Phase transition in swollen gels: 7. Effect of charge concentration on the temperature collapse of poly(*N,N*-diethylacrylamide) networks in water

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The swelling and mechanical behaviour of gels of the copolymer of diethylacrylamide (DEAAm) with a small quantity of sodium methacrylate (mole fraction $x_{\mathrm{MNa}} = 0$–0.067) swollen in water was investigated in the temperature range 1–80°C. For networks in the range $x_{\mathrm{MNa}} > 0.0095$ phase transition was observed; both the critical transition temperature $T_{c,c}$ and the extent of the collapse Δ_c increase with increasing x_{MNa}. The formation of associations in the collapsed state contributes to the overall extent of the transition; these structures give rise to stable turbid gels at elevated temperatures. Evidence for the formation of 'associated' structures is also supported by the observed independence of cloud temperature of the concentration of DEAAm, c, in the polymerization DEAAm–water mixture without the crosslinking agent in the range $c = 0.5$–80 vol%. While PDEAAm solutions are formed in the range $c < 4.5$–6 vol%, physical gels arise at higher concentrations.

(Keywords: phase transition; shear modulus; swelling ratio; swelling pressure; extent of collapse; critical temperature)

INTRODUCTION

For polyacrylamide networks swollen in acetone–water mixtures, phase transition (collapse) was observed, reflected by a pronounced change in the macroscopic dimensions of the gels (the volume varies from ten to hundred times) following an infinitesimal change in the composition of the solvent[1–3]. The presence of a low number of charges (~1 mol%) on the chain appeared to be a necessary condition for the collapse to take place[4]. The appearance of the charges may be due to a spontaneous hydrolysis of AAm groups of variously aged PAAm networks[1,3], or they may be introduced by the copolymerization of AAm with a suitable monomer, e.g. sodium methacrylate[2] (MNa), or with *N*-acryloxysuccinimide ester[5]. The extent of the phase transition and the acetone content at the point of collapse are reduced by increasing the content of the crosslinking agent[6] and reducing the water content[7], factors which are involved with the formation of PAAm networks.

These experimental conclusions are in semiquantitative agreement with the theory of swelling equilibria of polyelectrolyte networks[4]. It is a disadvantage to use a mixed solvent to produce the collapse of PAAm networks, when the possible preferential sorption of one component of the solvent is considered. The first results obtained with poly(*N,N'*-diethylacrylamide) (PDEAAm) gels with ≈3 mol% MNa showed[8] that transition can be induced in this polymer by a temperature change in pure water.

In this study we investigate the effect of charge concentration on the chain, on the swelling and mechanical equilibria of PDEAAm networks in the temperature range 1–80°C; the charge concentration is determined by copolymerization with a small amount of sodium methacrylate.

EXPERIMENTAL

Sample preparation

The networks were prepared by mixing 8 ml *N,N'*-diethylacrylamide (DEAAm), 0.5 g *N,N'*-methylenebisacrylamide (MBAAm), 150 μl *N,N'*-tetramethylethylenediamine (TEMED), 4 ml of a 1% aqueous solution of ammonium persulphate, sodium methacrylate (MNa) and redistilled water. A series of 8 networks, A–H, were prepared with mole fractions of sodium methacrylate $x_{\mathrm{MNa}} \times 100$; A = 0; B = 0.45; C = 0.95; D = 1.57; E = 2.34; F = 3.10; G = 4.32 and H = 6.67. All components with the exception of TEMED were dissolved in water so as to make the total content 100 ml, the solution was flushed with nitrogen and cooled to 1°C. After that, TEMED was added, the solution was stirred and placed in test tubes ≈1 cm in diameter. The solution was again flushed with nitrogen and sealed. The polymerization proceeded at 1°C for ≈12 h; thereafter the gels were removed from the test tubes, their diameter D^* was measured and they were cut into specimens ≈1 cm long. The specimens were extracted in redistilled water at room temperature for about 7 days.

