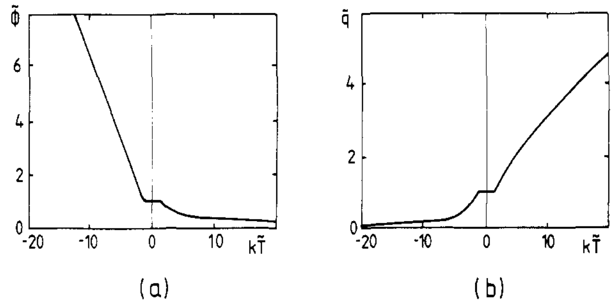


Figure 4. Scaled concentration (a) and the scaled swelling degree (b) as a function of the scaled temperature, according to eq 23. The scaled temperature is multiplied by the constant k.

The variable N_τ/N can also be expressed by the scaled temperature

$$N_\tau/N = (\text{const})(1/N\tau^2) = (\text{const})(\tau N^{1/2})^{-2} = (\text{const})(\tilde{T})^{-2} \tag{22}$$

Now the blob theory can already be applied for gels in the following form:

$$\tilde{\phi} = \left[(k\tilde{T})^{-4}(3 - 2(k\tilde{T})^{-2}) + 6(k\tilde{T})^{-2(1-2\nu)}\left(\frac{1 - (k\tilde{T})^{-2(2\nu+1)}}{2\nu + 1} - \frac{1 - (k\tilde{T})^{-4(\nu+1)}}{2(\nu + 1)} \right) \right]^{-3/2} \tag{23}$$

where k is a constant.

Figure 4 shows how $\tilde{\phi}$ and $\tilde{q}$ depend on $k\tilde{T}$. On the basis of the blob theory, three different behaviors can be distinguished. In the poor-solvent regime ϕ decreases almost linearly with T. This is followed by the Θ regime, where ϕ is independent of T, and in the good-solvent regime, ϕ also decreases further with T.

The asymptotic behavior of the $\tilde{\phi}$–$\tilde{T}$ or $\tilde{q}$–$\tilde{T}$ dependence can be easily calculated from eq 23 if $|k\tilde{T}| \gg 1$ is regarded. One obtains for good- and the poor-solvent limits

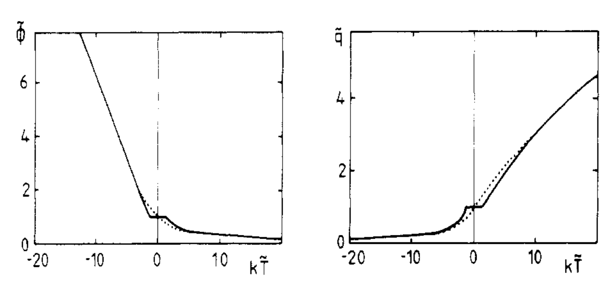
$$\tilde{\phi} = \left[\frac{3^{-3/2}}{(2 + 1)(\nu + 1)}(k\tilde{T})^{-3(2\nu-1)} \right] \tag{24}$$

Comparing eq 18, 19, and 24, one finds that in limit of $|k\tilde{T}| \gg 1$, the blob theory gives back the result of Daoud and Jannink.[27]

Comparison of the Results Obtained by the Mean-Field and Scaling Theories

One of our main conclusions is that, despite the completely different arguments, on which these theories are based, qualitative agreement can be observed in some respects.

Neither the classical James–Guth nor the modern blob theory predicts a first-order transition to appear. Both say that the scaled concentration is an universal function of the scaled temperature. Although the molecular mechanism of swelling behind the picture is different (affine in the case of JG, interspersion + affine in the case of the blob theory), the shape of the $\tilde{\phi}$–$\tilde{T}$ curves does not deviated considerably. The only difference can be seen in the vicinity of the Θ point, as shown in Figure 5. For the sake of direct comparison $k = 1.5c$ was choosen when



(a) (b)

Figure 5. Dependence of $\tilde\phi$ (a) and $\tilde q$ (b) on $\tilde T$. The dotted lines were calculated by eq 23, while the solid ones by eq 10.a and 10.b.

Table I
Characteristics of the PVAc Gels[a]

symbol	C_0, wt %	10^2X_c	symbol	C_0, wt %	10^2X_c
×	3	2	▲	9	0.5
●	6	2	▼	9	0.25
■	6	0.5	○	12	2
△	9	2	□	12	0.5
▽	9	1			

[a] The same symbols are used in the figures.

the plots of eq 10 were made.

