

# SAXS, SANS and photoelasticity of poly(*N,N*-diethylacrylamide) networks: 1. Structure changes after temperature jumps

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The development of microphase separation after temperature jumps in poly(*N,N*-diethylacrylamide) hydrogels was studied by means of small-angle neutron (SANS) and X-ray (SAXS) scattering. The curves of excess SANS and SAXS for temperature jumps from 25 to 30°C were different in character from those for jumps from 30 to 35°C. After the temperature jump from 25 to 30°C two polymer phases with different water content are formed (excess scattering intensity  $I_{ex} \sim q^{-2}$ , where  $q$  is the length of the scattering vector); however, after the jump from 30 to 35°C the dilute phase is formed by water droplets (pronounced two-phase structure,  $I_{ex} \sim q^{-4}$ ). Photoelastic measurements on the equilibrium swollen samples indicate that correlations exist between side groups at temperatures greater than or equal to 33°C. The association of side groups leads to microsineresis and to the differences observed in scattering behaviour.

(Keywords: hydrogel; microsineresis; poly(*N,N*-diethylacrylamide); small-angle X-ray scattering; small-angle neutron scattering; photoelasticity)

## INTRODUCTION

Due to polymer–diluent incompatibility, a sudden change in external conditions (such as temperature) usually leads to microphase separation of the solvent in swollen gels<sup>1–3</sup>. Depending on the amount of excess solvent, and size of heterogeneities, turbidity in the gel can be observed. In swollen non-polar networks an increase in swelling with increasing temperature is usually found. On the other hand, in hydrophilic networks swollen in water the opposite behaviour is observed, which means that the increase in temperature leads to phase separation. Heterogeneous structure and its development will eventually affect the physical properties of swollen networks.

With poly(2-hydroxyethyl methacrylate) (PHEMA) gels and with copolymers of HEMA and methacrylamide, in the range of incipient turbidity induced by the increase in temperature, a pronounced increase in the stress-optical coefficient  $C$  has been observed<sup>4,5</sup>. Also, with poly(*N,N*-diethylacrylamide) (PDEAAm) hydrogels, exhibiting a steep decrease of swelling with temperature<sup>6</sup>, a large dependence of their photoelastic behaviour on

microphase separation has been found<sup>7</sup>. While the mechanical behaviour is affected by the swollen gel matrix, optical characteristics are mainly influenced by droplets of the excluded liquid phase. PDEAAm hydrogels with a small number of charges on the chain (> 1 mol%) undergo a first-order phase transition (collapse) reflected in a change in the gel volume by two orders of magnitude following change in temperature<sup>8</sup>. SANS experiments have led to the conclusion that, while in the expanded state the chains are coil-shaped, in the collapsed state they have a compact globular structure<sup>9</sup>. The coil–globule transition at collapse was also proved with poly(*N*-isopropyl acrylamide) hydrogels using static and dynamic light scattering<sup>10</sup>. This thermoreversible collapse has been observed in many investigations<sup>11,12</sup>.

Among the methods for characterization of hydrogels, small-angle scattering of X-rays and neutrons (SAXS and SANS, respectively) play an important role due to their sensitivity to the polymer–polymer correlations and to the presence of inhomogeneities in gels<sup>13–15</sup>.

This study deals with the investigation of microphase separation in the PDEAAm hydrogels with jumps in temperature. SANS and SAXS experiments, together with swelling measurements, have been carried out.

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Photoelastic measurements of PDEAAm gels swollen to equilibrium were also performed in the same temperature region.

## EXPERIMENTAL

### Sample preparation

The network was prepared from a mixture containing 8 cm<sup>3</sup> *N,N*-diethylacrylamide (DEAAm), 0.02 g *N,N'*-methylenebisacrylamide (crosslinker), 2 cm<sup>3</sup> redistilled water, 200 μl tetramethylethylenediamine and 0.4 cm<sup>3</sup> of 1 wt% aqueous solution of ammonium persulfate. The solution was bubbled with nitrogen in an ampoule and then dosed into a glass mould, 10 × 10 × 0.1 cm<sup>3</sup> in size. The polymerization proceeded at room temperature for 5 h. The plate was then cut into specimens, 5 × 1 × 0.1 cm<sup>3</sup> in size.

