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Phase transition in swollen gels

13. Dynamic mechanical behaviour of poly (N, N-diethylacrylamide) networks and solutions in the collapse region

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Summary

The dynamic mechanical behaviour of 4% aqueous solutions and networks of poly(N,N-diethylacrylamide) and copolymers of diethylacrylamide with sodium methacrylate (MNa) (molar ratio x_{MNA}=0–0.05) swollen in water was measured in the temperature range 20–80°C. With increasing temperature, at T_c polymer chains collapse from random coil to more compact globular conformations. While in the region of coil conformations ($T > T_c$) the mechanical behaviour of solutions has a liquid-like character (the loss modulus G" is higher than the storage modulus G' for a constant frequency $\omega = 1$ Hz), in the region of globular conformations ($T > T_c$) a heterogeneous physical network is built in solutions, and the mechanical behaviour has a solid-like character (G' > G"). In networks the collapse is reflected in an increase of storage modulus G'; the magnitude of this increase decreases with ionization. The dependence of the loss modulus G" on the temperature of solutions and networks allows us to conclude that the magnitude of losses in the collapsed state is affected rather by x_{MNa} (the modulus G" increases with increasing ionization) than by the heterogeneous structure of the samples.

Introduction

Depending on temperature, poly(N,N-diethylacrylamide) (PDEAAm) networks with a small number of charges on the chain and swollen in water undergo the first-order phase transition (collapse), reflected in a jumpwise change in the gel volume following an infinitesimal change in temperature (1,2). Such collapse can also be brought about by a change in the ionization (3,4) (pH value), by applying an external electric field (5), by deformation (6) or by changing the composition of the mixed solvent in swollen gels (7,8). The jumpwise change in the gel volume is accompanied by a jumpwise change in both the equilibrium shear modulus (8) and the complex dielectrical permittivity (9), or in the stress-optical coefficient (10). In the first approximation the experimental data can be described in terms of the swelling equilibria of polyelectrolytic networks (11). SANS experiments (12) have led to a conclusion that, while in the expanded state the chains are coil-shaped, in the collapsed state they have a compact globular structure.

The transition from the expanded state into the collapsed one and vice versa is controlled by diffusion of the solvent in the gel (13,14). It was found (13) that the kinetics of swelling and deswelling of the gel is determined by local motions of the polymer network controlled by the diffusion equation, in which the diffusion coefficient D is given by the ratio of the bulk modulus of network, K, to the frictional factor f (between net-

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*To whom offprint requests should be sent work and liquid). Whereas in samples having the volume ~1 cm^3 the transition from one equilibrium state into another takes several days, for submicron spheres this time is several seconds only (15) (it was found that the relaxation time τ of transition of the network into equilibrium $\tau \sim R^2/D$, where R is the radius of the sphere).

This study deals with the measurement of the temperature dependence of a dynamic shear modulus $G^*(=G'+iG'')$ of ionized and nonionized solutions and networks of poly(N,N-diethylacrylamides) in the range of phase transition in water. Such measurements allow us to characterize both the resistance against deformation (storage modulus G') and the magnitude of mechanical losses (loss modulus G") in the collapse.

Experimental

Sample Preparation. Poly(N,N-diethylacrylamide) (PDEAAm) networks were prepared by the copolymerization of 8 ml DEAAm in the presence of 0.05 g N,N'-methylenebisacrylamide as the crosslinking agent, 100 µl N,N'-tetramethyethylene diamine, 2 ml 1 wt.% solution of ammonium persulfate and sodium methacrylate (MNa). To these components, redistilled water was added in order to complete the volume to 100 ml. Four networks with a varying MNa content were prepared so as to make the mole fraction of MNa in the chain x_{MNa} = 0, 0.01, 0.025, and 0.05. The PDEAAm solutions were prepared similarly, but without the crosslinking agent, using only 4 ml DEAAm for the polymerization; four solutions were prepared, having the same mole fraction of MNa as the networks. The polymerization of networks and solutions proceeded ~12 h at 1°C; conversion of the monomer was above 99%.

