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Phase transition in swollen gels

11. Small-angle neutron scattering from poly (N,N-diethylacrylamide) networks and solutions in the collapse region

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Summary

The temperature dependences of the small-angle neutron scattering (SANS) from solutions and networks of poly(N,N-diethylacrylamide) (PDEAAm), or from the copolymer of DEAAm and 5 mol.% sodium methacrylate (MNa) in deuterated water were measured. In the low-temperature range (T<30°C, expanded state) the SANS curves have features typical of scattering from polymer coils. At elevated temperatures (T>60°C, collapsed state) the character of SANS curves changes, indicating that in both networks and solutions compact globular structures are formed. The presence of MNa (i.e. of charges on the chains) shifts the temperature of the transition range from the expanded to the collapsed state towards higher temperature by 10-15°C.

Introduction

Polyacrylamide networks (PAAm), carrying a small amount of charges on the chain, and swollen in water-acetone mixtures undergo a phase transition (collapse) reflected in a jumpwise change in the gel volume after an infinitesimal change in the composition of the solvent (1-5). The charges were introduced into the chains either by a spontaneous hydrolysis of amide groups to carboxylic ones (1-3,5), or by the copolymerization of AAm with a suitable monomer - sodium methacrylate (4) or N-acryloxysuccinimide ester (6) (negative charge), or by the copolymerization of AAm with quaternary ammonium salts (7-9) (positive charge). The collapse may also be brought about by a change in ionization (10) or in the electric field applied to the gel (11), by a change in pH of the solvent (12), by a change in temperature (13,14) or in the external deformation (15). It was also found that the discontinuous change in the gel volume is accompanied by a similar change in the shear modulus and in the stress-optical coefficient of the network (16). The experimental swelling data of PAAm networks are in a good agreement with the theory of swelling equilibria of polyelectrolyte networks (17,18).

Ionized networks of poly(N,N-diethylacrylamide)(PDEAAm), which undergo a collapse in pure water, were found to be most suitable for the investigation of thermally induced phase transition (13,14). In this system the quality of the solvent decreases with increasing temperature so that at low temperatures (T<30°C) the network is in the expanded state, while at

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** To whom offprint requests should be sent high temperatures (T>60°C) the gel is collapsed. With PDEAAm networks the agreement between experiment and theory is poorer than with PAAm networks, due to the heterogeneous structure of the networks in the collapsed state (14).

The objective of this study is to point out the possibility of application of small-angle neutron scattering in the investigation of the phase transition of ionized and nonionized networks and solutions of poly(N,N-diethylacrylamide) in water.

Experimental

Sample preparation: The poly(N,N -diethylacrylamide) networks (PDEAAm) were prepared by the copolymerization of 10 ml DEAAm in presence of 0.125 g of N,N'-methylenebisacrylamide as the crosslinking agent, 150 µl of N,N'-tetramethylethylenediamine, 4 ml of 1 wt.-% solution of ammonium persulfate in deuterated water, and sodium methacrylate (MNa). Deuterated water D_2O (purity 99.6%) was added up to 100 ml. Two networks were prepared: one without MNa (sample N1), the other with the mole fraction of MNa $x_{MNa}=0.05$ (sample N2). The polymer solutions were prepared by a similar procedure, but without the crosslinking agent, and with total 4 wt.-% of DEAAm content. Two solutions were prepared again, one without MNa (solution S1) and the other with the MNa content $x_{MNa}=0.05$ (solution S2). The polymerization of solutions and networks proceeded ~12 h at 1°C; the monomer conversion was higher than 99%.

SANS measurements: The measurements were performed with a time-of-flight small-angle spectrometer (19) attached to a pulse reactor IBR 2 (20) in the Joint Institute of Nuclear Research, Dubna, U.S.S.R. The solutions and networks were placed in 2 mm quartz cells. The noncoherent part of scattering was estimated by means of light scattering from D_2O/H_2O mixtures, containing the same number of protons as the samples under investigation. Two data sets were recorded for each sample: (1) Scattering from the sample alone, (2) scattering from the sample and the vanadium standard placed in the primary beam between the sample and detector. By combining these two measurements, the differential effective cross-section of coherent scatter per unit volume of the sample was determined, $d\Sigma(q)/d\Omega$ for q in the range between 0.01 and 0.2 $Å^{-1}$ ($q=(4\pi/\Lambda)$ $\sin\Theta$ is the size of the scattering vector, Λ is the radiation wavelength and 2Θ is the scattering angle). Measurements of networks and solutions were carried out in the temperature interval 20-78°C, each time after the sample had been thermostated for five hours. The original samples of solutions S1,S2 were additionally diluted ten times with D_2O, so that the total polymer concentration in the solutions was 0.4 wt.-%.

