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Phase transition in swollen gels

14. The DC conductivity of swollen poly(N,N-diethylacrylamide) gels in the collapse region

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Summary

The DC conductivity of two networks — a poly(N,N-diethylacrylamide) network (N1) and a network prepared by the copolymerization of N,N-diethylacrylamide with 3 mol.% of sodium methacrylate (N2) — in deionized water in the temperature range 10 - 55°C was measured. While in the low-temperature range (expanded gel state) the volt - ampere (V - A) behaviour of both networks shows a semiconductive character (conductivity increases with increasing temperature), in the high-temperature range (collapsed gel state) the conductivity of the network N1 rapidly decreases with increasing temperature (metallic character). The presence of charges on the chain raises the conductivity and shifts the temperature of the change in conductivity to higher values. In the collapse region of the ionized network N2 anomalies were observed on the V - A characteristics.

Introduction

A number of swollen polymer networks, when subjected to a change in the external parameters (composition of the solvent, temperature and the like), undergo a phase transition of the first - order (collapse), at which the change in volume may range from one tenth to one thousand times (1 - 4). The transition may also be accompanied by jumpwise change in other physical characteristics of the gel, such as the shear modulus (3,4), the refractive index (5,6), the stress-optical coefficient (5) or components of the complex dielectrical permittivity (6). A change in the gel volume in the collapse is given by a change in the chain conformation. SANS experiments showed (7) that, while in the expanded state the chains have the shape of coils, in the collapsed state they have the shape of compact globular structures. The necessary conditions for occuring of the collapse is the presence of a small number ($\approx 1-5$ mol.%) of charges on the chain (3,4).

The majority of the experiments were carried out with polyacrylamide gels, where the charges were introduced on the chain either by a spontaneous hydrolysis of amide groups to carboxylic groups (1,4), or by the copolymerization with a suitable monomer (sodium methacrylate (3) or sodium acrylate (8)). In these gels the collapse may be brought about by a change in the composition of the mixed solvent water - acetone. On the other hand, in ionized networks of poly(N,N-diethylacrylamide) (PDEAAm) the collapse can be brought

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*To whom offprint requests should be sent about by a change in temperature in water alone (9). While in the low-temperature range water is a good solvent for PDEAAm chains (the interaction Flory – Huggins χ parameter is less than 0.5), with increasing temperature the polymer – water interaction deteriorates, and for $T > 35°C$ water is already a poor solvent ($\chi > 0.5$). Experimental swelling data for both systems have been compared with the theory of swelling equilibria of polyelectrolyte networks (10).

The measurement of the dielectric behaviour of PAAm networks showed (6) that a change in complex permittivity ϵ^* in the collapse depends not only on the magnitude of change in the gel volume, but also on frequency; this means that the ϵ^* value is also affected by the mobility of charge carriers. An investigation of the phase transition of submillimetre particles of poly(isopropylacrylamide) gels in water led to a conclusion (11) that in the critical point transition takes an infinite time, the thermal expansion becomes infinitely large, and the gels undergo internal critical density fluctuations. Moreover, it was found (12) that in a constant electrical field polyelectrolyte gels swollen in water and based on polymethacrylic acid show current oscillations with a frequency between 0.01 and 0.2 Hz.

This study is dealing with an investigation of the DC conductivity of nonionized and ionized poly(N,N-diethylacrylamide) networks swollen in water as a function of temperature.

Experimental

Sample preparation: The nonionized network (N1) was prepared from 100 ml of an aqueous solution which contained 8 ml N,N–diethylacrylamide (DEAAm), 0.05 g N,N'-methylenebisacrylamide (MBAAm, crosslinking agent), 120 μl N,N'-tetramethylethylene diamine, and 4 ml of a 1 wt.% solution of ammonium persulfate in water; in the case of the ionized network (N2), sodium methacrylate (MNa) was added so as to make the mole fraction of MNa on the chain equal 0.03. Deionized water was used in the preparation. The solutions were dosed into ampoules having the diameter 20 mm, cooled to 1°C and flushed with nitrogen. After that, the ampoules were sealed and the polymerization proceeded at 1°C for ≈ 12 h.