Dynamic Mechanical Measurements. The complex shear modulus $G^*(\omega)$ ($=G'+iG''$, where G' and G" respectively is the storage and loss modulus) was measured using a Rheometrics IV apparatus in a geometrical arrangement of parallel plates with the plate radius 2.5 cm. While with solutions a shear oscillation deformation mode was chosen (distance between the plates ~2 mm, angular deformation ~0.1), the networks were measured with dynamic compression mode (sample diameter ~2 cm, sample height ~2 cm; shear modulus $G^*=E^*/3$ was calculated from the measured complex Young modulus E^*). Two types of experiments were carried out at a constant frequency ω=1Hz:

a) measurement of temperature dependences of the components G', G" in the temperature range 20-80°C at a constant rate of heating of the sample ~1°C/min, and

b) measurement of time dependences of the components G', G" in the time interval 0-100 min at jumps of temperature; the measurement started at room temperature T_0=25°C, and at a time t=10 min the temperature was raised jumpwise from T_0 to T_x=52, 60, 70, and 80°C for networks and solutions having respectively x_{MNa}=0, 0.01, 0.025 and 0.05 ($T_x=T_c+20$°C, where T_c is the cloud temperature of the samples). At t=70 min, the temperature was decreased jumpwise from T_x to T_0=25°C. All measurements were carried out with samples after completed polymerization.

Results and Discussion

Temperature and Time Behaviour of Solutions. From the temperature dependences of the moduli of solutions (Fig. 1) one can see that at low temperatures the loss modulus G" is higher than G', which is a characteristic feature of the dynamic mechanical behaviour of liquids. With the solutions of PDEAAm alone, both G' and G" increase quickly at T_c=32°C and both dependences intersect each other, so that for T > 32°C we already have G' > G". Also, the solution turns milky at T_c (2). As follows from SANS experiments (12), at T_c the conformation of PDEAAm chains in water changes (collapse of the chains) from random coils ($T < T_c$) to globular structures

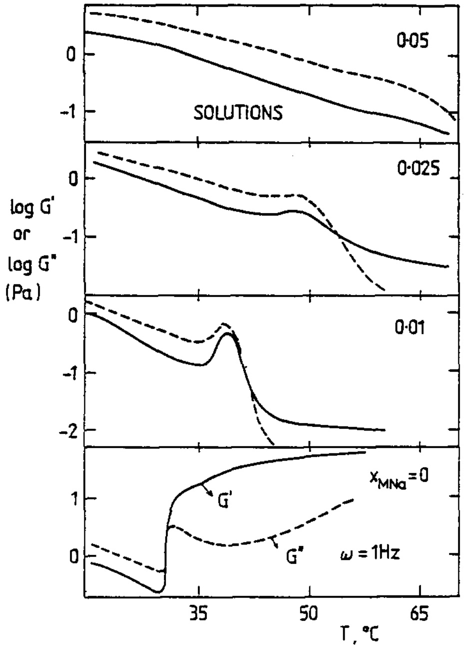

Fig. 1. Dependence of the storage G'(Pa) and loss G"(Pa) component of the dynamic modulus on temperature for PDEAAm solutions

($T > T_c$). This is a consequence of the decreasing quality of water-PDEAAm chains interaction (the Flory-Huggins interaction parameter χ increases). Dynamic mechanical measurements show that the globular structure of PDEAAm chains leads to the formation of a physical network, and thus to G' > G", which is characteristic of the solid-like mechanical behaviour. Turbidity of the sample suggests, however, that the structure thus arising is a heterogeneous one: domains of separated water probably exist inside the network. The increase in the storage modulus G' with temperature in the range $T > T_c$ can be interpreted by the increasing quality (stronger interactions or increasing concentration of the contacts) of the arising heterogeneous physical network with temperature. The good quality of the network is also indicated by the G' value for $T > T_c$, which is higher by an order of magnitude, compared with G' in the range $T < T_c$.