From the theory of small-angle scattering we have that at low q (i.e., $qR_z<<1$) the scattering from any particles may be approximated as (21,22) $d\Sigma/d\Omega\sim M_w\exp(-q^2R_z^2/3)$, where R_z is the z-average of the radius of gyration, M_w is the weight average molecular weight. At higher q, the values $d\Sigma/d\Omega$ depend on the conformation of the macromolecule (23). For Gaussian coils, the dependence (24) $d\Sigma/d\Omega\sim q^{-2}$ is characteristic, while for compact particles we expect (25) $d\Sigma/d\Omega\sim q^{-4}$.

Light scattering: Both polymer solutions, S1 and S2, in heavy water were diluted with distilled water and then with the same volume of 2M KSCN aqueous solution. The presence of an inorganic salt is needed to suppress the polyelectrolyte effect (especially for copolymers containing MNa) in the molecular characterization. Light scattering was measured with a Sofica 42 000 apparatus (vertically polarized primary beam, wavelength 5460 Å, 25°C). The polymer solutions were optically purified by centrifugation. The refractive index increment of PDEAAm in 1 M KSCN was $(dn/dc)_\mu = 0.141$ cm^3/g (after the establishment of osmotic equilibrium between the polymer solution and solvent; 25°C, 5460 Å). After the usual treatment by the Zimm method, the results of light scattering measurements gave the weight average molecular weight M_w and the z-average of the radius of gyration R_z.

Results and Discussion

Experimental dependences of the effective scattering

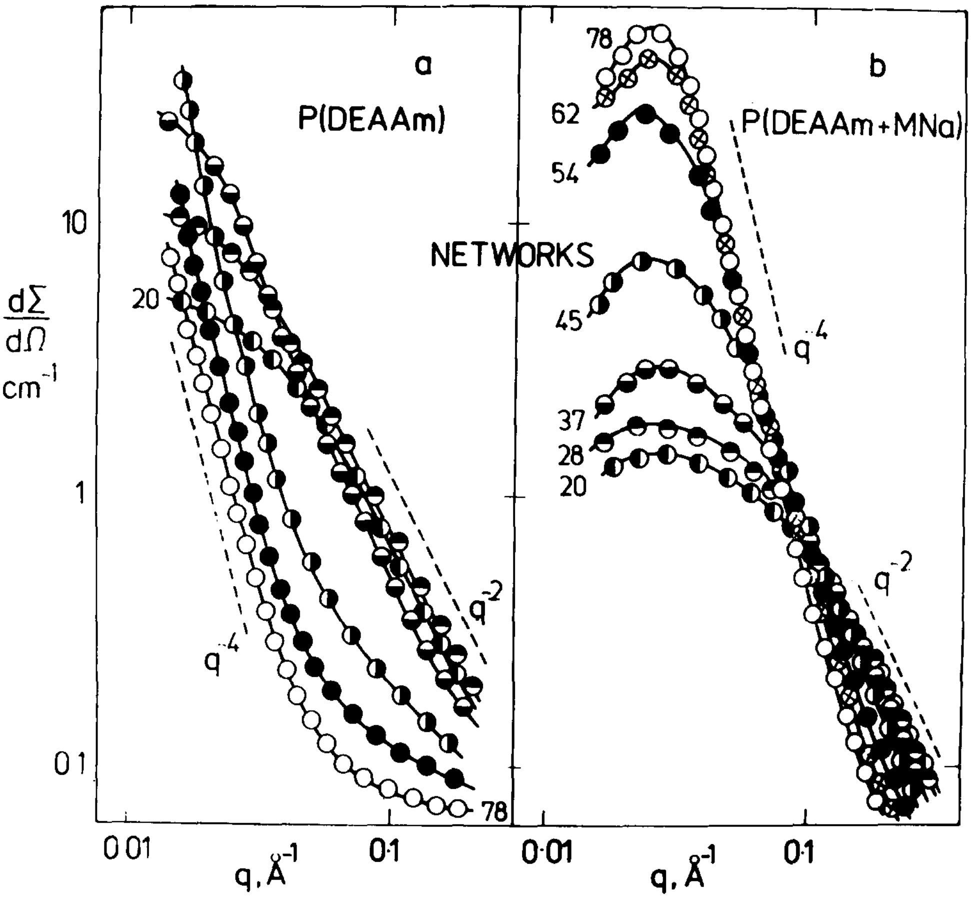

Figure 1. SANS curves of swollen networks: a) PDEAAm network, b) P(DEAAm+MNa) network. Temperature of measurement: ◐ 20°C, ◓ 28°C, ◒ 37°C, ◑ 45°C, ● 54°C, ⊗ 62°C, ○ 78°C