### Swelling

The specimens used for determination of the degree of swelling were first dried in vacuum to constant weight and then left in ampoules in ~100 cm<sup>3</sup> redistilled water at the given temperature to attain equilibrium. The volume fraction of the polymer in the swollen gel,  $v_2$ , was determined from the weight of the dry and swollen sample, assuming additivity of the polymer and water volumes. The temperature dependence of equilibrium swelling (characterized by  $v_2(T)$ ), together with the time dependences of swelling after temperature jumps from  $T_1$  to  $T_2$  (characterized by the ratio  $w(t)/w(t=0)$ , where  $w$  is the weight of swollen sample) were determined.

### Photoelastic measurement

The photoelastic characteristics in unidirectional extension were determined by using an apparatus described earlier<sup>16</sup>, where together with the force  $f$ , the optical retardation  $\delta$  in a de Sénarmont compensator could also be detected. The sample was deformed to an elongation  $\lambda$  ( $=l/l_0$ , where  $l$  and  $l_0$  are deformed and initial sample length, respectively). After 90 s of relaxation, the force  $f$  and optical retardation  $\delta$  were determined, the elongation was increased (in the range  $1 < \lambda < 1.2$ ), and the whole procedure was repeated. The modulus  $G$ , deformation-optical function  $A$ , and the stress-optical coefficient  $C = A/G$  were determined from<sup>16</sup>:

$$\sigma = f/S = G(\lambda^2 - \lambda^{-1}) \quad (1)$$

$$\Delta n = \delta\kappa_0/2\pi d = A(\lambda^2 - \lambda^{-1}) \quad (2)$$

where  $\sigma$  is the stress related to the deformed cross-section  $S$ ,  $\kappa_0 = 546.1$  nm is the wavelength of the light used,  $\Delta n$  is the birefringence and  $d$  is the deformed sample thickness. The measurements were performed on the equilibrium swollen samples immersed in water in the temperature range 20–60°C. The cross-section and thickness of the deformed sample were calculated from the respective undeformed characteristics, assuming that the volume of the sample in the rubbery state is constant during deformation.

### Small-angle X-ray scattering

Scattering curves were registered on a Kratky Compact camera (A. Paar, Graz, Austria) equipped with a position-sensitive detector (OED-50, MBraun, Munich, Germany) using Ni-filtered CuK $\alpha$  radiation (wavelength 1.54 Å) from a conventional X-ray tube (Philips,

Eindhoven, The Netherlands). The scattering curves were corrected for collimation errors by means of Glatter's desmearing program DESMGLAT<sup>17</sup>.

### Small-angle neutron scattering

Measurements were made with a time-of-flight small-angle spectrometer attached to the IBR-2 pulsed reactor. A more detailed description of the experimental procedures can be found in an earlier paper<sup>18</sup>. Scattering intensities  $I$  are presented as a function of the length of the scattering vector:

$$q = (4\pi/\lambda) \sin \theta$$

where  $\lambda$  is the wavelength of neutrons and  $2\theta$  is the scattering angle. Measurements were carried out on samples swollen with D<sub>2</sub>O. Background correction was based on the measured scattering from mixtures with different H<sub>2</sub>O/D<sub>2</sub>O ratios. The intensity corresponding to a H<sub>2</sub>O/D<sub>2</sub>O mixture containing the same number of hydrogen atoms in the irradiated volume as the gel investigated, was determined using interpolation and subtracted from the intensity scattered from the gel. For this purpose, time variations of the sample thickness and the volume fraction of the polymer were calculated from the results of swelling experiments. The use of H<sub>2</sub>O/D<sub>2</sub>O solutions for background correction is not quite rigorous. However, we believe that our results are not significantly affected by a possible inaccuracy in background subtraction because the signal-to-noise ratio is favourable (1.5 in the worst case).

