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Studies on Mechanical and Swelling Behavior of Polymer Networks on the Basis of the Scaling Concept. 5. Crossover Effects above and below the Θ Temperature

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ABSTRACT: The temperature dependence of elastic moduli and the equilibrium concentration of swollen poly(vinyl acetate) gels were studied. For gels swollen to equilibrium in a good diluent (toluene), the power law exponent of the elastic moduli, m, was found to be independent of the temperature and to be close to the value predicted by scaling theory. Poly(vinyl acetate) gels equilibrated with isopropyl alcohol in the vicinity of Θ temperature were studied. In the crossover regimes (below and above the Θ temperature), the apparent power law exponent of the elastic moduli varied between the values of 2.31 and 13.3. At the Θ temperature $m = 3.04$ was obtained. Supposing that the third power of the expansion factor of network chains can be expressed as the ratio of the equilibrium concentration of the gel at Θ temperature ($\varphi_{e,\Theta}$) to the actual concentration (φ_e) either below or above Θ, it was verified that $\varphi_{e,\Theta}/\varphi_e$ is the only function of $\tau N^{1/2}$ (where τ and N are the reduced temperature and the degree of polymerization, respectively). Analysis of the experimental data on the basis of thermal blob theory indicated a satisfactory agreement at $N/N_\tau > 10$; however, at smaller N/N_τ values considerable deviation occurred (N_τ is the temperature-dependent cutoff distance which separates the scales of Gaussian and non-Gaussian behavior within the same chain).

Introduction

The concepts of scaling and universality have been proved to be highly appropriate tools in understanding the physical properties of polymer systems.[1] These concepts are taken from the theory of phase transitions. The basic work of de Gennes, des Cloizeaux, Daoud, and Jannink has established the connection between the phase transition problem and the description of polymer solutions. Recently, many efforts have been devoted to deduce the elastic and swelling properties of swollen network systems from scaling considerations.[2] This approach is mainly used to predict which aspects of the observed phenomena are universal, that is, independent of single variables like temperature or chemical details of the chains and the surrounding media.

One of the universal properties of swollen gels made of flexible chains is the dependence of the elastic modulus, G, on the equilibrium concentration, φ_e:

$$G = A(\varphi_e)^m \tag{1}$$

In eq 1 the prefactor, A, contains the nonuniversal properties of the studied system, while the power law exponent, m, is independent on such "irrelevant" details. A scaling law (eq 2) gives the correspondence between m and the excluded volume exponent, ν, of the free polymer chains:[1]

$$m = \frac{3\nu}{3\nu - 1} \tag{2}$$

In eq 2, ν is a characteristic critical exponent which expresses the radius of gyration, R, in the well-known form

$$R = aN^\nu \tag{3}$$

where a is the effective segment length and N is the degree of polymerization. Many analytical and numerical calculations[3,4] as well as experimental results support this power law.

The values of ν and naturally those of m are primarily determined by the effective monomer–monomer interaction. Three distinct behaviors can be discussed as limiting cases for sufficiently high N values:

(a) In good solvents, the interaction between monomers is repulsive and tends to swell the coil. For years it has been thought that the value of ν in this case equals $^3/_5$ (Flory value[4]), but renoromalization group techniques[5] have given $\nu = 0.588$. Careful light scattering experiments[6,7] as well as computer simulation of selfavoiding walk[3,8] support this value. For gels the power law exponent, m, of the elastic modulus is equal to $^9/_4$ (or else 2.31 if $\nu = 0.588$ is taken).

(b) In a Θ solvent the attractive and repulsive forces compensate each other, and chains are quasi-ideal[4]—thus $\nu = {}^1/_2$ and $m = 3$.

(c) In a poor solvent the monomer–monomer interaction is attractive, and the complete collapse of chains are hindered only by steric repulsion between segments.[4,9-11] In this case $\nu = {}^1/_3$ and $m = \infty$.

The universality of exponents means that in a wide range of interaction the value of ν and m is constant, but crossover effects may occur. By suitable changes in temperature or in solvent composition the chains can crossover from an extended swollen coil to a collapsed globule. In this sense one can speak about the temperature or composition dependence of the exponents. The value of the exponents changes in the crossover regime where a gradual transition from one regime to another occurs. It should be mentioned when chains are not sufficiently long we are also in the crossover domain. The width of this regime is not a rigorously defined quantity and has very little universality. The crossover from Θ condition to a good or a poor solvent occurs in a region of temperature which becomes progressively narrower as the molecular mass increases.[12] The transition between behaviors designated by letters a, b, and c is a subject of great current theoretical and experimental interest.

Much less investigated and understood is the elastic and swelling behavior of swollen gel systems in the transition regime. To the best of our knowledge no experimental work has been reported in this respect, despite the fact that many efforts have been focused on the collapse phenomena of gels. The latter has attracted a great deal of both theoretical[13-15] and experimental[15-20] attention.