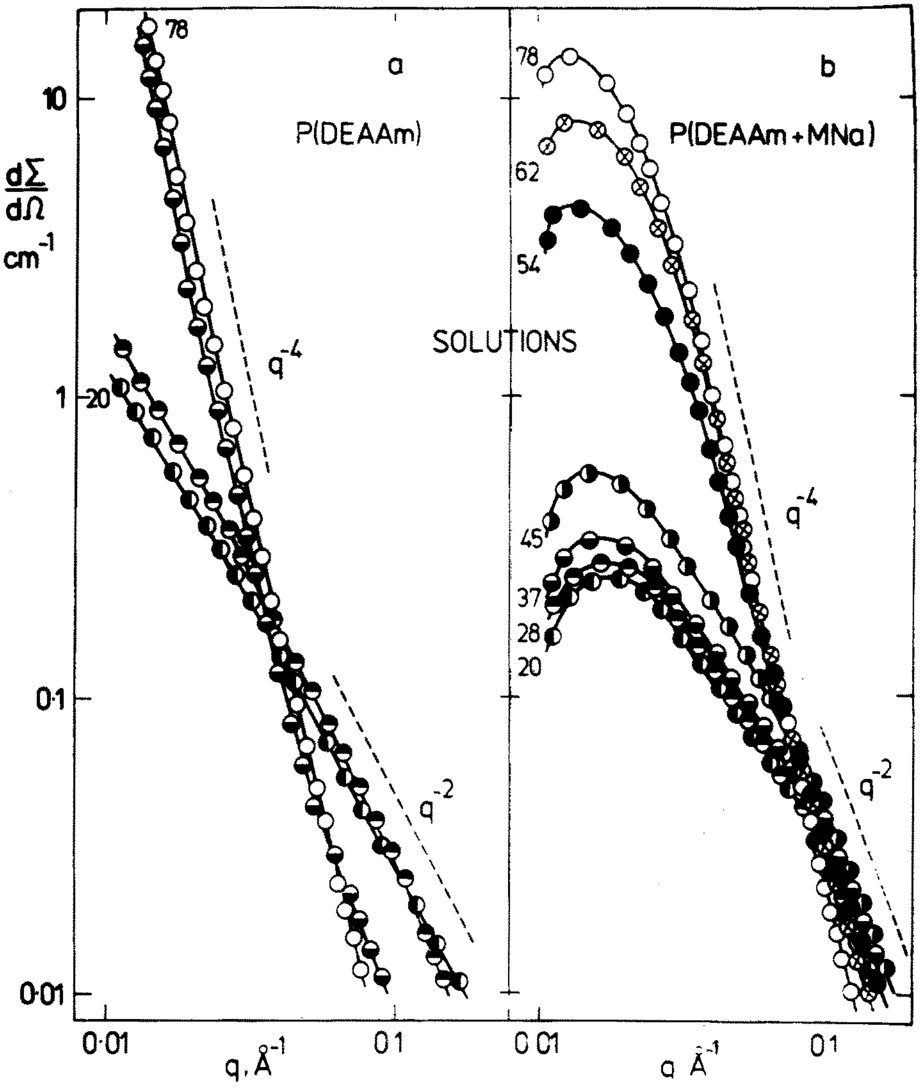

Figure 2. SANS curves of 0.4 wt.-%, a) PDEAAm, b) P(DEAAm+MNa) solution. Temperature of measurement: ◐ 20°C, ◓ 28°C, ◒ 37°C, ◑ 45°C, ● 54°C, ⊗ 62°C, ○ 78°C

cross-section dΣ/dΩ of all PDEAAm samples are strongly temperature-dependent (Figs 1 and 2). The basic features of the scattering behaviour are common for networks and solutions. At low temperatures the scattering curves have a range in which $d\Sigma/d\Omega \sim q^{-2}$. This dependence is characteristic of scattering from polymer coils; a similar behaviour may also be expected for strongly swollen networks. At high temperatures the scattering curves have a region in which $d\Sigma/d\Omega \sim q^{-4}$. Such faster decrease corresponds to the presence of more compact structures in solutions and gels, compared with that at low temperatures. Thus, a change in the exponent from -2 to -4 reflects the transition from the expanded into the collapsed state of the network or chain.

The dependence of the slope $S=d(d\Sigma/d\Omega)/dq$ for networks and solutions on temperature can be seen in Fig.3. It is obvious that in the case of the ionized network N2 and solution S2 the transition from the expanded to the collapsed state proceeds at a temperature by 10-15°C higher than for uncharged samples; the transition temperature is the same for both the network and the solution. The transition is shifted to higher temperature due to the presence of charges on the chain. The swelling and mechanical measurements of PDEAAm networks led to the same conclusions (14).