As for the limit behavior, both theories result in the same dependence. At low temperatures ($\tau \ll 0$), eq 10.a and eq 24 give

$$\tilde\phi = -(\text{const})\tilde T \quad (25)$$

while in the good-solvent limit they result in

$$\tilde\phi = (\text{const})(\tilde T)^{-3/5} \quad (26)$$

A completely different swelling behavior is expected on the basis of the Flory–Hermans–Wall–Kuhn theory. It is predicted that equlibrium concentration (or swelling degree) of network homologues cannot be described by an universal function, and if the $B\nu^*\bar V/w\phi_\Theta^2$ exceeds its critical value, a first-order transition marked by a sudden change in ϕ or q can occur.

Experimental Section

For the experiments, gel systems of poly(vinyl acetate) (PVAc) swollen to equilibrium in isopropyl alcohol were used. At room temperature the isopropyl alcohol can be considered as a poor solvent for PVAc. Hence by heating or cooling the gels, the poor-solvent and the good-solvent regimes can be scanned. The Θ temperature of PVAc/isopropyl alcohol gels was found to be 54.7 °C in one of our previous works.[10] A more critical analysis of the data has shown that $\Theta = 52 \pm 2$ °C. Thus for the calculations, $\Theta = 325$ K is used.

Materials. A hydrolyzed Poval 420 (Japan) poly(vinyl alcohol) (PVA) sample was fractionated in a mixture of *n*-propyl alcohol–water in order to get a narrow molecular mass distribution. Some characteristics of the fractionated sample are $\bar M_\eta = 100\,000$, $\bar M_w = 110\,000$ (determined by ultracentrifugation), and $|\eta| = 0.68$ dL g^{-1}.

PVA solutions of different concentrations (c = 3.0, 6.0, 9.0, and 12.0 wt %) were cross-linked with glutaraldehyde (Merck, GFR) at pH 1.5 and $T = 298 \pm 0.1$ K with water as solvent.

Networks with different cross-linking densities were prepared.[10,30,31] The cross-linking density, X_c, which is the mole fraction of the cross-linking agent (now the glutaraldehyde) in the dry network, was varied from 2×10^{-3} to 2×10^{-2}. (For the calculation of X_c the moles of monomer units of PVA were taken into account.)

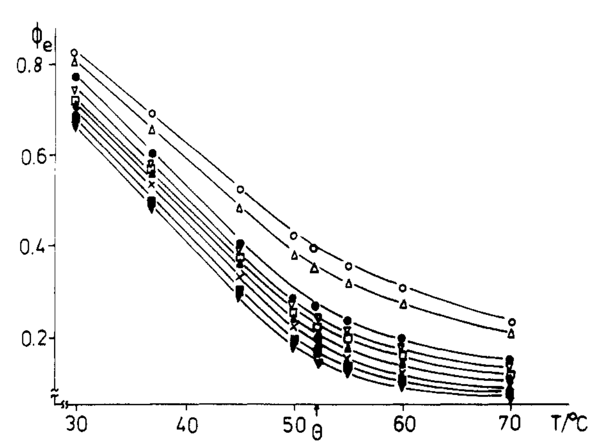


Figure 6. Concentration versus temperature diagram for the PVAc/isopropyl alcohol gels. Solid lines are a guide for eyes. For identification of the symbols, see Table I.

Cylindrical network specimens 1 cm in diameter and 1 cm in height were prepared in cylindrical containers of a suitable frame. The mixture of polymer, cross-linking agent, and catalyst (2 N HCl solution) was stirred by means of a magnetic stirrer and then it was poured into the containers. Some characteristics of the PVA gels are summarized in Table I.

After the cross-linking reaction the gels were removed from the frame and the traces of foreign matter (e.g., HCl) were washed by distilled water several times. Then the media of the gels were replaced by a mixture of acetic anhydride (40 vol%)–acetic acid (10 vol%)–pyridine (50 vol%). The acetylation reaction was continued at 363 K for 8 h. The acetylation mixture was renewed hourly. In the last 3 h the acetic acid was omitted from the fresh mixture, in order to shift the equilibrium in the direction of acetate formation. After several solvent exchanges, each taking 48 h or more, no traces of pyridine, acetic acid, acetic anhydride, or water appeared in the wash. The complete wash cycle involved not less than 10 solvent exchanges and took over 1 month. After solvent exchanges, the gels were carefully dried. The extent of acetylation was checked and an agreement within 1–2% was found between the calculated and experimentally determined values. The dry networks were swollen to equilibrium with isopropyl alcohol (Reanal, Hungary). The gels were stored not less than 1 month at each temperature before testing.