Conductivity measurements: The DC volt – ampere (V – A) characteristics were measured with a microcomputer – controlled Keithley 617 electrometer. The sample was placed in a thermostated measuring capacitor (Fig.1). The core of the capacitor is made from polymethylmethacrylate, the external jacket is of brass; the sample inside the capacitor is fully closed to avoid its deswelling during the measurement. Electrodes (flat for current measurement and needle – shaped for voltage measurement are made from platinum. The distance between the current electrodes is 30 mm, that between voltage electrodes is 10 mm. The V – A characteristics were measured by the four – points metod (cf. scheme Fig.2) using samples with the diameter 20 mm, directly after completion of the polymerization. Such procedure restricts the effect of the space charge and of the polarization of the electrodes. The measurements were carried out in the temperature range 10 – 55°C, from the lowest temperature upwards. The sample was thermostated ≈ 30 min before each measurement. At each temperature about 10 – 15 values of voltage U and current I were measured.

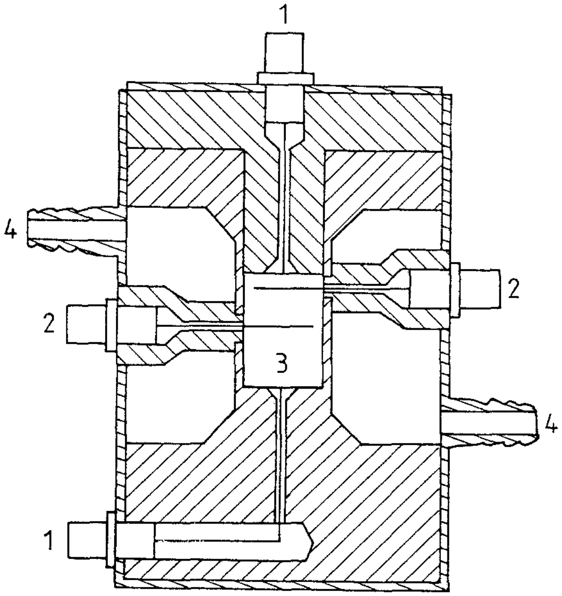

Figure 1: Sectional view of the measuring capacitor for measurements of volt – ampere characteristics. 1 – flat electrodes, 2 – needle electrodes, 3 – sample, 4 – temperance

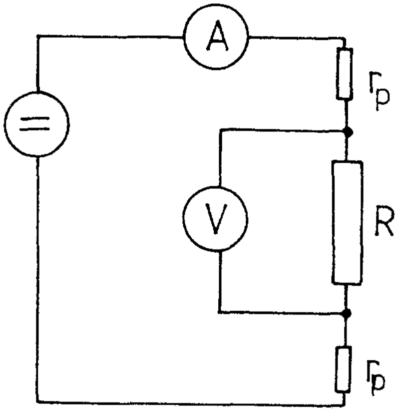

Figure 2: Substitute scheme of the four – point method of measurement. R – sample resistance, r_p – resistance of supply leads and electrodes

Results and Discussion

An example of the measured V – A characteristics of the nonionized network N1 can be seen in Fig.3. With increasing value of the field applied to the sample the current I passing through it linearly increases with the increasing voltage U on the needle electrodes, for all constant temperature measured. A somewhat different behaviour can be observed with the ionized network N2. In the low-temperature range (expanded state below the critical temperature of collapse, T_c) the conductivity behaviour of the network N2 resembles that of the network N1. In the temperature range corresponding to the collapse ($T_c \approx 52 - 54$°C) the V – A characteristics ceases to be linear and the behaviour of the gel changes (Fig.4). One can see that starting from a certain limiting value of the field applied to the sample, its further increase is accompanied by a decrease in both the current I passing through the sample and in the voltage U between the needle electrodes, which may be due to the polarization of the electrodes. This finding impeded the measurement of the V – A characteristics of the ionized network for temperatures $T > 55$°C.