Elastic moduli of different network systems swollen in good and Θ solvents have already been studied in order

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to determine the value of m. In most of the cases the observed m was found to be close to the predicted 2.31 value in good solvent condition. Some examples are given in ref 2. At the Θ point, the elastic behavior of gels is rather rarely studied. Geissler and Hecht measured the shear and longitudinal elastic moduli of polyacrylamide–methanol–water gels as a function of the equilibrium concentration at Θ temperature. The power law exponent was found to be 3.12 and 3.07, respectively.[21]

In this work we intended to study the equilibrium concentration and shear moduli of chemically cross-linked swollen gels, prepared in different way, both in the excluded volume limit (at good solvent condition) and in the crossover regimes, below and above Θ temperature. Our purposes were (1) to examine the universality of the power law exponent of elastic modulus in good solvent condition (in the excluded volume limit), (2) to verify whether the power law dependence of elastic moduli remain valid in the crossover regime, (3) to determine the apparent exponents in the crossover regimes, (4) to study the equilibrium concentration of gels with respect to the collapse phenomena, and (5) to check whether the concentration of gels scales (or not) as the scaling theory predicts.

Theoretical Background

Polymer gels in swelling equilibrium with a pure diluent can be considered as a set of closely packed coils kept together by cross-links.[1] de Gennes has postulated that the equilibrium polymer concentration, φ_e, of a swollen network can be expressed in terms of overlap concentration, φ^*, of the solution of a polymer having the same molecular mass as the network chains:

$$\varphi_e = k(z)\varphi^* \tag{4}$$

where $k(z)$ is a constant of order of unity depending only on the functionality, z, of the cross-links. The overlap concentration is defined as

$$\varphi^* = \frac{N}{R^3} \propto N^{1-3\nu} \tag{5}$$

where R is the radius of gyration of the equivalent polymer chain in dilute solution. The relation, eq 4, which has been called the "c* theorem" has also been derived from the classical Flory theory[4] by Brochard[22] and from the scaling theory by Bastide et al.[43] According to these treatments, the equilibrium concentration of a gel primarily depends on the interactions that determine the chain dimensions in dilute solutions. The above statements are strongly supported by recent small-angle neutron scattering measurements. Beltzung et al.[23] measured the radius of gyration of elastic chains in swollen poly(dimethylsiloxane) networks as well as in their equivalent solutions. It was found that the radii of gyration of the elastic chains in the swollen networks were within the limits of experimental accuracy, like those of the corresponding free chains in the dilute regime. However, other neutron scattering experiments are in contradiction with the packing condition given by eq 4. According to these results,[39–41] the average radius of gyration of the labeled network chains was found to vary with the swelling degree to a much lesser extent than would have been expected on the basis of affine deformation as a result of swelling. A new mechanism was put forward to explain the experimental results: the elementary coils are widely interspersed, and an important contribution to the swelling mechanism could arise from topological rearrangements.[42] A phenomenological theory has been developed[43] and another expression of the de Gennes c* theorem has been constituted for gels swollen in good solvent.

In poor solvents detailed experiments as well as theories are missing.

Our analysis is based on the assumption that the equilibrium concentration of a gel at different temperatures (above and below the Θ temperature) can be described by the expansion factor, α, of the radius of gyration of network chains in the following way (compare eq 4 and 5):

$$\frac{\varphi_{e,\Theta}}{\varphi_e} = \frac{R^3}{R_\Theta^{\,3}} = \alpha^3 \tag{6}$$

where $\varphi_{e,\Theta}$ and φ_e are the equilibrium concentrations of the gel, and R_Θ is the dimension of the equivalent chain in dilute solution at Θ temperature. For good solvent conditions the expansion factor can be expressed by a mean field theory due to Flory.[9] Similar calculations were developed for negative excluded volume.[11,29,30] In both cases α was found to depend on one variable of $\tau N^{1/2}$ (τ is the reduced temperature).[24]

In the development of scaling relationships in dilute polymer solution, Daoud and Jannink[12] have shown that R is given by

$$R \sim |\tau|^{-1} f(N^{-1}\tau^{-2}) \tag{7}$$

where the $f(N^{-1}\tau^{-2})$ function in the asymptotic limit ($N\tau^2$ large) can be written as a ν power of $N\tau^2$. The exponent, ν, takes the value $^3/_5$, $^1/_2$, and $^1/_3$ for T greater than, equal to, or less than Θ, respectively. However, this is not necessarily the case when $N\tau^2$ is not sufficiently large. To prepare polymer networks having long chains is rather difficult. (Typical values of N in networks are from 50 to 1000.) Due to spinodal decomposition, achieving the asymptotic limit below the Θ temperature is much more difficult than achieving the excluded volume limit. This could be the reason for lack of experimental evidence for collapse of neutral gels made of flexible chains. So if we are interested in the behavior of gels near the Θ temperature we must investigate the crossover regimes.