Methods

In order to determine the swelling equilibrium concentration, the gels were weighed, then evaporated to dryness, and weighed again. Densities of the dry networks and that of the isopropyl alcohol were also determined as a function of temperature. The volume fraction of the polymer in the equilibrated gels was calculated from the measured mass and density value, supposing the additivity of the specific volumes. The error of concentration measurements did not exceed 0.2%. The equilibrium concentrations of nine network homologues were determined at nine different temperatures, 25, 30, 37, 45, 50, 52, 55, 60, and 70 °C.

Results and Discussion

In Figure 6, we plot the equilibrium concentration versus temperature for the studied systems. It can be seen that none of the gels show the macroscopic collapse phenomenon within the studied temperature range. For all the gels a continuous monotonically decreasing curve was obtained. One should think that collapse could occur at lower temperatures. However, experimental results, not involved in this article, show that it could not. The reason why we do not pay any attention to the temperatures below 25 °C is that upon cooling, all gels exhibit optical, and many of them also structural, changes that can be observed visually. The originally transparent gels become turbid as the temperature is decreased. Beside turbidity, profound structural changes can also be observed. When crossing the cloud point, there are no drastic changes in the concentration. Below the cloud-point temperature, relaxation

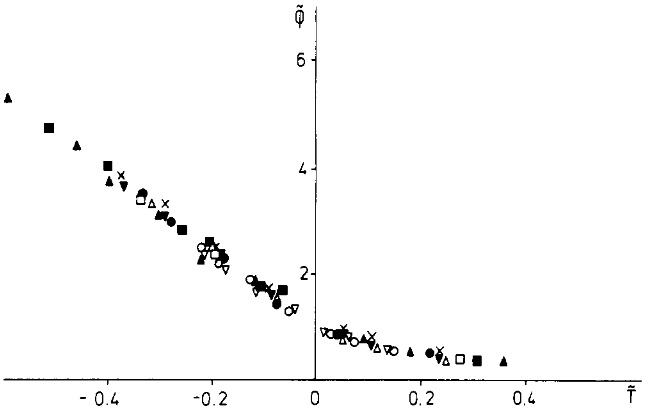


Figure 7. Scaled concentration versus the scaled temperature for the PVAc/isopropyl alcohol gels.

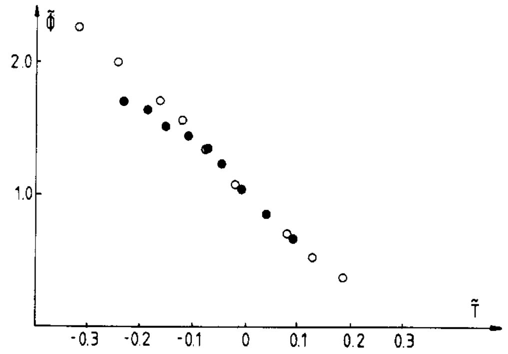


Figure 8. Scaled concentration versus the scaled temperature for poly(styrene)/cyclohexane networks. These data are taken from a paper of Erman and Baysal.[12]

Table II
Concentration of Gels at $T = \Theta$ and the Calculated $B\nu^*\bar{V}/w\phi_\Theta^2$ Data[a]

$C_0/10^2X_c$	ϕ_Θ	$B\nu^*\bar{V}/w\phi_\Theta^2$
3/2	0.172	76.3
6/2	0.253	23.1
6/0.5	0.149	16.3
9/2	0.330	14.8
9/1	0.237	11.9
9/0.5	0.201	10.7
9/0.25	0.146	8.6
12/2	0.365	10.2
12/0.5	0.219	7.3

[a] For the calculation, $B = 1$ and w = 0.078 were used. The $\nu^*\bar{V}$ values were obtained from unidirectional compression measurements.[32,33]

phenomena enormously slow down, and to attain equilibrium would take years.

In order to compare the experimental results with the prediction of different theories, the scaled concentration is plotted against the scaled temperature in Figure 7. For the calculation of the scaled quantities, the concentration of gels at Θ condition was needed. these are summarized in Table II.

In Figure 7 one sees that within experimental accuracy, all points (72 points) are on the same curve.

Figure 8 shows the same representation of data obtained by Erman et al.[12] who investigated polystyrene networks swollen to equilibrium in cyclohexane. The temperature dependence of the equilibrium concentration of the two network homologues seems to be gathered also in the same curve except the last three filled circles on the left-hand side of Figure 8. These points correspond to low temperatures where the relaxation of network chains can be so long that the time (24 h) allowed for attaining the equilibrium might be too short. These results support the validity of eq 10.a and 23, since $\tilde{\phi}$ seems to depend only on one variable, $\tilde{T}$. This means that both the James–Guth and the scaling (blob) theories are adequate to predict the equilibrium concentration–temperature dependence of PVAc/isopropyl alcohol gels.