## RESULTS AND DISCUSSION

### Swelling behaviour

A considerable deswelling of PDEAAm network occurs (Figure 1) with increasing temperature; the equilibrium volume fraction of the polymer in swollen state  $v_2$  increases from 0.15 to 0.7 within the temperature range 22–45°C, which is in accord with the results obtained earlier<sup>6</sup>. Both the degree of swelling and the temperature were sufficient to maintain the network in the rubber-like state and to obtain equilibrium values of photoelastic

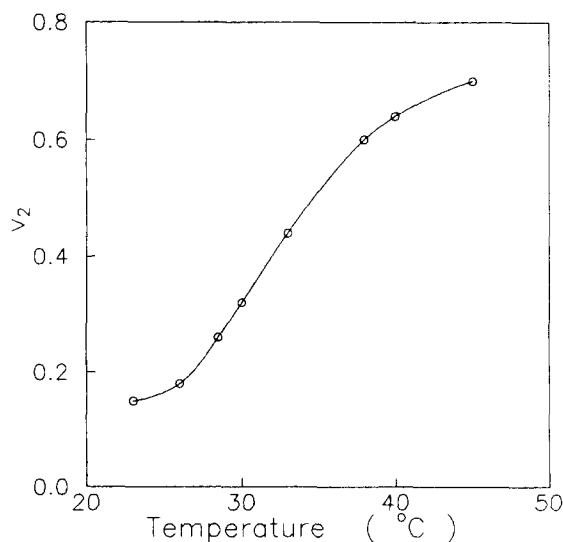


Figure 1 Temperature dependence of the volume fraction of polymer in the swollen gel,  $v_2$

functions. The time dependences of the swelling given by the ratio  $w(t)/w(t=0)$  after two temperature jumps from 25 to 30°C and 30 to 35°C are shown in Figure 2. In both cases, the jump in temperature gave rise to turbidity of the sample. Turbidity diminished with time and, after reaching a new equilibrium at the higher temperature, the sample became transparent again. The pronounced deswelling with temperature means that with increasing temperature polymer-polymer interactions are preferred to polymer-water interactions; the gel behaves as a system with a lower critical solution temperature<sup>19</sup>.

*Small-angle X-ray scattering*

Figure 3 shows the SAXS curve of PDEAAm gel in the equilibrium state at 25°C and the curves after the temperature jumps from 25 to 30°C or from 25 to 33°C recorded for 3 min. The equilibrium curves exhibit the expected behaviour. In the high- $q$  region, scattering comes from concentration fluctuations with correlation length of the order of several nanometres. The increase in scattered intensity at the lowest  $q$  values can be ascribed to long-range inhomogeneities in the gel<sup>20-22</sup>. After the temperature jump, a considerable increase in scattered

intensity is observed. This indicates that the presence of excess water (excess over the equilibrium water content at the higher temperature) leads to the formation of a non-equilibrium heterogeneous structure.

It is worth mentioning the different character of the excess scattering for the temperature jump from 25 to 30°C compared to that for the jump from 25 to 33°C (Figure 3). In the former case, the scattering intensity is proportional to  $q^{-2}$ , while after the jump to the higher temperature a much steeper descent ( $q^{-4}$ ) is observed. A possible reason of this distinction in scattering behaviour may consist in different compositions of the newly formed non-equilibrium phases. It is likely that, in the former case, the polymer content in the new phase is large enough to give rise to a Lorentzian-type excess scattering. In the latter case, the excess water is probably present as droplets with a minimum polymer content so that a distinct two-phase structure is formed. With a relatively sharp boundary between water and polymer phase this would lead to the observed scattering behaviour ( $I \sim q^{-4}$ ).

The excess scattering intensity decreases with time. This is accompanied by diminishing turbidity of the gel. The time needed to reach equilibrium depends on the sample dimensions. For the samples used in the SAXS experiments, with characteristic thickness of the order of 1 mm, an equilibrium state is reached in several hours.

Our SAXS data are rather uncertain at both margins of the  $q$ -range explored. The main sources of this uncertainty are the necessity to perform collimation corrections, and the relatively low scattering contrast between the polymer and solvent. In both aspects, employment of SANS is more advantageous for the system under study. For this reason, the SANS data will be used to obtain more detailed quantitative information on the structure changes in swollen PDEAAm network.