Variously concentrated solutions and physical gels were obtained by the polymerization of various amounts of the monomer (0.5–80 vol% DEAAm) in water under the same conditions as those used in networks preparation, but without the crosslinking agent. Two series of samples were prepared with the comonomer content $x_{\mathrm{MNa}} = 0$ and 0.03, respectively.

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Swelling and mechanical characteristics

After extraction the networks were swollen in deionized water in closed glass ampoules at 1°C; one part of the samples were predried and swollen at 80°C. After swelling at 1°C for 7 days the diameter of the samples, D, was determined and used for calculation of the swelling ratio X

$$X=(D^*/D)^3=V^*/V \qquad (1)$$

where V and V^* repectively are the sample volumes after swelling and after preparation. Simultaneously with the measurement of D, the deformational behaviour in unidirectional compression was measured using an apparatus described previously[9]; the shear modulus G was determined from the dependence of force on compression (the measurement is described in detail elsewhere[4]). The temperature was then raised by 2–5°C, and after 3 days of swelling at a new temperature the whole procedure was repeated. The same procedure of measurement of D and of the modulus G was employed with partly dried networks swollen at 80°C. In this case, however, the temperature was decreased by 2–5°C.

Solution–physical gel transition

Sealed ampoules containing solutions after polymerization were used in the measurement. To determine the solution–gel transition, we used the test tube 'tilting' method[10] which is identical to the ball-drop method[11]. The temperature of the ampoules was raised at a rate of $\approx 0.5°\mathrm{C\,min}^{-1}$; the temperature of gelation T_{GL} was regarded as a temperature at which, on turning the test tube, a jumpwise change in the solution viscosity took place: the flowing solution became a nonflowing gel (in some cases, the gel stability was checked for 24 h). The cloud temperature T_c of the solution or gel at which phase separation occurred was also determined.

RESULTS AND DISCUSSION

Temperature and concentration behaviour of PDEAAm without the crosslinking agent in water

In view of the unusual behaviour of PDEAAm networks in the collapsed state, we examined the temperature and concentration behaviour of the water–PDEAAm system without the crosslinking agent. The phase diagram in *Figure 1* in which the temperature of gelation (or the cloud temperature) is plotted vs. the DEAAm concentration in the polymerization mixture, c, shows that:

(a) The PDEAAm solutions may be obtained only at the lowest DEAAm contents in the polymerization mixture. In the range of DEAAm concentrations $c>6$ vol% gels are already formed (in the temperature range $T\sim 1°\mathrm{C}$). The critical concentration c_k at which the gel is formed is only slightly temperature-dependent ($c_k \sim 4.5$–6.0 vol% as the temperature changes from ~45–1°C).

(b) With increasing temperature the PDEAAm solutions and gels become turbid; the cloud temperature T_c is independent of the monomer content in the polymerization mixture in the range $c=0.5$–80 vol% DEAAm.

(c) An addition of 3 mol% sodium methacrylate (on the DEAAm in the monomer mixture) is reflected in the phase diagram in a rise in the cloud temperature (by ~13°C); the concentration region of gelation remains virtually unaffected.

The gels thus formed are reversible with respect to temperature, but with respect to the solvent concentration they are stable and cannot be dissolved in an excess of water.

Similar behaviour was observed previously for atactic polystyrene gels in a number of solvents[11]; it was found that the molecular weight and the molecular structure of the solvent affect the ease of gel formation and gel stability. In gel formation PDEAAm differs from polyacrylamide (PAAm), for which aqueous solutions can be observed in the concentration range $c=0.5$–50 wt% AAm in the polymerization mixture. This finding also suggests that the PDEAAm gels thus formed are of a physical rather than chemical nature (they do not contain chemical junctions which might arise in the polymerization by transfer), even though no solvent has been found which would dissolve the gel (the latter swells most in water near 0°C). The rise in the cloud temperature with 3 mol% sodium methacrylate is a result of an increase in the polarity of the chain.