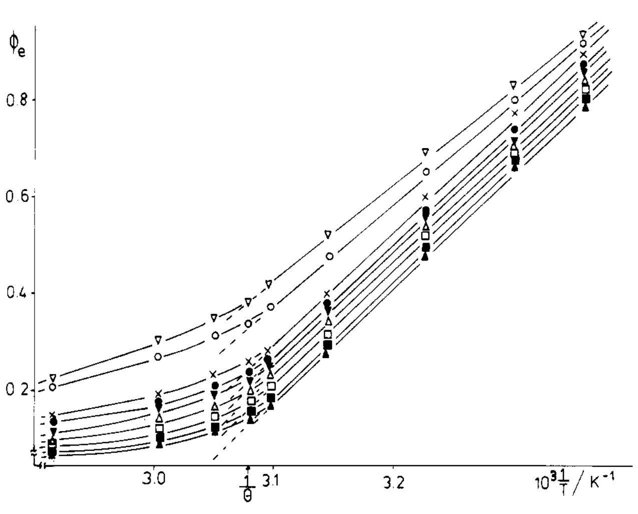


Figure 9. Equilibrium concentration versus the reciprocal temperature for PVAc/isopropyl alcohol gels.

It must be mentioned that our experimental results are diametrically opposed to the predictions of eq 13.a; that is, the theory based on the approach of Flory, Hermans, Wall, and Kuhn seems to be less consistent with the results observed for PVAc/isopropyl alcohol gel systems. The differences in $b/w\phi_\Theta^2$ values are so high (see Table II) that according to eq 13.a the $\tilde{\phi}$–$\tilde{T}$ curves belonging to a given network should have been separated to a much greater extent than that due to experimental error. These findings can be regarded as an independent confirmation of our previous results in which $B = 0$ was proven.[19,20]

It is worth mentioning that considerably below the Θ point, $\tilde{T} > -0.15$, the dependence of $\tilde{\phi}$ on $\tilde{T}$ seems to be linear, as predicted for the limit behavior by both the JG and the blob theories (see eq 25). This means that at temperatures between Θ and the spinodal decomposition, the temperature dependence of the equilibrium concentration can be given as follows:

$$\phi = c_\tau \Theta/T + a_\tau \phi_\Theta - c_\tau \qquad (27)$$

where c_τ and a_τ are constants.

On the basis of eq 27, one expects a linear relationship between the equilibrium concentration and the reciprocal temperature. This representation is shown in Figure 9. It can be seen that below the Θ point the linearity holds, and the straight lines have—within experimental accuracy—the same slopes and different intercepts as predicted by eq 27.

In order to compare the observed experimental result with those predicted by theory, one would need the value of the constants c and k in eq 10.a and 23, respectively, which can only be determined by direct comparison.

For the PVA/isopropyl alcohol gels the best fit was obtained at $c = 0.1$ and $k = 15$. Figure 10 shows how the theories can give the temperature dependence of the equilibrium concentration of swollen network systems. It can be seen that the agreement is quite satisfactory.

Summary

We have studied the temperature dependence of equilibrium concentrations of loosely cross-linked swollen networks. Three basically different approaches, the James–Guth, the Flory–Hermans–Wall–Kuhn, and the

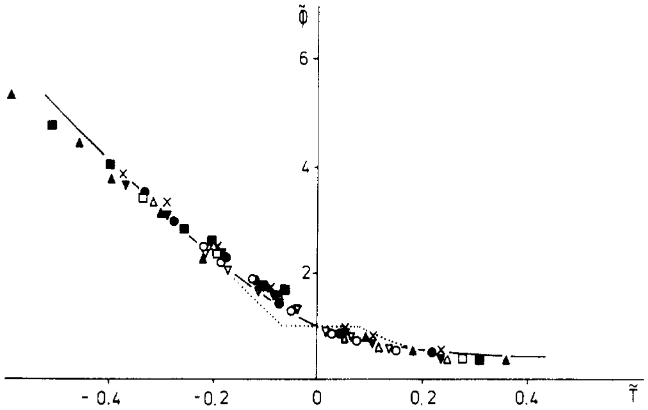


Figure 10. Comparison of theoretical results with the experiments. The solid line was calculated by eq 10.a, while the dotted one by eq 23. The values of the constants are given in the text.

thermal blob theories were considered. We have shown that the James–Guth theory exhibits scaling behavior. As a result of this, one can construct a universal function for the dependence of the scaled quantities. It has been shown that in the limiting cases the scaling functions belonging to either the James–Guth or the thermal blob theories coincide.