*Small-angle neutron scattering*

Time variation of the SANS curves after two temperature jumps, namely from 25 to 30°C (Figure 4a) and from 30 to 35°C (Figure 4b) was measured. The data collection time for one curve was 10 min at the beginning of each experiment. It will be shown later that this time is much shorter than the characteristic time of the process ( $10^2$  min).

A large increase (one to two orders of magnitude) in scattering intensity in comparison to the equilibrium state was observed at the smallest angles (Figure 4). It indicates inhomogeneity of the gel after temperature jumps. Similarly to the SAXS experiment, a striking difference is seen between the scattering behaviour after the jump to 30°C ( $I \sim q^{-2}$ ) and that for the jump to 35°C ( $I \sim q^{-4}$ ).

To facilitate presentation of the time variation of scattering behaviour, we characterized the excess scattering intensity (excess over the equilibrium scattering curves at higher temperature) by one parameter. For the jump to a final temperature of 30°C, we did not find any proper parameter simply related to some structure characteristics, and at the same time applicable to all of the recorded scattering curves. Therefore, we shall characterize the excess scattering intensity by its value at  $q = 0.02 \text{ \AA}^{-1}$ ,  $I_{ex}(0.02)$ . After the jump to 35°C, the excess scattering curves for  $q < 0.025 \text{ \AA}^{-1}$  are well fitted to the relation:

$$I_{ex} = A + C_4 q^4 \tag{3}$$

with  $A$  and  $C_4$  being constants describing asymptotic

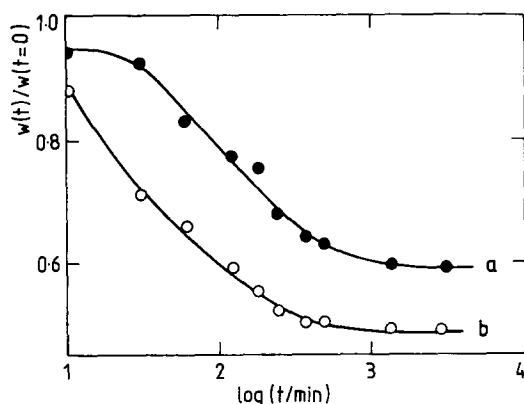


Figure 2 Time dependence of the weight ratio  $w(t)/w(t=0)$  at the temperature jump: a, from 25 to 30°C; b, from 30 to 35°C

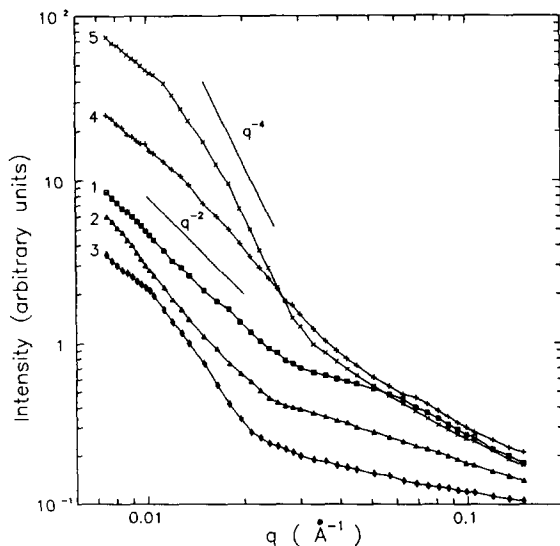
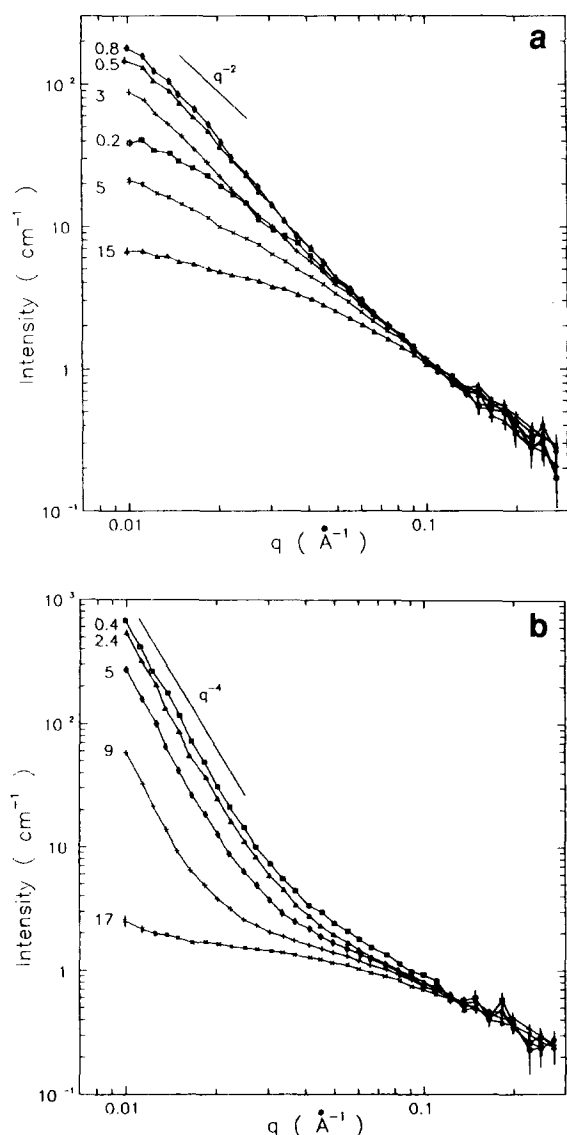


