Polymer Bulletin 7, 107–113 (1982)

Polymer Bulletin

Phase Transition in Swollen Gels

3. The Temperature Collapse and Mechanical Behaviour of Poly (N,N-diethylacrylamide) Networks in Water

M. Ilavský, J. Hrouz and K. Ulbrich

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
CS-16206 Prague 6, Czechoslovakia

Summary

The temperature dependence of the swelling and mechanical behaviour of two poly(N,N-diethylacrylamide) networks has been investigated in aqueous solutions at pH ≈ 7.5. While one network was prepared by the copolymerization of N,N-diethylacrylamide with N,N′-methylenebisacrylamide in the presence of 92 vol.% water, 3 mol.% sodium methacrylate was added to the mixture used in the preparation of the second network. In the network without charges on the chain, both the swelling ratio and modulus were found to be continuously dependent on temperature. On the other hand, the ionized network containing sodium methacrylate showed a pronounced phase transition at the temperature T ≈ 51 °C connected with a jumpwise change in both the volume and modulus of the network.

Introduction

A theoretical analysis of the classical relation describing free energy of a swollen polymer network ΔF showed (DUŠEK and PATTERSON 1968) that under certain (though experimentally inaccessible) conditions, two phases may coexist in the network differing in the conformation of chains and concentration of the segments. It was demonstrated experimentally that the presence of charges on the chain is necessary in order to produce phase transition (collapse) in polyacrylamide (PAAm) networks in acetone-water mixtures; these charges may arise either due to the ageing of the network (TANAKA et al. 1980, STEJSKAL et al. 1980, JANAS et al. 1980), which causes a spontaneous hydrolysis of the PAAm chain, or they may be introduced by the copolymerization of AAm with sodium methacrylate (ILAVSKÝ 1982). It was shown theoretically that ≈1 mol.% of charges on the chain are sufficient to affect free energy of the network ΔF in such a way that collapse occurs under suitable conditions; the increasing ionization increases the extent of phase transition (ILAVSKÝ 1981). These theoretical conclusions were also confirm-

0170-0839/82/0007/0107/$01.40

ed experimentally (ILAVSKÝ 1982), and it was found that the jumpwise change in the gel volume accompanying the collapse produced a similar change in the mechanical characteristics (i.e. in the network modulus).

A disadvantage, especially in a quantitative comparison of experimental data obtained on PAAm networks with theory, consists in the necessity to employ a two-component solvent acetone-water which is approximated by a single liquid (preferential solvation and interactions between molecules of the solvent are neglected). Also, the comparatively easy and uncontrollable hydrolysis of the PAAm chain is a certain shortcoming of the system. Within an extensive investigation of acryl- or methacrylamide polymers suited for biomedical applications (ULBRICH et al. 1977, ULBRICH et al. 1978), we examined the swelling and mechanical behaviour of poly (N,N-diethylacrylamide) networks (HROUZ et al. 1981). A pronounced dependence of the swelling on temperature in water (with increasing temperature the network deswells quickly, i.e. the gel behaves as a system with the lower critical solution temperature) makes the system attractive for the study of phase transition. It may be expected that in such networks with a small number of ionized groups the collapse could be achieved by a change in temperature in pure water; at the same time, bulky substituents on the amide nitrogen atom will considerably slow down the spontaneous hydrolysis of the chain (compared with the PAAm chain).

In this paper we report the results of swelling and mechanical equilibria in water as a function of temperature, both for the nonionized and ionized poly (N,N-diethylacrylamide) networks; the latter was prepared by the copolymerization of N,N-diethylacrylamide with a small amount of sodium methacrylate.

Experimental

Sample preparation: The gels were prepared from 100 ml of a mixture which contained 8 ml of the monomer N,N-diethylacrylamide (DEAAm), (monomer density $\rho =$ 0.923 g cm^{3}), 0.2 g of the crosslinking agent N,N-methylenebisacrylamide (MBAAm), 20 mg ammonium persulphate and 20 mg sodium pyrosulphite. To prepare an ionized network, 1.94 ml of a 0.96 M solution of sodium methacrylate (MNa), which corresponds to the molar ratio $x_{MNa} = 0.03$, was added to the mixture above mentioned. All components with the exception of sodium pyrosulphite were dissolved in redistilled water and flushed with nitrogen. After that, pyrosulphite was added, the solution was stirred and dosed into glass test tubes, ≈1 cm in diameter; the test tubes were again flushed and sealed. The polymerization proceeded at 6°C for 24 h; the gels were removed and cut into cylinders ≈1 cm long. The samples were kept for 12 hours in a 0.005 M aqueous solution of sodium nitrite which was later washed out in redistilled water.