The blob theory[1] permits the calculation of chain dimensions in the crossover regimes. It is assumed that 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. (The chains have Gaussian statistics inside the blobs and excluded volume statistics outside the blobs.) N_τ is the temperature-dependent cutoff separating the Gaussian and excluded volume regimes and can be written as

$$N_\tau = \beta\tau^{-2} \tag{8}$$

where the β proportionality factor depends on the kind of polymer and solvent, an adjustable parameter which has to be determined from direct comparison between theory and experiment.[24] In eq 8, τ is a reduced temperature defined as

$$\tau = \frac{T - \Theta}{T}$$

Several authors[24–26] have calculated the temperature and molecular mass dependence of the static expansion factor. They all obtained the same result in terms of one variable, $x = N_\tau/N$

$$\alpha^2 = \frac{R^2}{R_\Theta^{\,2}} = x^2(3 - 2x) + 6x^{1-2\nu}\left(\frac{1 - x^{2\nu+1}}{2\nu + 1} - \frac{1 - x^{2(\nu+1)}}{2(\nu + 1)}\right) \tag{9}$$

It can be supposed that eq 9 gives a symmetric description

Table I
Characteristics of the PVA Gels

c_0, wt %	DC			
3	50			
6	50		200	
9	50	100	200	400
12	50		200	

of the chain conformation above ($\nu \simeq 3/5$) and below Θ ($\nu \simeq {}^1/_3$). Below the Θ point, the chain has Gaussian statistics at short distances and globular statistics at long distances. The asymptotic behavior of α both in the good- and poor-solvent limit ($x \gg 1$) can be easily calculated from eq 9

$$\alpha = \left(\frac{3}{(2\nu + 1)(\nu + 1)}\right)^{1/2}\left(\frac{N}{N_\tau}\right)^{\nu-1/2} \tag{10}$$

This result—except the numerical factors—is consistent with that of Daoud and Jannink.[12]

There is no theoretical basis to believe that eq 1 and 3 remain valid in the crossover regimes below and above the Θ point. However, one can define similar relations with apparent indices as an approximation of the real unknown functions. Thus, the forms eq 1 and 3 are considered, but instead of ν and m their apparent values, ν_a and m_a, are used. These are defined as

$$\nu_a = \frac{\partial \ln R}{\partial \ln N} \tag{11}$$

$$m_a = \frac{\partial \ln G}{\partial \ln \varphi_e} \tag{12}$$

The above statements include that the exponents are considered as continuous functions as was supposed by Francois et al.[27] and des Cloizeaux.[28]

Experimental Section

For the experiments, gel systems of poly(vinyl acetate) (PVAc) swollen to equilibrium in toluene and in isopropyl alcohol were used. PVAc gel samples were prepared by total acetylation of poly(vinyl alcohol) (PVA) gels according to a method described in ref 31 and 32.

Purification and characterization of materials as well as network formation procedure were also described previously.[33] A hydrolyzed Poval 420 (Japan) PVA sample was fractionated in a mixture of n-propyl alcohol–water. Some characteristics of the fractionated sample are $\bar{M}_\eta = 100\,000$, $\bar{M}_w = 110\,000$ (determined by ultracentrifuge), and $[\eta]_{303} = 0.68$ dL g^{-1}.

PVA was cross-linked with glutaraldehyde (Merck, GFR) at pH 1.5 and 298 ± 0.1 K in water as solvent. Networks characterized by different degrees of cross-linking (DC) values were formed at four different polymer concentrations (c_0 = 3.0, 6.0, 9.0, and 12.0 wt %) (DC means the moles of monomer units per mole of cross-linking agent).

Cylindrical network specimens 1 cm in diameter and 1 cm in height were prepared in cylindrical containers of a suitable frame. The mixture of the 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. Then the media of the gels was 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 before it was terminated. The acetylation mixture was renewed in each hour. 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. Then the reaction mixture was cooled and washed with acetone. After several solvent exchanges, each taking 48 h or more, there appeared in the wash no traces of pyridine, acetic acid, acetic anhydride, and water. 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.[31] The dry networks were swollen to equilibrium with isopropyl alcohol and toluene, respectively. The swollen gels were stored not less than 1 month at each temperature before testing.

Table II
Temperatures of Mechanical Measurements

system	temp, °C							
PVAc/isopropyl alcohol	25	30	37	45	50	55	60	70
PVAc/toluene	25	30	37	45	50	55	60	70

Unidirectional compression measurements were carried out on swollen network samples at eight different temperatures given in Table II.

Stress–compression measurements were performed with an apparatus sensitive to ±0.1 mN and ±6 μm, respectively.[33] The gel cylinders were subjected to deformation between two flat glass plates in a thermostable sample holder. Stress–compression curves were determined for networks at equilibrium in each diluent at each temperature.

The stress–compression measurements were analyzed according to the Mooney–Rivlin equation

$$\sigma = 2C_1(\Lambda - \Lambda^{-2}) + 2C_2(\Lambda - \Lambda^{-2})\Lambda^{-1}$$

where σ is the nominal stress, Λ is the experimental deformation ratio, and C_1 and C_2 are constants. For all the PVAc gels, independent of the swelling agent and temperature, C_2 was found to be equal to zero, and thus $2C_1$ was considered as the elastic (shear) modulus of gels ($G = 2C_1$).

It should be noted that the absence of volume changes and barrel distortion during unidirectional compression as well as the reversibility of stress–strain behavior were also checked. The reproducibility of mechanical measurements was found within 5%.