Figure 3 SAXS curves of PDEAAm hydrogel in the equilibrium state at 25°C (1), 30°C (2), 33°C (3) and those recorded for 3 min after the temperature jump from 25 to 30°C (4) and from 25 to 33°C (5)



**Figure 4** Time variation of SANS curves of PDEAAm hydrogel after temperature jumps from 25 to 30°C (a) and from 30 to 35°C (b). Numbers denote time elapsed in hours

scattering behaviour for a real two-phase system<sup>23</sup>. The parameter  $C_4$ , which is a measure of the interphase surface, has been chosen for characterization of the excess scattering intensity in this case.

Figures 5a and b show time dependence of the excess scattering characteristics ( $I_{ex}(0.02)$  and  $C_4$ ) together with that of the weight fraction of excess water  $w_{ex} = (w(t) - w(eq))/w(t)$  (excess over the equilibrium weight of the sample at final temperature,  $w(eq)$ ), obtained by extrapolation of the data from Figure 2). It can be seen that the time decrease of the scattering characteristics follows that of the weight fraction of excess water,  $w_{ex}$ , quite well for both temperature jumps. This suggests that the observed heterogeneity is closely related to the presence of excess water in the gel. An increase in  $I_{ex}(0.02)$  is observed for  $t < 1$  h after the jump from 25 to 30°C (Figure 5a); this can be explained by a finite rate of development of the new non-equilibrium phase.

The characteristic time,  $\tau$ , based on the assumption of exponential decay of the excess quantities  $w_{ex}$ ,  $C_4$  and  $I_{ex}(0.02)$  was determined to describe the approach to equilibrium after temperature jumps. The characteristic times for the excess water release were 110 and 220 min for the jumps to 30°C and 35°C, respectively. Very similar

values ( $\tau = 90$  and 220 min) have been obtained for the corresponding excess scattering characteristics.