From linear part of the V – A dependences (Figs 3 and 4) the resistance values $R = U/I$ were determined, where U is the voltage on the needle electrodes and I is the current passing through the sample. Hence, R is the resistance value of a 1 cm sample having the diameter 2 cm. It can be seen in Fig.5 that depending on temperature, two distinctly different conductivity regions can be found in the nonionized network N1. While in the region of the

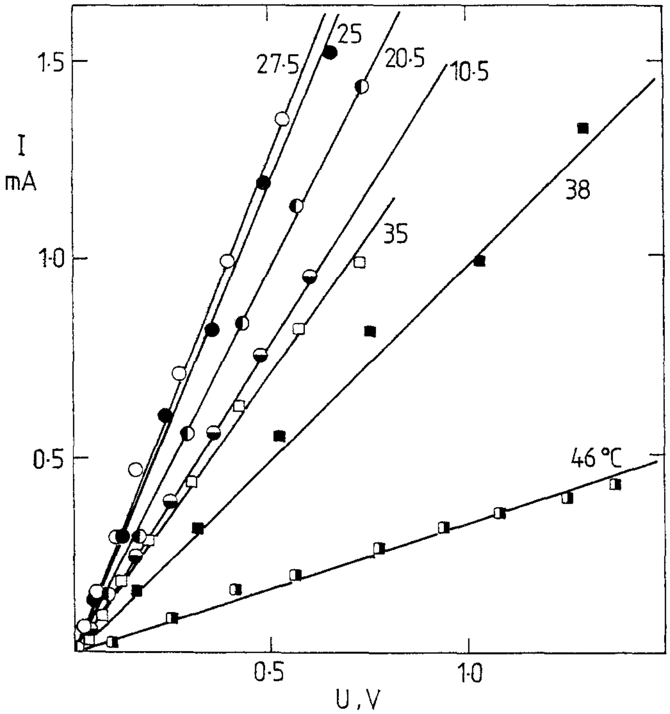

Figure 3: Volt – ampere characteristics of the nonionized network N1. Numbers at straight lines denote the temperature of measurement in °C

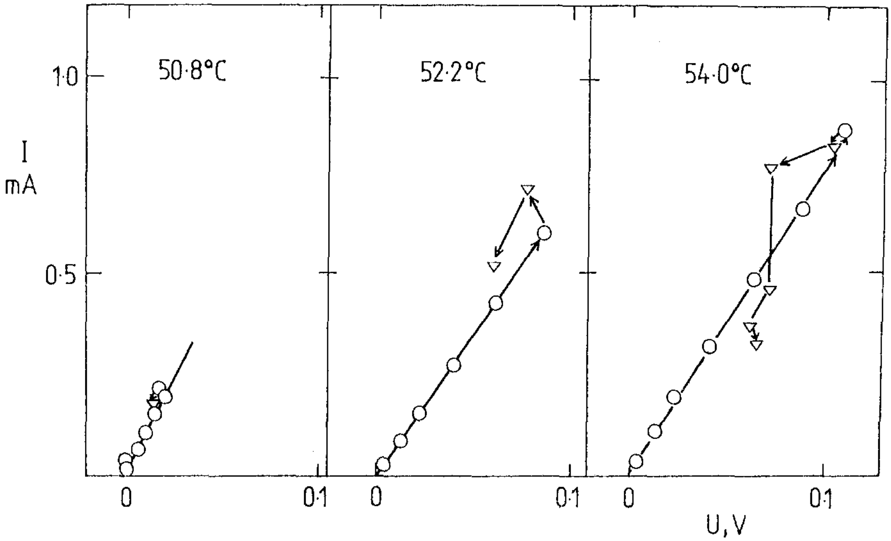

Figure 4: Volt – ampere characteristics of the ionized network N2 for temperatures in the collapse region. Arrows denote the order of measurement

expanded state ($T < 30°C$) a decrease in the resistance R can be observed with increasing temperature (semiconductivite character of conductivity),in the range of the collapsed state ($T > 35°C$) R increases with increasing temperature (metallic character of conductivity). Due to the insufficient thermostating time of the sample in the range $T > 35°C$, a heterogeneous structure is formed and the network is turbid ($\approx$ 50 - 100 days are needed to reach the equilibrium degree of swelling in this region).