In addition, densities of dry networks and diluents and network volume fractions at swelling equilibrium were determined at each temperature from subsidiary experiments. The specific volumes of the solvent and polymer were assumed to be additive in the whole temperature interval studied. In order to determine the swelling equilibrium concentration of the gels, the samples were weighed, evaporated to dryness, and weighed again. The accuracy of concentration measurements did not exceed 0.2%.

Results and Discussion

In order to study and to compare the elastic and swelling behavior of gels at different conditions, a good and a poor diluent were chosen as swelling agents. For PVAc networks, toluene can be considered as a good solvent, while isopropyl alcohol is a poor one. (The Θ temperature of PVAc/isopropyl alcohol systems was found to be 54.7 °C.[17,20]) Thus the behavior of gels at the excluded volume limit can be studied on PVAc/toluene gels while at Θ condition and in the crossover regimes (below and above Θ) on PVAc/isopropyl alcohol gels.

Concentration Dependence of Elastic Moduli at Different Temperatures at Good Solvent Condition

First we discuss the elastic properties of PVAc/toluene systems. In two of our previous papers[34,35] we reported the power law behavior of these gels. For 53 different networks the exponent was found to be 2.38 at 25 °C. Now for the experiments we used "only" nine of these gels, but the elastic moduli and the equilibrium concentration were determined at eight different temperatures varying from 25 to 70 °C (see Table II). At each temperature the dependence given by eq 1 has been proved to be valid. The exponent, m, the prefactor, A, and the correlation coef-

Table III
Power Law Exponents, Prefactors, and Correlation Coefficients for the Elastic Moduli of PVAc/Toluene Gel Systems at Different Temperatures[a]

T, °C	m	log A	r
25	2.23	3.31_2	0.994
30	2.29	3.35_9	0.995
37	2.28	3.36_3	0.994
45	2.29	3.37_6	0.995
50	2.28	3.37_2	0.995
55	2.27	3.36_7	0.994
60	2.25	3.35_7	0.994
70	2.25	3.36_1	0.994

[a] For the calculations, G was expressed in kPa units.

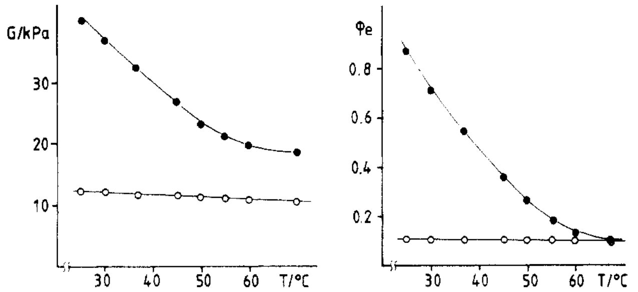

Figure 1. Temperature dependence of elastic modulus and equilibrium concentration of 9/200 PVAc/toluene (○) and 9/200 PVAc/isopropyl alcohol (●) gel sample.

ficient obtained by least-squares fitting are given in Table III. One can see that the value of m is independent of the temperature within the experimental accuracy and does not differ considerably from the theoretical value of 2.31 corresponding to the excluded volume limit. The difference between the value of 2.38 reported previously[34-36] and the exponent found recently may be attributed to the fact that in the earlier analysis gel systems prepared by cross-linking of primary chains differing in molecular mass and molecular mass distribution were also included. The effect of molecular heterogeneity of the primary chains affects both the elastic and the swelling equilibrium concentration of the gels and may have resulted in a slight alteration in the value of the exponent.[2]

It should be noted that neither the equilibrium concentration nor the elastic moduli of gels were very sensitive to the temperature (see Figure 1).

Concentration Dependence of Elastic Moduli above and below the Θ Temperature

Quite a different behavior was found for PVAc/isopropyl alcohol gels. Both the modulus and equilibrium concentration strongly varied with temperature. Figure 1 shows the temperature dependence of elastic moduli (a) and equilibrium concentration (b) of some selected gel samples.

At each temprature for the PVAc/isopropyl alcohol gels, the power law described by eq 1 was found to be valid. In Figure 2 the log–log plot of elastic modulus as a function of equilibrium polymer concentration at different temperatures can be seen. It is obvious that the power law behavior remains valid within the experimental accuracy; however, the apparent exponent defined by eq 2 depends on the temperature. The values of m and A, as well as the correlation coefficients for PVAc/isopropyl alcohol gels, are listed in Table IV.

One can see that the value of m increases and that of A decreases with decreasing temperature. The nonmonotonic character of A dependence on temperature is probably due to experimental inaccuracy. It can also been established that at Θ temperature m is equal to 3.04, in good agreement with the prediction of both classical and scaling theories. At 70 °C $m_a = 2.31$, which corresponds to the value given by scaling theory (eq 2). At lower temperatures, m_a considerably exceeds the excluded volume limit and the Θ value.