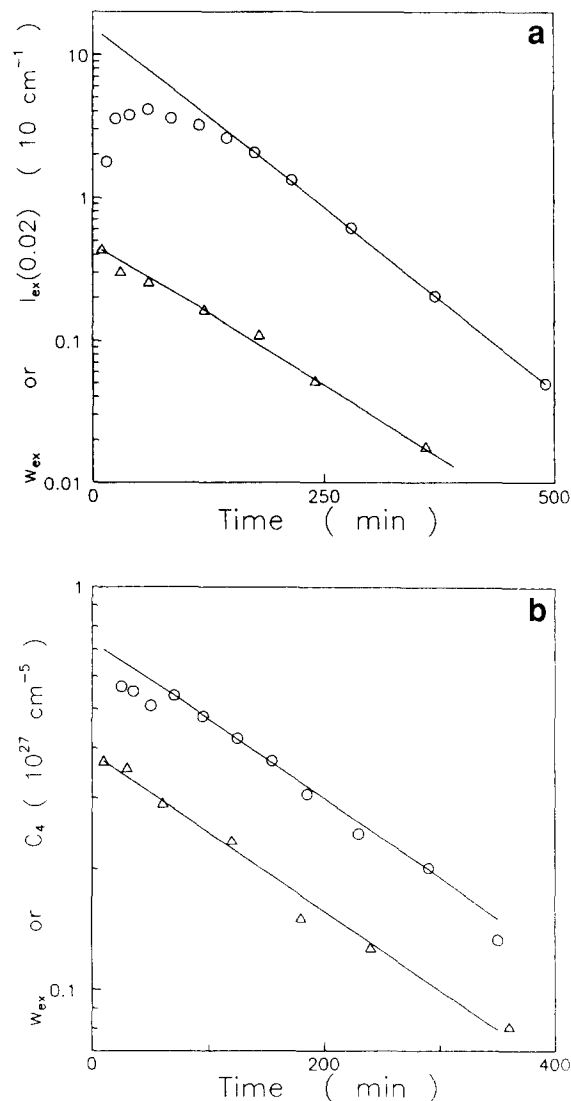
The higher  $\tau$  value found for the jump from 30 to 35°C, compared to that for the jump from 25 to 30°C, is probably connected with the difference in structure of non-equilibrium dilute phases. Photoelastic measurements suggest associations between side groups of PDEAAm at temperatures above 33°C, which probably increase the effective crosslinking density (see below). The phenomenon can also influence the rate of the deswelling process.

A certain time is needed to expel excess water from the gel, therefore regions enriched with water are expected to be formed. In further discussion we shall assume that after temperature jumps the gel contains two phases distinguished by their water content.

After the jump to 30°C the polymer content of both phases is high enough to give rise to Lorentzian-type scattering:

$$I(q) = I(0)/(1 + q^2\xi^2) \quad (4)$$

where  $\xi$  is the correlation length. An attempt was made to fit the SANS data to the sum of two Lorentzians.



**Figure 5** Time dependences of the weight fraction of excess water  $w_{ex}$  ( $\Delta$ ) and of the excess scattering characteristics ( $\circ$ ) after the temperature jumps from 25 to 30°C (a) and from 30 to 35°C (b). The solid lines represent an exponential fit. See text for respective characteristic times

Two Lorentzians ( $\xi_1=15\text{--}22\text{ \AA}$  for the dense phase,  $\xi_2=70\text{--}200\text{ \AA}$  for the dilute phase) were resolved in the curves recorded at  $t \leq 0.2\text{ h}$  and  $t \geq 3.5\text{ h}$  after the temperature jump. The correlation lengths obtained for the dense phase are close to the equilibrium value at the final temperature ( $\xi=21\text{ \AA}$ ), where the corresponding scattering curve is reasonably well described by one Lorentzian. At the intermediate times, the correlation length of the dilute phase,  $\xi_2$ , is too high to be detectable in the  $q$ -range covered by the present experiment. This means that a maximum is present in the time dependence of  $\xi_2$ . An example of the fitting is given in Figure 6. A departure from Lorentzian behaviour appears at  $q > 0.1\text{ \AA}^{-1}$ , where the single-chain effect begins to dominate<sup>20</sup>. This corresponds to a persistence length of about  $20\text{ \AA}$ , a value comparable to the correlation length in the dense phase.