Swelling and mechanical characteristics: The samples were swollen in redistilled water simultanously in five thermostats with the initial temperatures 30, 40, 50, 60 and 70°C in closed glass ampoules ≈3 cm in diameter (each containing some three samples). Partly predried samples were used for the swelling. After swelling for one week, pH of water in the ampoules was adjusted to 7.5 with concentrated NaOH (pH≈7.5 guarantees that ionization equals the molar fraction of MNa with an accuracy higher than 0.5 % of the originally weighted amount of MNa). After another three days of swelling, the swelling ratio X of all gels related to the state of network formation was determined by using the relation

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

where D and D^{*} respectively are diameters of the sample after swelling and after preparation, and V and V^{*} respectively are gel volumes after swelling and after preparation. The temperature of all thermostats was then decreased by 2-5°C, and after another three days of swelling at a lower temperature the whole procedure was repeated. Each point on the temperature dependence X given in Fig.1 represents an average from three measurements. Using the swelling ratio X, it is possible to calculate the volume fraction of the polymer in the swollen state φ_2 $(=V_d/V_s = \varphi^{o}X$, where V_d and V_s respectively is the volume of the dry and swollen sample, and $\varphi^{o} = 0.07$ is the volume fraction of the polymer at network formation calculated from the density of the dry polymer $\rho_d = 1.06$ g cm^{-3}).

Simultanously with the swelling measurements, the deformational characteristics were measured with an apparatus described earlier (HROUZ et al. 1979), operating in a unidirectional compression. The measurement was performed at a corresponding temperature in water at pH≈7.5 flushed with nitrogen. A cylindrical sample was compressed between teflon surfaces to the compression λ , and the force f was determined after 30 s relaxation, 10 values of λ were measured in the range $0.7 < \lambda < 1$. From these measurements, the shear modulus G was determined using the relation

$$G = f/S_{o}(\lambda^{-2} - \lambda) \qquad (2)$$

in which S_o is the initial cross-section of the sample. The dependence of G on temperature is given in Fig.2.

Results and Discussion

Swelling and mechanical characteristics

The dependence of the swelling ratio X on temperature shown in Fig.1 indicates that while the dependence of X on T for the nonionized network is a continuous one, the network with $x_{MNa} = 0.03$ has a pronounced discontinuity in the range T ≈ 51°C, corresponding to the phase transition. The extent of this transition $\Delta \log X \approx 1.1$ ($\Delta \log X = \log X'' - \log X'$, cf.Fig.1) is comparable with the collapse observed for polyacrylamide (PAAm) network after ageing for ≈6 days at pH=12 (cf. Fig.1, from TANAKA et al. 1980), or for PAAm network with a ≈2 mol.% content of sodium methacrylate (cf.Fig.2 from ILAVSKÝ 1982).

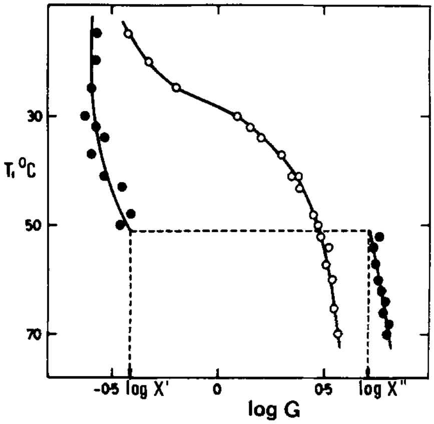

Fig.1 Temperature dependence of the swelling ratio X ○ nonionized network, ● ionized network

Similarly to the swelling ratio X, the dependence of the modulus G on temperature is also continuous for the nonionized network (Fig.2). In the range of phase transition of the ionized network the modulus also undergoes a jumpwise change which takes place as a result

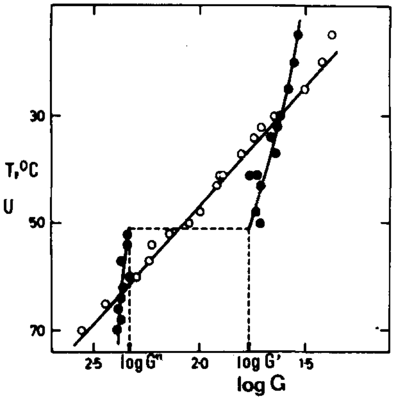

Fig.2 Temperature dependence of the modulus G ($g\ cm^{-2}$) ○ nonionized network, ● ionized network

of the similar change in the gel volume. The magnitude of this change $\Delta \log G \approx 0.55$ ($\Delta \log G = \log G'' - \log G'$, cf.Fig.2) can be correlated with $\Delta \log X$, it being valid that $\Delta \log G = 0.5 \times \Delta \log X$. A similar correlation between the change in the modulus and volume in the collapse has been observed earlier with ionized PAAm gels in the acetone-water mixture (ILAVSKÝ 1982).