An unexpected result is the independence of the cloud temperature T_c on the monomer concentration in the polymerization mixture, both for PDEAAm alone and for the copolymer with sodium methacrylate. In this respect the system under study differs from the classical critical behaviour of solutions[12] and from the behaviour of swollen physical[11] or chemically crosslinked[13] gels, the critical temperature T_c of which depends considerably on the polymer concentration. In some cases it was observed, however, that macromolecules in solution (depending on the quality of the solvent) tend to associate and form ordered structures[14]. These structures usually produce extended chain conformations, and after removal of the solvent, a partly crystalline phase. We believe that in our case similar associations are formed in solutions and gels of PDEAAm at temperatures $T>T_c$. Even though measurements of X-ray scattering from clouded solutions and gels of PDEAAm did not reveal the presence of the crystalline phase, it is known[15] that some substituted polyacrylamides (e.g., *N*,*N*-dibutyl or *N*-isopropyl) have the ability to crystallize.

Swelling and mechanical behaviour of PDEAAm networks

The swelling ratio X and the shear modulus G of samples A and B vary continuously with temperature, but in networks C–H ($x_{\mathrm{MNa}}>0.009$) a phase transition takes

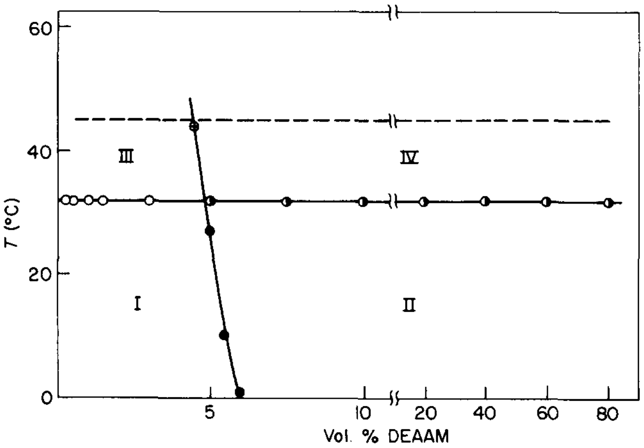

Figure 1 Phase diagram of PDEAAm in water. I: range of homogeneous solutions; II: range of homogeneous physical gels; III: range of clouded solutions; IV: range of clouded physical gels; (-----) cloud temperature for PDEAAm with $x_{\mathrm{MNa}}=0.03$