For a description of the structure changes after the temperature jumps from  $30$  to  $35^\circ\text{C}$  we also use a two-phase model. Contrary to the previous case, however, we suppose that the dilute phase is formed by water droplets. The diameter of the droplets,  $D$ , can be estimated from the relation:

$$D = \frac{6}{S/V} \quad (5)$$

where the specific surface,  $S/V$ , is calculated from  $C_4$ , defined in equation (3) as<sup>24</sup>:

$$S/V = \frac{C_4/v}{2\pi(\rho_1 - \rho_2)^2} \quad (6)$$

where  $v$  is the volume fraction of droplets, and  $\rho_1$  and  $\rho_2$  are the scattering densities of the phases. In our case, the values of the scattering densities are assumed to be  $\rho_1 = 3.4 \times 10^{10}\text{ cm}^{-2}$  (mean scattering density of the gel at  $35^\circ\text{C}$  swollen to equilibrium) and  $\rho_2 = 6.3 \times 10^{10}\text{ cm}^{-2}$  (scattering density of  $\text{D}_2\text{O}$ ). Supposing that the droplets contain all the excess water,  $v$  is approximately equal to the weight fraction of the excess water,  $w_{\text{ex}}$ . The mean diameter of the droplets, as determined using equations (5) and (6) and the assumptions made above, slightly decreases with time from  $2000\text{ \AA}$  at the beginning

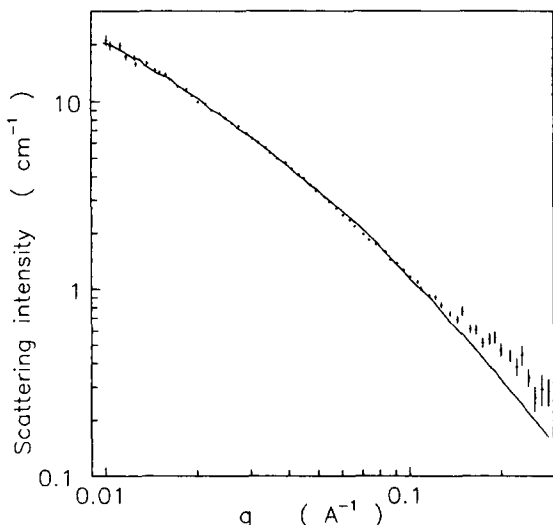


Figure 6 Scattering curve of PDEAAm hydrogel 5 h after the temperature jump from  $30$  to  $35^\circ\text{C}$ ; the solid line is a two-Lorentzian fit with  $I_1(0)=3.9(9)\text{ cm}^{-1}$ ,  $\xi_1=20(3)\text{ \AA}$  (dense phase) and  $I_2(0)=31(2)\text{ cm}^{-1}$ ,  $\xi_2=92(9)\text{ \AA}$  (dilute phase); see equation (4)

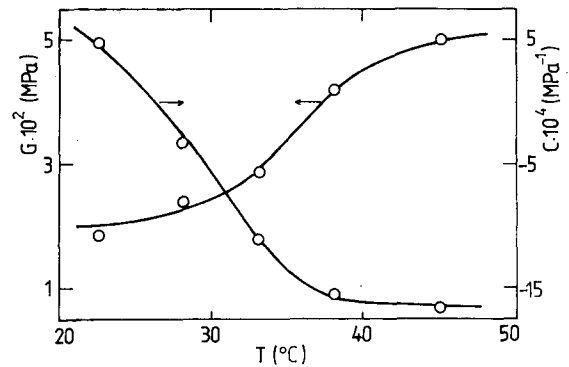


Figure 7 Temperature dependences of the modulus,  $G$ , and of the stress-optical coefficient,  $C$ , for the PDEAAm hydrogel in the equilibrium state

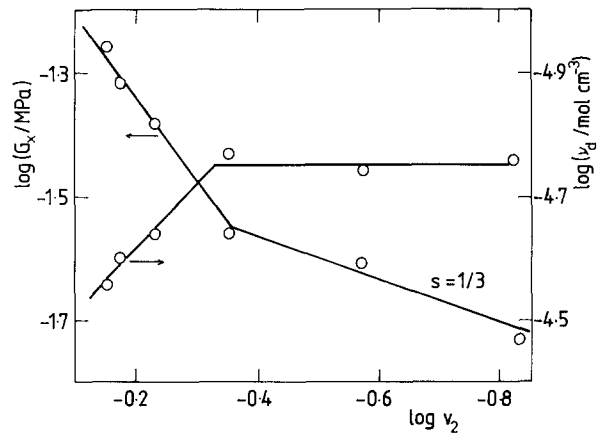


Figure 8 Dependence of the reduced modulus,  $G_x$ , and of the crosslinking density,  $v_d$ , on the volume fraction of polymer,  $v_2$ , for the PDEAAm hydrogel in the equilibrium state

of deswelling to  $1600\text{ \AA}$  after 5 h. This size is of the same order of magnitude as that observed by Huglin and Yip in poly(2-hydroxyethyl methacrylate) hydrogels<sup>25</sup>.