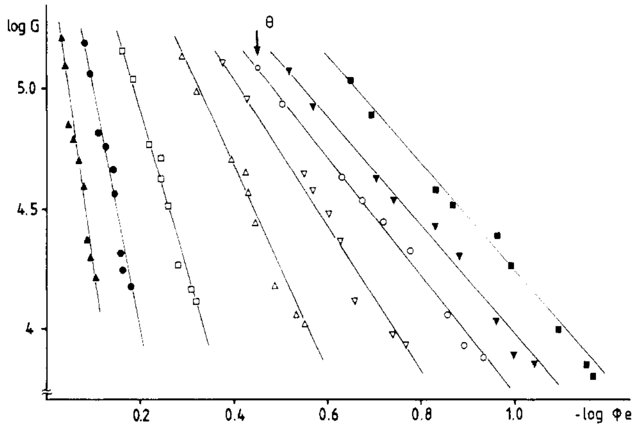

Figure 2. Log–log plot of the elastic modulus as a function of the equilibrium concentration at different temperatures (25 °C (▲), 30 °C (●), 37 °C (□), 45 °C (△), 50 °C (▽), 55 °C (○), 60 °C (▼), 70 °C (■)). Solid lines are guide for eyes.

Table IV
Power Law Exponents, Prefactors, and the Correlation Coefficients of the Elastic Moduli of PVAc/Isopropyl Alcohol Gels at Different Temperatures

T, °C	m_a	log A	r
25	13.3	2.58	0.986
30	10.5	3.05	0.974
37	6.92	3.31	0.988
45	4.39	3.42	0.989
50	3.17	3.34	0.989
Θ	3.04	3.65	0.974
60	2.33	3.28	0.996
70	2.31	3.53	0.997

Collapse Phenomena and the Temperature Dependence of Equilibrium Concentrations

It is worth mentioning that upon cooling all PVAc/isopropyl alcohol gels exhibit optical changes, and some of them structural changes, that can be visible to the naked eye. The originally transparent PVAc gels swollen in isopropyl alcohol become turbid as the temperature decreases below a certain value. This cloud point temperature was found to depend only on concentration of gel. For the gels used for the present experiments turbidity occurred at about 25 °C. (Some gels were turbid even at 25 °C and no one above it.) A more detailed description of the appearance of turbidity and structural changes can be found in two earlier papers.[17,20]

In order to find the variation of the apparent excluded volume exponent of the network chains as a function of temperature, we calculated ν_a from m_a by using eq 2. The result can be seen in Figure 3. It can be concluded that the calculated apparent excluded volume exponents for PVAc/isopropyl alcohol systems tend toward the universal value of 2.31 and $^1/_3$, respectively. We do not exclude the possibility of the existence of the Θ domain where the exponent is independent of temperature; however, the verification of it would require more accurate measurements in a much narrower temperature interval. It is rather surprising that ν_a tends to $^1/_3$ (the smallest value of it is 0.36), since none of the gels has shown the macroscopic collapse phenomenon. For all the network systems a continuous concentration–temperature curve was found, as can be seen in Figure 4.

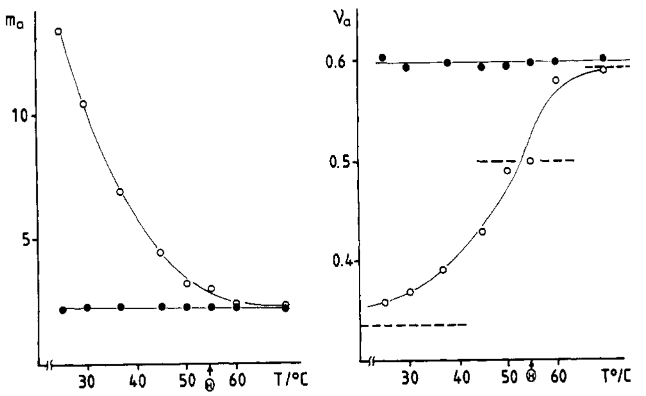

Figure 3. Temperature dependence of the apparent exponents for PVAc/toluene (●) and for PVAc/isopropyl alcohol (○) gels. Solid lines are guide for eyes; dotted line represents the theoretical value belonging to the three limiting cases.

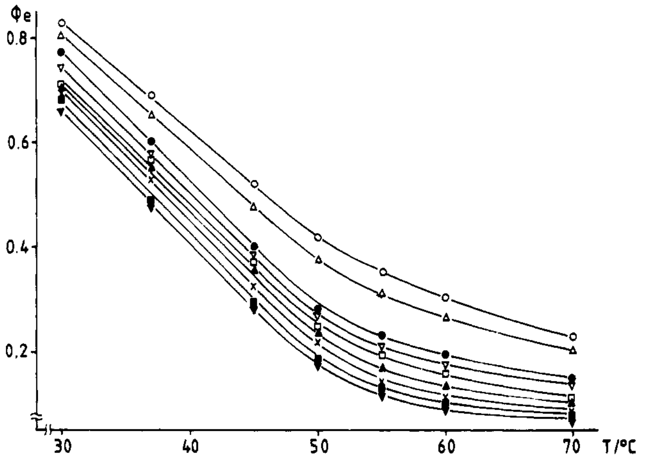

Figure 4. Temperature vs. concentration diagram for PVAc/isopropyl alcohol gels. Solid lines are guide for eyes (12/50 (○), 12/200 (□), 9/50 (△), 9/100 (▽), 9/200 (▲), 9/400 (▼), 6/50 (●), 6/200 (■), 3/50 (×)).