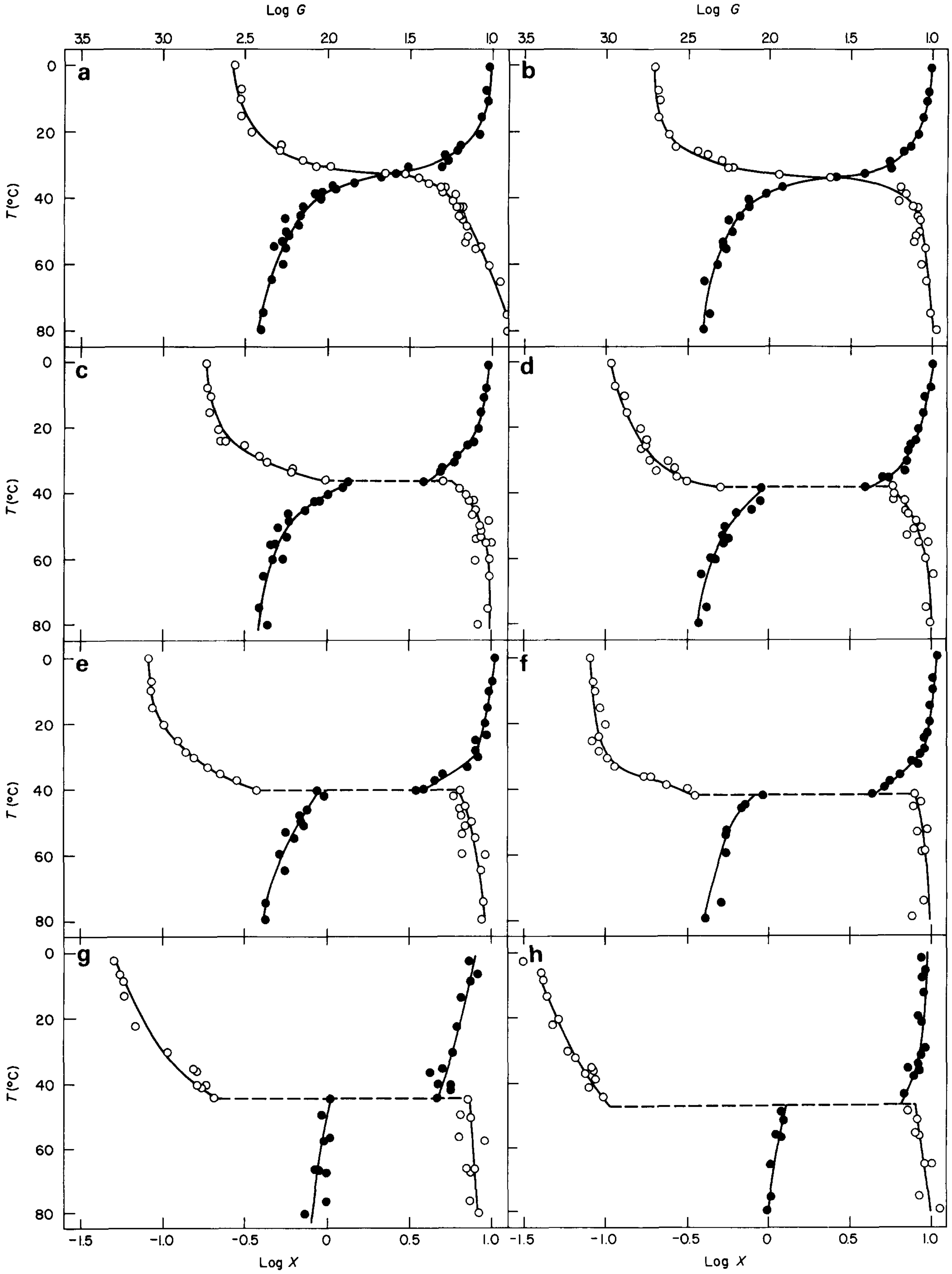

Figure 2 Temperature dependence of swelling ratio X and shear modulus G (g cm^{-2}) for the gel series A–H which correspond to the networks in *Table 1*. (○) X values, (●) G values

Table 1 Basic characteristics and parameters of phase transition

Series	$x^a_{\mathrm{MNa}}\cdot 100$ (mol%)	G^b_0 (g cm^{-2})	G^c_1 (g cm^{-2})	$\nu^d_d\cdot 10^5$ (mol cm^{-3})	$T^e_{c,e}$ (°C)	Δ^f_e	χ^g_c	$T^h_{c,t}$ (°C)	Δ^i_t	ϕ^j
A	0	23.0	28.2	1.55	–	–	–	–	–	–
B	0.45	20.0	30.2	1.66	–	–	–	–	–	0.56
C	0.95	20.4	28.2	1.55	36	0.303	0.546	32.0	0.100	0.32
D	1.57	18.9	35.5	1.95	38	0.376	0.565	33.5	0.144	0.46
E	2.34	20.2	39.8	2.19	40	0.427	0.592	35.5	0.200	0.49
F	3.10	17.6	42.7	2.35	42	0.502	0.610	37.5	0.229	0.41
G	4.32	19.0	42.7	2.35	44	0.506	0.655	40.5	0.315	0.48
H	6.67	18.8	44.7	2.45	47.5	0.512	0.687	43.0	0.357	0.38

[a] Content of sodium methacrylate in the polymerization mixture

[b] Gel modulus after preparation

[c] Gel modulus after swelling extrapolated for $X=1$

[d] Network density

[e] Experimental temperature value at phase transition

[f] $\Delta_e = v'_2 - v''_2$ (*Figure 4*) is a change in the gel volume at collapse

[g] Critical value of the interaction parameter at collapse determined by using Maxwell's construction of experimental data χ vs. v_2 (*Figure 4*)