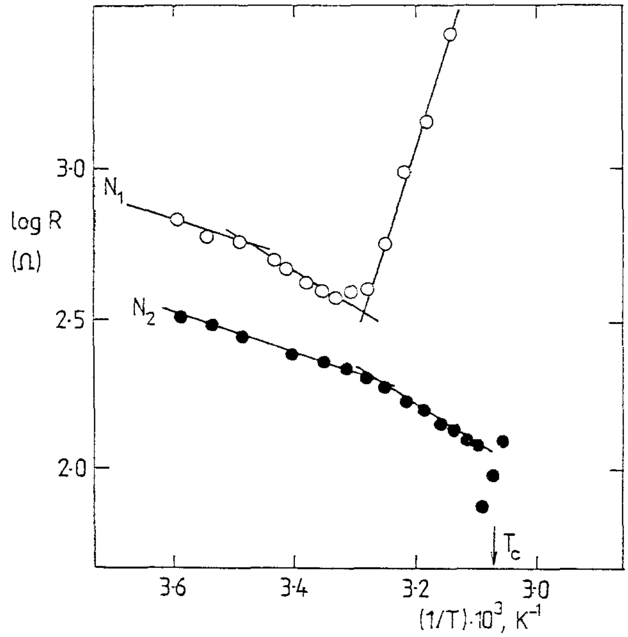

Figure 5: Dependence of resistance $R(\Omega)$ on reciprocal temperature $1/T$ (K^{-1}). T_c - the temperature of collapse

In the region of the semiconductive behaviour of the network N1 (Fig.5) two regions can be found, possessing somewhat different activation energies, $\Delta U_1 = -0.13$ eV and $\Delta U_2 = -0.24$ eV (the change takes place at $T \approx 15°C$). The change in the activation energy of conductivity, which probably has a proton character, may be related to a change in the mobility of PDEAAm chains. On the other hand, the region of metallic conductivity ($T > 35°C$) is characterized by a high positive activation energy $\Delta U_3 = 1.24$ eV. The rise in the resistance with temperature, i.e. the change in the character of conductivity in the collapsed state is probably related to the heterogeneous structure of the gel. According to this view, conductivity would be given by jumps of the proton between the individual water clusters separated in particular regions of the heterogeneous structure of the gel.

The conductivity behaviour of the ionized network N2 at temperatures $T < T_c$ (expanded state) resembles that of the network N1 (Fig.5). Much lower values of resistivity R and the observed change in conductivity at the higher temperature in comparison with the network N1 is given by the presence of MNa during network formation (9). The torn-off free counterions Na^+ raise the conductivity of the gel and improve the P(DEAAm - MNa) - water interactions (the critical temperature of collapse increases $T_c \approx 50°C$). In this case too in the expanded state of the ionized gel (semiconductive behaviour, $T < 45°C$) two regions can be observed possessing the same activation energies ΔU_1 and ΔU_2 as in the network N1. The independence of the activation energies of the presence of MNa suggests that the change in ΔU is probably given by a change in the mobility of PDEAAm chains in the network.

Although measurements in the collapse region of the ionized network N2 ($T \approx 52-54°C$) are not exact, it seems that a further increase in conductivity takes place here (Fig.5). To prove the character of conductivity of the network N2 in the collapse region and at even higher temperatures ($T > T_c$) other types of measurements will have to be employed (e.g., the contact - free method of measurement of alternating conductivity by using mutual inductance). Work in this respect is underway.

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