Comparison between theory and experiment

A characteristic feature of phase transition is the existence of the van der Waals loop in the dependence of the swelling pressure P or of the interaction parameter $\bar{\chi}$ on the volume fraction of the polymer φ_2. The composition of phases (φ_2' and φ_2'') is given by the condition (ILAVSKÝ 1981)

$$\int_{\varphi_2'}^{\varphi_2''} (\bar{\chi} - \chi_c) d\varphi_2 = 0 \quad , \qquad (3)$$

the dependence of the interaction parameter $\bar{\chi}$ on the composition of the gel (given by φ_2) is determined from an experiment for free swelling, i.e. P=0 (for a detailed expression of the swelling pressure P in molecular parameters see Eqs. (1)-(5) of the paper ILAVSKÝ 1981), and χ_c is the critical value of the interaction parameter at which collapse takes place. Hence, Eq.(3) determines, in addition to the phase compositions φ_2' and φ_2'', also the critical value χ_c (Maxwell's construction is applied to the $\bar{\chi}$ vs. φ_2 dependence).

Using the known molecular parameters: molecular weight of the monomer unit $M_o = 127$, polymer density $\rho_d = 1.06$ g cm^{-3}, $\varphi^o = 0.07$, dielectric constant D = 80, molar volume of water $V_1 = 18.1$, network density in the dry state $\nu = 2.1 \times 10^{-5}$ mol cm^{-3} and 4.6×10^{-5} mol cm^{-3} for the nonionized and ionized networks respectively (ν is calculated from the modulus G measured after preparation at X = 1) and the respective degree of ionization $i = x_{MNa} = 0$ and 0.03, the dependence of $\bar{\chi}$ vs. φ_2 was calculated from the condition for free swelling, i.e. P=0 (Fig.3).

While for the nonionized network the $\bar{\chi}$ vs. φ_2 dependence is continuous, discontinuity appears with ionized gels as expected. The application of Eq.(3) to $\bar{\chi}$ vs. φ_2 of the ionized network allowed us to determine the theoretical composition of phases φ_2', φ_2'' and also χ_c (Fig.3). Fig.3 also shows the plot of critical values φ_{2s}' and φ_{2s}'' determined by the spinodal condition $(\partial P/\partial \varphi_2) = 0$. The value $\chi_c = 0.585$ is in good agreement with $\bar{\chi} = 0.58$ of the nonionized network determined for 51°C. A shift of the experimental value of φ_{2e}' to a region in the direction of the spidonal φ_{2s}' has been observed earlier with PAAm networks (ILAVSKÝ 1982). The high

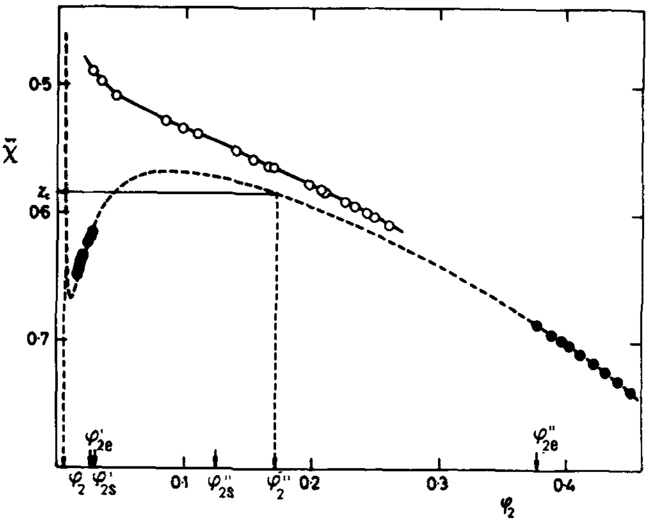

Fig.3 Dependence of the interaction parameter $\bar{\chi}$ on the volume fraction of the polymer in the swollen state φ_2
○ nonionized network; ● ionized network;
---- dependence determined by the condition that the swelling pressure P=0, parameters φ_2' and φ_2'' determined by Eq.(3), parameters φ_{2s}' and φ_{2s}'' determined by Eq.(3), parameters φ_{2s}' and φ_{2s}'' are determined by a spinodal condition $\partial P/\partial \varphi_2 = 0$

experimental value of $\varphi_{2e}'' > \varphi_{2s}''$ (collapsed state) is however surprising, because earlier (ILAVSKÝ 1982) for the PAAm networks the value φ_{2e}'' has been observed to be somewhat shifted towards φ_{2s}''.

It can be said, in conclusion, that the existence of phase transition is not restricted to PAAm networks in the mixture acetone-water, but if the required physical conditions are fulfilled (in particular, the presence of a small number of charges on the chain and the possibility of preparation of homogeneous systems at high dilution at network formation), this phenomenon can be expected also for other systems. The collapse may then be provoked by a change in conditions causing a pronounced change in the polymer-solvent interaction (and thus, due to a change in the interaction parameter).

Acknowledgment. The authors are indebted to Mrs. R.Mejstříková for careful assistance in experimental work.

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Received March 12, accepted March 15, 1982

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