[h] Critical temperature at collapse determined from χ_c

[i] Extent of collapse determined from Maxwell's construction

[j] Semi-empirical correction factor

place, and the dependence of X and G on T is discontinuous (*Figure 2*). With increasing charge concentration on the chain, both the extent of phase transition, Δ_c (defined as a change in the sample volume at collapse: $\Delta_e = v'_2 - v''_2$, where v'_2 and v''_2 respectively are the volume fraction of the polymer in the collapsed and expanded state; $v_2 = Xv^0$ and $v^0 = 0.07$ is the volume fraction of the polymer at network formation), and the critical temperature of phase transition T_{cc} increase (*Table 1*). Qualitatively similar changes have been observed earlier[2] on polyacrylamide networks which contained MNa in acetone–water mixtures (instead of an increase in $T_{c,e}$, the acetone concentration in the mixture increased with increasing x_{MNa} at collapse).

Samples swollen to equilibrium in series A for $T > 32$°C, series B for $T > 33$°C, and series C–H in the collapsed state were always turbid, regardless of their initial state (predried or swollen). At the beginning, swelling of the predried samples in the collapsed state proceeded homogeneously, and samples were transparent. On reaching ~80% of the equilibrium amount of water, the samples become opalescent and eventually turbid, which suggested a heterogeneous equilibrium structure. In this respect the P(DEAAm–MNa) networks differ from the P(AAm–MNa) networks for which homogeneous transparent samples could be obtained in the collapsed state[2], by swelling of predried samples. We believe that also in the case of P(DEAAm–MNa) networks (similarly to solutions and physical gels) associations are formed at elevated temperatures, so that a two-phase equilibrium structure is obtained. Due to the low network density (low value of the modulus G) and large dilution at network formation ($v^0 = 0.07$), the associations are stable. It has been observed earlier[16] that in the case of an approx. 20 times higher G and at $v^0 = 0.75$, homogeneous networks swollen in water to equilibrium could be prepared throughout the temperature range 20–95°C. The large negative deformational birefringence of these networks suggested, however, the existence of interactions, between side chains, which were destroyed by increasing swelling[17].

The continuous dependence of both X and G on temperature in series A and B (*Figure 2*) indicates that associations do not cause any distinct jump in these characteristics. Also, the dependence of log G on log X in series A and B is continuous, and in the range log $X < 0.8$ it may be represented by a straight line with slope $s = 0.65$ (*Figure 3*). In series C–H the jumpwise change in volume accompanying the collapse correlates with a change in the modulus; it was found that $\Delta\log G \doteq 0.65\ \Delta\log X$. The same slope s and correlation between Δlog G and Δlog X was found earlier for P(AAm–MNa) networks[2,3].

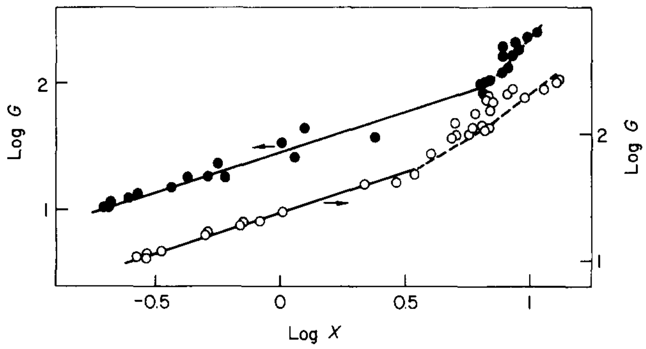

Figure 3 Dependence of shear modulus G (g cm^{-2}) on swelling ratio X (○) series A; (●) series B

For all networks the values of modulus G_1 were extrapolated for $X = 1$ from the log G vs. log X dependence (*Table 1*). While the modulus after preparation, G_0, (before swelling at various temperatures) is constant in the series A–H, the modulus G_1 increases with increasing MNa content by as much as ~50%; a similar increase has been observed earlier for P(AAm–MNa) networks[2,3]. The concentrations of elastically active chains in the dry state, $\nu_d = G_1/v^0RT$ were calculated from the modulus G_1 (*Table 1*); the low ν_d values suggest the low efficiency of the crosslinking reaction.