With increasing MNa content the magnitude of the increase in G' and G" decreases, and both dependences intersect each other at higher T_c values ($T_c \doteq 40$° or 50°C for $x_{MNa} = 0.01$ or 0.025 respectively). The rise in the T_c values of ionized solutions is a result of the increasing chain polarity with increasing x_{MNa}. The smaller increase in the storage modulus G' and its further decrease with temperature in the range $T > T_c$ suggest that the introduction of ionized groups into the chain interferes with the structure of the heterogeneous physical network, causing the network quality to decrease. The finding that the solution with the highest x_{MNa}=0.05 value behaves as a liquid within the whole range of measurement (G" > G') without turning milky also satisfies the interpretation given above.

One can see in Fig. 2 that jumpwise changes in temperature are markedly reflected in the time dependence of both components of the modulus of all solutions. In all cases at T_0=25°C and times t < 10 min, G" > G'. A rise in temperature from T_0 to T_x (=T_c+20°C) in a nonionized solution leads to a a rise in the modulus G' and a drop in G" with G' > G" within the whole time

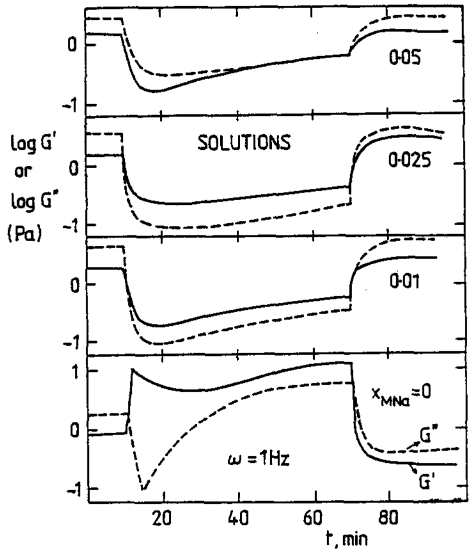

Fig. 2. Dependence of the storage G'(Pa) and loss G"(Pa) component of the dynamic modulus on time at a jumpwise change in temperature from T_o to T_x (t=10 min) and from T_x to T_o (t=70 min) for PDEAAm solutions

interval 10 < t < 70 min. The dependence of G' and G" on time in this interval suggests that after the rise in temperature the quality of the heterogeneous physical network is highest (high G', low G"). With increasing time G' first decreases, then slightly increases; G" increases within the whole time interval. Such dependences are given by the development of the structure of the heterogeneous physical network. A jumpwise decrease in temperature from T_x to T_o causes a decrease in both components of the modulus, and for t > 70 min the nonionized sample again behaves as a liquid (G" > G'). The lower G" and G' values in the range t > 70 min compared with the initial G" and G' values (in the range t < 10 min) suggest that somewhat more coiled conformations of polymer coils than those present at the beginning are preserved in solution.

With ionized solutions, a rise in temperature from T_o to T_x causes a decrease in both components of the modulus (Fig. 2), and the time dependences intersect each other. The lower values of both G' and G" in this region compared with the initial ones indicate that the heterogeneous physical network shows resistance against deformation and losses lower than the initial solution. A somewhat different behaviour in this region has been observed with the sample having x_{MNa}=0.05. The liquid character of the deformational behaviour is maintained also after the jumpwise rise in temperature, and the observed agreement between both components of the modulus (G'=G") in times t > 30 min seems to suggest that an infinite structure (analogy of the gel point) has just been formed in the sample. Decrease in temperature from T_x to T_o makes both components of the modulus increase in all the three ionized samples, reaching roughly the same values as at the beginning. As expected, in this range (t > 70 min) the deformational behaviour of the samples is again of the liquid type.