Another interesting finding deserves more attention. In Figure 4 one can see that equilibrium concentration–temperature curves seem not to gather at low temperature. If one considers a network made of collapsed chains ($R \propto N^{1/3}$) and estimates its concentration by eq 4 and 5 then one finds that the equilibrium concentration does not depend on N. So the equilibrium concentration of gels made of globulas is determined only by the interactions between the monomer and solvent molecules; the cross-linking density does not play any role. This is not the case. Neutron scattering measurements could provide direct evidence for collapsed chains in the network.

Comparison of the Experiments with the Thermal Blob Theory

From now on we focus on the equilibrium concentration of gels and try to compare the experimental results and the blob theory. To do this we need the knowledge of N, N_τ, and τ. Unfortunately only the last quantity is known. To find the degree of polymerization of network chains is easy in the case of end-linked networks but is difficult in all other cases. One possibility is to suppose that the number of network chains is proportional to the number of cross-linking molecules; however, the formation of physical entanglements cannot be excluded. Generally there is no linear relationship between G (or the number of elastically active network chains) and the amount of cross-linking agent added to the system.[37] This means that on the basis of the stoichiometry of the cross-linking reaction one cannot estimate the value of N with satisfactory accuracy.

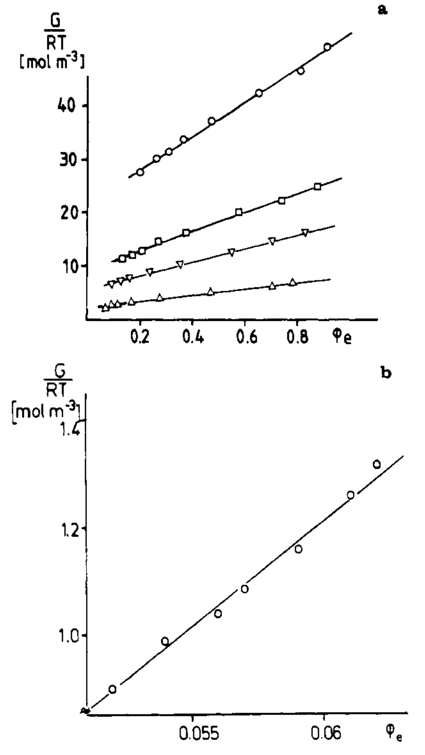

Figure 5. The dependence of G/RT on $\varphi_e(T)$ for gels. (a) PVAc/isopropyl alcohol. Solid lines were calculated by least-squares fitting through the experimental points (9/50 (○), 9/100 (□), 9/200 (▽), 9/400 (△)). (b) PVAc/toluene (6/200 (○)).

Table V
Values of δ/N, ψ, and Correlation Coefficients for PVAc/Isopropyl Alcohol Gels

sample	δ/N, mol/m^3	ψ, mol/m^3	r
3/50	7.72	3.08	0.998
6/50	19.49	11.23	0.999
6/200	7.37	2.09	0.999
9/50	31.68	22.00	0.999
9/100	18.21	9.45	0.999
9/200	12.97	5.54	0.998
9/400	6.07	2.06	0.995
12/50	38.30	31.34	0.997
12/200	15.90	7.29	0.996

The c* theorem enables us to determine a quantity which is linearly proportional to N. According to the theories,[1,2,4] the elastic moduli of swollen gels can be expressed by the concentration of network chains:

$$\frac{G}{RT} = \delta\frac{\varphi_e}{N} \qquad (13)$$

where the δ proportionality factor is not known. If eq 13 is valid, the slope of $G/RT - \varphi_e(T)$ curves gives δ/N. In Figure 5 the dependence of G/RT on the equilibrium concentration can be seen for both PVAc/toluene and PVAc/isopropyl alcohol gels. Straight lines are found for both kinds of systems with positive intercepts at infinite dilution ($\varphi_e = 0$). This means that eq 13 is not strictly valid; the intercepts (ψ) must be taken into account ($G/RT = \delta(\varphi_e/N) + \psi$). Since eq 1 is strongly supported by experimental evidences, the validity of it requires that the intercept should depend on N as follows: $\psi \propto N^{-3\nu}$. (Only this dependence together with eq 4 and 5 yields eq 1.) A more detailed analysis can be found in our other paper.[44]

In Table V the values of δ/N and ψ, as well as the correlation coefficients obtained by least-squares fitting,

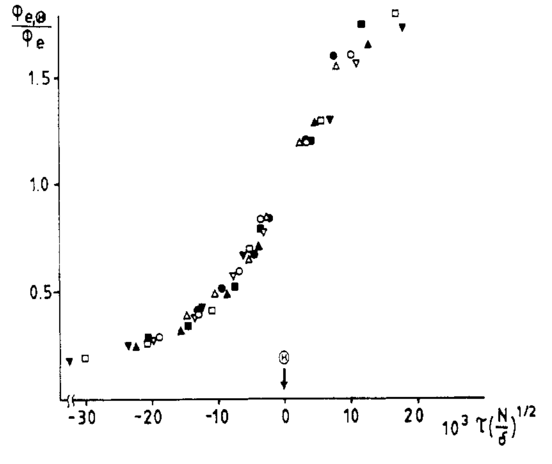

Figure 6. Dependence of $\varphi_{e,\Theta}/\varphi_e$ on $\tau(N/\delta)^{1/2}$ for PVAc/isopropyl alcohol gels (6/50 (○), 6/200 (□), 9/50 (△), 9/100 (▽), 9/200 (▲), 9/400 (▼), 12/50 (●), 12/200 (■)).