Comparison between theory and experiment

The inclusion of electrostatic interactions into the kinetic theory of rubber elasticity has led to an expression for the swelling pressure[4] P of the form

$$P = P_m + P_{el} + P_{os} + P_{els} \qquad (2)$$

where P_m corresponds to the mixing of the chain segments with the solvent (the Flory–Huggins term with the

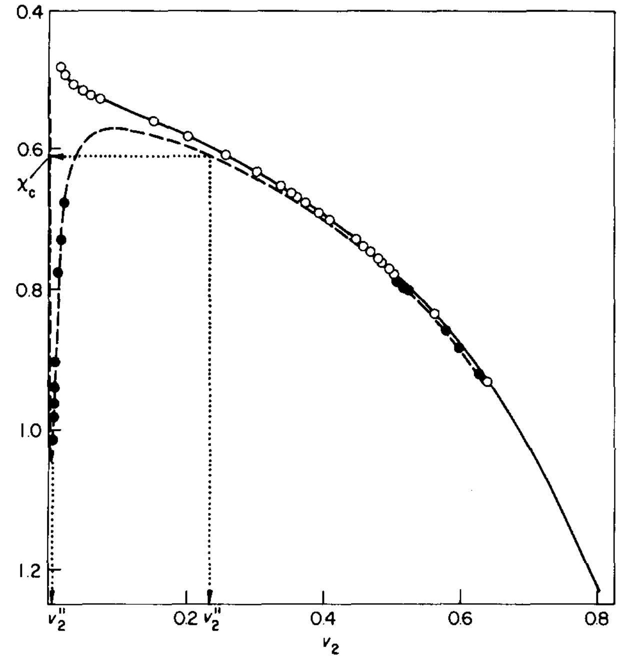

Figure 4 Dependence of the interaction parameter χ on the volume fraction of the polymer in the swollen state v_2. (———) dependence obtained earlier on homogeneous networks[15]; (○): data of series A; (●): data of series F; (-----): dependence determined from equation (2) for $P=0$; χ_c, v'_2 and v''_2 are phase transition parameters determined by Maxwell's construction of the χ vs. v_2 dependence for series F

interaction parameter χ), P_{el} corresponds to a change in the elastic energy with swelling, P_{os} is given by mixing of gel ions with the solvent, and P_{els} corresponds to a change in electrostatic interactions with swelling. A detail meaning of P_i in molecular parameters of the network is given in equations (2)–(5), (see ref. 4).

By using experimental parameters (density of the dry polymer $\rho=1.07$ g cm^{-3}, $v^0=0.07$, the molar volume of water $V_1=18.1$ cm^3 g^{-1}, the experimental network density v_d, the degree of ionization x_{MNa}, v_2 and T values), and the dependence of χ on v_2 (for free swelling, $P=0$) can be calculated from equation (2). In series A with $x_{MNa}=0$, χ was 0.476, 0.482 and 0.488 at 1, 10 and 20°C respectively (the networks are homogeneous). For ionized networks B–H at the same temperatures the values of χ were much higher, i.e. 0.5–3.65. As χ is a measure of the polymer–solvent affinity when all the charges are screened (the charge effect on the degree of swelling is included in P_{os} and P_{els}), it may be expected that χ should not be affected by the presence of a small number of charges to any considerable extent. The requirement that χ at 1, 10 and 20°C should be the same for both ionized and non-ionized networks may be satisfied by assuming that the effective degree of ionization α is lower than x_{MNa}, i.e. $\alpha=\phi x_{MNa}$ and ϕ is the semiempirical correction factor (*Table 1*). The need to introduce a correction factor $\phi<1$ was seen earlier from an analysis of swelling data of variously aged PAAm networks[3] and PAAm networks containing hydrolysed ester of *N*-acryloxysuccinimide[5].