#### Photoelastic behaviour

As expected, the equilibrium modulus  $G$  increases with increasing temperature due to a pronounced deswelling (Figure 7). The dependence of the reduced modulus  $G_x = GT_x/T$  (where  $T_x = 298\text{ K}$  and  $T$  is the temperature of measurement) on the volume fraction  $v_2$  is shown in Figure 8. The slope  $s = 1/3$  in the dependence of  $\log G_x$  on  $\log v_2$  predicted by the kinetic theory of rubber elasticity<sup>19</sup> can be observed only in the region of high swelling (at low temperatures); at low swelling the increase of  $\log G_x$  with  $\log v_2$  is much faster ( $s \sim 1.3$ ). Owing to this fact, the concentration of elastically active network chains related to the dry volume  $v_d = G_x \times v_2^{-1/3} / v^0 RT_x$  (where  $v^0 = 0.77$  is the volume fraction of the polymer at network formation and  $R$  is the gas constant) is independent of  $v_2$  only at low temperatures ( $T < 33^\circ\text{C}$ ). However, at high temperatures ( $T > 33^\circ\text{C}$ ) it increases (Figure 8).

While the theory of Gaussian networks<sup>7,14,19</sup> predicts independence of the stress-optical coefficient  $C$  on  $v_2$ , Figure 7 shows a distinct decrease of  $C$  with deswelling of the network. A pronounced decrease can be observed in the low-temperature region ( $T < 35^\circ\text{C}$ ), where  $C$  decreases from the positive value  $5 \times 10^{-4}\text{ MPa}^{-1}$  to the negative value  $-15 \times 10^{-4}\text{ MPa}^{-1}$ . The high negative  $C$  value may be explained by assuming correlations between

side groups<sup>6</sup>. These correlations can cause the observed increase in the crosslinking density  $\nu_d$  in the high-temperature region (Figure 8). The association of side groups at low swelling is also supported by the earlier<sup>8</sup> observed independence of cloud-point temperature on the concentration of DEAAm in the polymerization DEAAm-water mixture without the crosslinker.

Therefore, we can conclude that the change in the dependence of the photoelastic functions of PDEAAm network swollen to equilibrium at  $T \geq 33^\circ\text{C}$  supports the observed differences between the scattering behaviour at the temperature jump from 25 to  $30^\circ\text{C}$ , and that at the jump from 30 to  $35^\circ\text{C}$ . The suggested associations at  $T > 33^\circ\text{C}$  lead to microsineresis, which causes more pronounced two-phase structure; as a result of this the small-angle scattering intensity is proportional to  $q^{-4}$  after the jump from 30 to  $35^\circ\text{C}$ .

## CONCLUSIONS

After a jump to higher temperature, the PDEAAm hydrogels become inhomogeneous due to the presence of excess water. The formation of heterogeneous structure is reflected in a strong small-angle scattering and turbidity of the sample. Both turbidity and scattering intensity decrease with time until a new equilibrium at the higher temperature is reached.

SANS curves indicate that in a non-equilibrium state, the hydrogel contains two phases, differing in their polymer contents. The dense phase probably corresponds to the equilibrium structure at the final temperature. The character of the non-equilibrium, dilute phase, formed after the temperature jump from 25 to  $30^\circ\text{C}$ , is different from that after the jump from 30 to  $35^\circ\text{C}$ . In the former case, the polymer content in the dilute phase is high enough to give rise to Lorentzian-type scattering, typical of swollen networks. In the latter case, the excess water is probably present as droplets with a diameter of roughly 2000 Å, with a minimum polymer content.

The change in the temperature variation of the equilibrium photoelastic functions, observed at  $33^\circ\text{C}$ ,

corroborates the concept of the association of side groups in PDEAAm gel at higher temperatures.

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