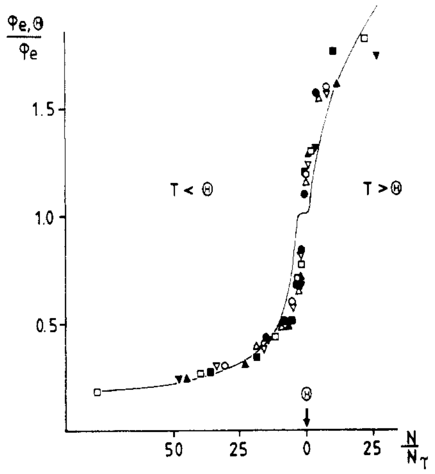

Figure 7. Linear plot of $\varphi_{e,\Theta}/\varphi_e$ vs. N/N_τ for different PVAc/isopropyl alcohol gels. Solid line was calculated according to the blob theory. Symbols are the same as used in Figure 6.

are given for PVAc/isopropyl alcohol gels. To check whether the concentration dependence of gels can be described by the blob theory or not, one must know the quantity N/N_τ for gels. The exact value of this ratio is not known since neither N nor N_τ can be calculated from the available data. Instead of N/N_τ, we know $(N/\delta)\tau^2$ which is proportional to it. In order to make sure that the ratio $\varphi_{e,\Theta}/\varphi_e$ scales with $N\tau^2$ (or $N^{1/2}\tau$), as classical and scaling theories predict, in Figure 6 we plotted $\varphi_{e,\Theta}/\varphi_e$ against $(N/\delta)^{1/2}\tau$. It can be seen that within the experimental error all points are on the same curve. This result qualitatively supports the theoretical prediction, since $\varphi_{e,\Theta}/\varphi_e$ seems to depend only on one variable, $\tau N^{1/2}$.

In order to compare the experiments with theory, one must express N/N_τ in terms of δ/N and τ. According to eq 8, we can write

$$\frac{N}{N_\tau} = \delta\beta^{-1}\left(\frac{N}{\delta}\right)\tau^2 \qquad (14)$$

The $\delta\beta^{-1}$ product is now the only adjustable parameter needed for direct comparison between theory and experiments. The best fit was obtained at $\delta\beta^{-1} = 8.8 \times 10^4$ for PVAc/isopropyl alcohol gels.

In Figure 7 the theoretical and experimental curves are shown. The solid line was calculated by the aid of eq 9. Above Θ, $\nu = 0.588$, and below Θ, $\nu = {}^1/_3$ was used. The agreement between experimental and theoretical predictions is quite satisfactory for higher N/N_τ values, while at low values of N/N_τ slight differences occur. It can also be seen that the width of the Θ domain is not much bigger than the experimental accuracy itself.

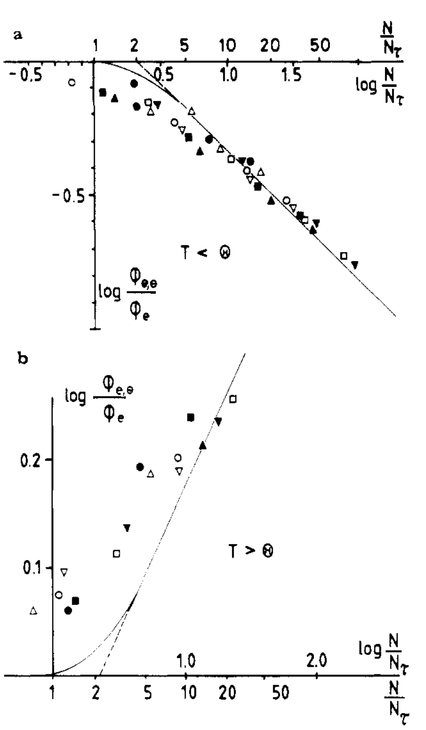

Figure 8. log $\varphi_{e,\Theta}/\varphi_e$ vs. N/N_τ for $T < \Theta$ (a) and for $T > \Theta$ (b). Symbols are the same as used in Figure 6.

In order to establish what states of gels which exhibit the asymptotic limit behavior, a log–log plot of $\varphi_{e,\Theta}/\varphi_e$ vs. N/N_τ is shown in Figure 8. Figure 8a contains the experimental points below Θ while Figure 8b contains the experimental points above Θ. The continuous curve was calculated on the basis of blob theory; the dotted line gives the asymptotic behavior referring to high N/N_τ values (eq 10). It can be concluded that for $N/N_\tau > 6$ we are in the asymptotic limit. The points belonging to the highest N/N_τ values indicate that the good- and poor-solvent limits have been reached. In case of $N/N_\tau > 10$, the agreement between the experiments and theory is quite satisfactory, while for smaller values of N/N_τ the difference is significant.