The dependence of χ on v_2 of the system PDEAAm–water was obtained earlier by measuring variously crosslinked and diluted homogeneous networks[16]. It is interesting that the χ vs. v_2 dependence obtained from measurements in series A virtually coincides with a dependence measured earlier also in the range of heterogeneous samples (i.e. for temperatures T > 32°C). *Figure 4* shows also the χ vs. v_2 dependence for the ionized series F calculated by means of equation (2) from the dependence of v_2 on temperature using $\alpha=x_{MNa}$ within the whole temperature range under investigation (the samples are turbid in the collapsed state). As expected[2], the χ vs. v_2 dependence for the ionized network F has the form of the van der Waals loop. By applying Maxwell's construction to this loop, it is possible to determine both the critical value of the interaction parameter $\chi_c=0.610$ and the extent of the collapse $\Delta_t=v'_2-v''_2=0.229$; (a detailed procedure is described elsewhere[2,4]). The χ_c value corresponds to χ of the non-ionized network for $T_{c,t}=37.5$°C (*Table 1*).

It can be seen from *Table 1* that while values of the critical temperatures $T_{c,e}$ and $T_{c,t}$ correlate comparatively well ($T_{c,e}\approx T_{c,t}+4$°C), the experimental extents of transition Δ_e are much larger than of Δ_t. The use of $\alpha=\phi x_{MNa}$ would lead to still greater differences between Δ_e and Δ_t (the fit between Δ_e and Δ_t would require $\alpha \gg x_{MNa}$). On the other hand, an analysis of swelling data of samples in the expanded state required $\alpha<x_{MNa}$. It may be said, therefore, that the fit between theory and experiment for PDEAAm networks is much poorer than for PAAm networks. We believe that this difference is due to the formation of associated structures of PDEAAm gels in the collapsed state which contribute to the overall extent of the phase transition.

It may be said in conclusion, that the existence of phase transition is not restricted to PAAm networks in acetone–water mixture. Assuming that the required physical conditions are satisfied (the gels have a low crosslinking density and contain a low number of charges on the chain), transition can be observed also in other systems. The collapse can be brought about by a change of conditions which lead to a pronounced change in the polymer–solvent interaction. In systems in which ordered structures (or partial crystallinity) exist in the collapsed state the extent of collapse may be expected to increase.

REFERENCES

1 Tanaka, T. *Polymer* 1979, **20**, 1404
2 Ilavský, M. *Macromolecules* 1982, **15**, 782
3 Ilavský, M., Hrouz, J., Stejskal, J. and Bouchal, K. *Macromolecules*, 1984, **17**, 2868
4 Ilavský, M. *Polymer* 1981, **22**, 1687
5 Nicoli, D., Young, C., Tanaka, T., Pollak, A. and Whitesides, G. *Macromolecules* 1983, **16**, 887
6 Ilavský, M. and Hrouz, J. *Polym. Bull.* 1982, **8**, 387
7 Ilavský, M. and Hrouz, J. *Polym. Bull.* 1983, **9**, 159
8 Ilavský, M., Hrouz, J. and Ulbrich, K. *Polym. Bull.* 1982, **7**, 107
9 Hrouz, J., Ilavský, M., Havlíček, I. and Dušek, K. *Coll. Czech. Chem. Commun.* 1979, **44**, 1942
10 Wellinghoff, S., Shaw, J. and Baer, E. *Macromolecules* 1979, **12**, 932
11 Tan, Hui-Min, Moet, A., Hiltner, A. and Baer, E. *Macromolecules* 1983, **16**, 28
12 Flory, P. J. in 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
13 Zrinyi, M. and Wolfram, E. *J. Coll. Inter. Science* 1982, **90**, 34
14 Sedláček, B., Spěváček, J., Mrkvičková, L., Stejskal, J., Horská, J., Baldrián, J. and Quadrat, O. *Macromolecules* 1984, **17**, 825
15 Brandrup, J. and Immergut, E. H. in 'Polymer Handbook', Wiley, New York, 1966, p. III-8
16 Hrouz, J., Ilavský, M., Ulbrich, K. and Kopeček, J. *Eur. Polym. J.* 1981, **17**, 361
17 Ilavský, M., Hrouz, J. and Dušek, K. *J. Macromol. Sci.* 1981, **B19**, 227