Temperature and Time Behaviour of Networks. As expected for permanent networks, in all cases G' > G", with the observed dependences of the components of the modulus on temperature and time being simpler than analogous dependences observed with solutions (Figs 3 and 4). With increasing temperature the storage modulus G' increases (Fig. 3). The dependences are S-shaped; with increasing MNa content the inflexion point of the curves Ti

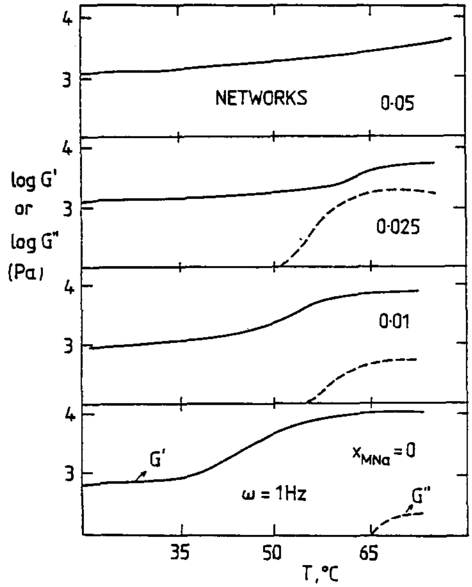

Fig. 3. Dependence of the storage G'(Pa) and loss G"(Pa) component of the dynamic modulus on temperature for PDEAAm networks

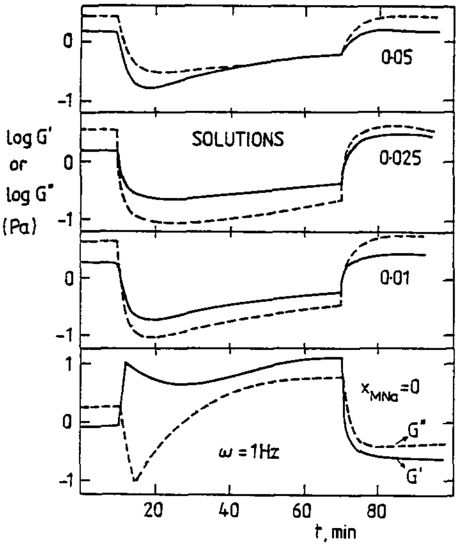

Fig. 4. Dependence of the storage G'(Pa) and loss G"(Pa) component of the dynamic modulus on time at the jumpwise change from T_o to T_x (t= 10 min) and from T_x to T_o (t=70 min)

is shifted to higher temperatures (T_i = 44°, 52° and 62°C for networks having x_{MNa}=0, 0.01 and 0.025), and the magnitude of increase of the modulus G' decreases. The increase in G' is due to the formation of a heterogeneous structure in the networks, and the temperatures T_i correlate with the cloud points of the samples T_c ($T_i=T_c$+12°), which are the same as those of the corresponding solutions (beginning of the increase in G' is situated roughly at T_c values). With the most ionized network (similarly to an analogous solution) no heterogeneous structure is formed (the sample is slightly opalescent, and the G' vs. T dependence is not S-shaped).

It is of interest that with increasing ionization the temperature at which the loss modulus G" increases above 10^2 Pa is shifted to lower values, and the magnitude of the increase in G" increases. Thus, it seems that the magnitude of the losses is rather affected by the number of polar groups on the chain than by the heterogeneous structure of the samples (networks after the preparation have approximately the same modulus G'=10^3Pa, which means that their network densities are virtually identical). An exception in this respect can again be observed with the most ionized network, the G" values of which are very low within the whole range of temperatures.

In all cases the jumpwise change in temperature from T_o to T_x leads to an increase in the storage modulus G' (Fig. 4); the magnitude of the increase decreases with increasing ionization. In the time interval $10 < t < 70$ min the heterogeneous structure of the networks has higher G' values than those in the homogeneous state. A further decrease in temperature from T_x to T_o at t=70 min reduces the modulus G' to roughly the same value as that at the beginning. In this case too (similarly to the temperature dependences) one can see that with increasing ionization both the magnitude of the losses (absolute G" value) and the time interval in which the loss modulus G" > 10^2 Pa increase. In this case too the most ionized sample is an exception, and its modulus G" < 10^2 Pa within the whole time interval used in the measurement.

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