Since $\varphi_{e,\Theta}/\varphi_e$ for gels in the poor- or good-solvent limit can be expressed as a single power of N/N_τ (see eq 10)

$$\frac{\varphi_{e,\Theta}}{\varphi_e} = \left(\frac{3}{(2\nu + 1)(\nu + 1)}\right)^{3/2}\left(\frac{N}{N_\tau}\right)^{3(\nu-1/2)} \qquad (15)$$

one can compare φ_e and $\varphi_{e,\Theta}$ both in the poor- and good-solvent limit. At fixed temperature (N_τ is constant), N can be given in terms of φ_e (see eq 4 and 5) and one gets

$$\varphi_{e,\Theta} \propto \varphi_e^{[2(3\nu-1)]^{-1}} \qquad (16)$$

Equation 16 for good solvents yields the same result that was derived by Canadau et al.[38] on the basis of Flory's theory. In the excluded volume limit $\varphi_{e,\Theta} \propto \varphi_e^{5/8}$, while in the poor-solvent limit $\varphi_{e,\Theta} \propto \varphi_e^{b}$, where the exponent b goes to infinity as ν goes to ${}^1/_3$. For the PVAc/isopropyl alcohol gels at 30 °C, $\nu_a = 0.37$ was found, which corresponds to $b = 4.54$. In Figure 9 log–log plots of $\varphi_{e,\Theta}$ vs. φ_e obtained at 70 and 30 °C respectively are shown. For gels at 70 °C, $\varphi_{e,\Theta} = 0.784\varphi_e^{0.87}$, and at 30 °C, $\varphi_{e,\Theta} = 1.13\varphi_e^{4.96}$ were found with the respective correlation coefficients of 0.997 and 0.985. In good-solvent condition, instead of the theoretical

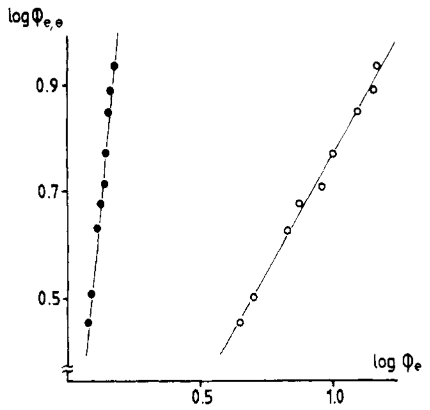

Figure 9. Dependence of log $\varphi_{e,\Theta}$ on log φ_e for PVAc/isopropyl alcohol gels at two temperatures (30 °C (●), 70 °C (○)).

0.62, the value of 0.87 was obtained.

Conclusions

In this work we have demonstrated the applicability of scaling theory for the elastic moduli and equilibrium polymer concentration of cross-linked poly(vinyl acetate) gels swollen to equilibrium either in a good (toluene) or a Θ diluent (isopropyl alcohol, Θ = 54.7 °C). Mechanical and equilibrium concentration measurements were performed in the temperature range from 25 to 70 °C in both solvents.

In the excluded volume limit (good-solvent condition) the exponent of the elastic moduli (m_a) exhibited the universal value predicted by the scaling theory. We found that m_a did not depend on the temperature within the limits of the experimental accuracy. In the case of PVAc/isopropyl alcohol gels, the power law behavior remained valid; however, considerable temperature dependence of the apparent exponent was detected. Supposing the validity of the scaling law between m_a and ν_a in the crossover domain (above and below the Θ temperature), one can calculate the apparent excluded volume exponent for the network chains. With decreasing temperature, m_a was found to vary from 2.31 to 13.3 which corresponds to $0.59 > \nu_a > 0.36$. At the Θ temperature we got $m = 3.04$ and thus $\nu = 0.5$. Despite the considerable changes in ν_a, no macroscopic collapse of the gel systems was observed.

On the basis of the supposed analogy between α^3 and $\varphi_{e,\Theta}/\varphi_e$, it was demonstrated that this ratio is the only function of $\tau N^{1/2}$ predicted by both the classical and scaling theories. Instead of quantity N, another one (N/δ), linearly proportional to it, was used.

For all the gel systems studied, straight lines were found for the experimental $G/RT - \varphi_e(T)$ data, and thus their slopes were considered inversely proportional to N. It should be mentioned that these lines lead to nonzero values of the moduli at infinite dilution, that is, in contradiction with gel thermodynamics in general.

In order to check whether the ratio $\varphi_{e,\Theta}/\varphi_e$ can be described by the thermal blob theory, a comparison was made between theoretical and experimental dependences of $\varphi_{e,\Theta}/\varphi_e$ on N/N_τ. We concluded that the agreement between predicted and experimental results is satisfactory when the ratio of $N/N_\tau > 10$, while for $N/N_\tau < 10$ the deviation is significant.

Taking into account the asymptotic limit behavior of blob theory, a relationship was derived between $\varphi_{e,\Theta}$ and φ_e; the latter refers to the asymptotic limit either below or above Θ. A qualitative agreement was found as the experimental and calculated exponents slightly differed from one another.

Registry No. Poly(vinyl acetate) (homopolymer), 9003-20-7.

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