Fig.3 and the scattering curves at higher $q \sim 0.1$ Å^{-1} seem to indicate that in all samples the transition from the coil to more compact structures is a continuous one, and that it is less steep in the case of an ionized solution and network than in the case of uncharged samples. The continuous transition of the ionized network is somewhat surprising, because it was found (14) that the presence of charges is a necessary condition for jumpwise changes in the swelling and mechanical properties of PDEAAm networks. This finding is probably related with the time régime of the SANS measurements, which did not allow the swelling equilibria to be achieved in the collapsed state in both networks. At high temperatures, the network N2 with MNa component may lie further from the quilibrium than the network N1 without charges; the time needed to reach equi-

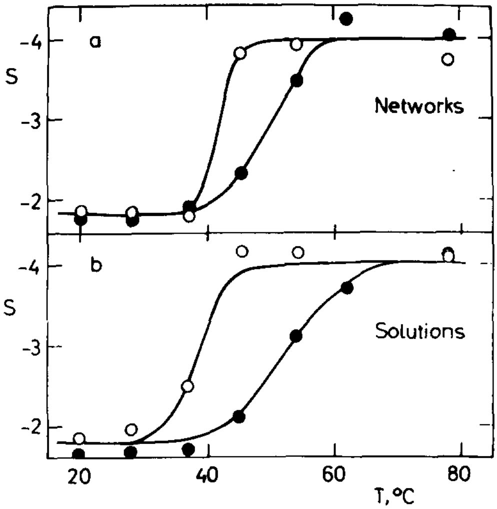

Figure 3. Temperature dependence of the slope $S=d(d\Sigma/d\Omega)/dq$ of a) PDEAAm networks, b) PDEAAm solutions. ○ PDEAAm, ● P(DEAAm+MNa)

librium in the collapsed state of the gel is weeks by the order of magnitude.

The scattering curves of samples with charges have a maximum at $q \sim 0.025$ Å^{-1} (network N2 - Fig.1b), or at $q \sim 0.012$ Å^{-1} (solution S2 - Fig.2b) at all temperatures. It is likely that here we have an analogy of the maximum observed in SANS from polyelectrolyte solutions, where already a very small charge density (~1% of charged monomer units) leads to considerable changes in the intermolecular correlation of segments, compared with the neutral polymer (27). So far, there is no satisfactory explanation of the finding that structural changes produced by a collapse are not accompanied by a shift of the maximum.

From the tail of scattering curves measured at room temperature, the weight per unit length of the chain, M_L, and the radius of gyration of the chain cross-section, R_C, were determined (26) for both networks, $M_L = 48$ and 47 Å^{-1}, and $R_C = 5.5$ and 4.9 Å, respectively, for the networks N1 and N2. From the structure of the monomer unit it is possible to estimate M_L=51 Å^{-1} and the minimal value R_C=3.6 Å for the PDEAAm chains (assuming a circular homogeneous cross-section of the chain). The determined M_L values are close to the theoretical value, and R_C is reasonably higher than the estimated minimal value. This suggests that at room temperature the local chain structure in the network does not essentially differ from the local chain structure in solution.

The situation in solutions is complicated by the fact that at the given molecular weights the sizes of macromolecules in the expanded state are too large from the SANS viewpoint. At temperature below the transition, the apparent radii of gyration R_z and the molecular weights M_w obtained from the SANS curves are, respectively, lower by one order of magnitude and by two orders of magnitude than those obtained by light scattering. This results from the fact that the SANS data are available only for $q \geq 0.01$ Å. Table 1 therefore contains values of the parameters R_z and M_w determined from SANS data of the

Table 1

z-Average radius of gyration of particles, R_z, and particle weight, M_w, determined from SANS curves of solutions

T [°C]	R_z [A]	M_wx10^{-6}	R_z [A]	M_wx10^{-6}
	PDEAAm-S1		P(DEAAm+MNa)-S2	
25	950*	4.4*	670*	1.8*
37	180	7.0	-	-
45	185	11.1	-	-
54	185	12.4	92	0.58
62	-	-	95	1.20
70	-	-	104	1.70
78	186	10.4	103	2.20

*Values determined by light scattering in 1 M KSCN.

solutions only for temperatures in the transition range and higher, where the determined weights of the particles are comparable to, or higher than, the molecular weight of macromolecules. R_z and M_w values determined by light scattering are given in Table 1 for 25°C.

In the collapsed state (above the transition temperature) the particle sizes are roughly five times smaller than in the expanded state. From M_w and R_z, the polymer density in the particle can be estimated ($d \sim M_w/R_z^3$). In the expanded state we obtain $d \approx 0.001$ g/cm^3, while in the collapsed state it is higher by two orders of magnitude ($d \cong 0.1-0.4$ g/cm^3). These estimates were obtained without taking into account non-uniformity in the molecular weights of particles, which would lead to a still higher particle density in the collapsed state.

In may be said, in conclusion, that the small-angle neutron scattering is sufficiently sensitive for the determination of phase transition in swollen polymer networks. In particular, it may contribute to the determination of detailed chain conformation in both the expanded and collapsed state.

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