The Flory–Hermans–Wall–Kuhn theory gives basically different swelling behavior: below the Θ temperature a first-order phase transition is predicted and no scaling behavior has been observed.

Experimental results obtained for chemically cross-linked PVAc networks swollen to equilibrium in isopropyl alcohol are in agreement with the prediction of both James–Guth and thermal blob theories.

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Registry No. (VA)(glutaraldehyde) (copolymer), 32630-65-2.

References and Notes

(1) Dušek, K.; Patterson, D. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1209.
(2) Dušek, K.; Prins, W. *Adv. Polym. Sci.* **1969** *6*, 1.
(3) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(4) Khoklov, A. R. *Polymer* **1980**, *21*, 376.
(5) Ilavsky, M. *Polymer* **1981**, *22*, 1678.
(6) Janas, V. F.; Rodriguez, F.; Cohen, F. *Macromolecules* **1980**, *13*, 977.
(7) Aharoni, S. M.; Wertz, D. H. *J. Macromol. Sci., Phys.* **1983**, *B22*, 129.
(8) Zrinyi, M.; Molnár, T.; Horváth, E. *Polymer* **1981**, *22*, 429.
(9) Zrinyi, M.; Wolfram, E. *J. Colloid Interface Sci.* **1982**, *90*, 1.
(10) Zrinyi, M.; Horkay, F. *Macromolecules* **1984**, *17*, 2805.
(11) Zrinyi, M.; Wolfram, E. *Prog. Colloid Polym. Sci.* **1985**, *71*, 20.
(12) Erman, B.; Baysal, B. M. *Macromolecules* **1985**, *18*, 1696.
(13) Candau, S.; Munch, J. P.; Hild, G. *J. Phys. (Les Ulis, Fr.)* **1980**, *41*, 1031.
(14) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(15) Van der Kraats, E. J.; Winkeler, M. A. M.; Potters, J. M.; Prins, W. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 449.
(16) Froelich, D.; Crawford, D.; Rozek, T.; Prins, W. *Macromolecules* **1972**, *5*, 100.
(17) Pennings, A. J.; Prins, W. *Polym. Sci.* **1961**, *49*, 507.
(18) Rijke, A. M. *J. Polym. Sci.* **1966**, *4*, 131.
(19) Horkay, F.; Nagy, M. *Acta Chim. Hung.* **1984**, *115*, 305.
(20) Horkay, F.; Nagy, M.; Zrinyi, M. *Acta Chim. Acad. Sci. Hung.* **1981**, *108*, 287.
(21) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(22) Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1979**, *40*, 1049.
(23) Candau, S.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 27.
(24) Beltzung, M.; Herz, J.; Picot, C. *Macromolecules* **1983**, *15*, 1594.
(25) Bastide, J.; Picot, S.; Candau, S. *J. Macromol. Sci., Phys.* **1981**, *B19*, 13.
(26) Bastide, J.; Herz, J.; Boué, F. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, 1967.
(27) Daoud, M.; Jannink, G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 973.
(28) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.
(29) Weill, G.; des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1979**, *40*, 99.
(30) Horkay, F.; Zrinyi, M. *Macromolecules* **1982**, *15*, 1306.
(31) Horkay, F.; Zrinyi, M. *J. Macromol. Sci., Phys.* **1986**, *B25*, 307.
(32) Horkay, F.; Nagy, M. *Polym. Bull (Berlin)* **1980**, *3*, 457.
(33) Horkay, F.; Nagy, M. *Acta Chim. Acad. Sci. Hung.* **1981**, *107*, 321.

Gelation Process by Size-Exclusion Chromatography Coupled with Light Scattering

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ABSTRACT: We study the sol–gel transition obtained by cross-linking of polymer solutions. We measure the size distribution function of diluted pregel samples by size-exclusion chromatography coupled with light scattering. With this technique a very good approximation of molecular weight distribution function is obtained although the separation criterion in the columns is the hydrodynamic volume of the molecules. Experimental results are found to be consistent with a scaling description of the sol–gel transition.

I. Introduction

Although polymeric gels are widely used materials, an extended comprehension of their properties is far from being reached. In particular, the relationship between the structure and the properties of gels is not yet clearly understood, even in neutral gels.[1-5] Probably this complicated relationship originates in the method of synthesis of the gels, in the very beginning of gel formation. Therefore, among the large amount of experimental and theoretical work on gels, particular attention has been paid to gel