Photoelastic Behaviour

Phase Transition in Swollen Gels.
8. The Photoelastic Behaviour of Polyacrylamide Networks in the Collapse Region

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Summary

The photoelastic behaviour of two networks – polyacryl-
amide (PAAm) and of a network prepared by the copolymerization
of acrylamide with 5 mol.% sodium methacrylate – was investi-
gated in water-acetone mixtures. For the PAAm network the
dependence of all photoelastic characteristics on the com-
position of the mixture is continuous. At 54 vol.% acetone in
the mixture, the ionized network undergoes a transition which
gives rise to jumpwise changes in the shear modulus, defor-
mational-optical coefficient, C, and in the refractive index
of the gel, n_g. While in the collapsed state the optical
anisotropy of the statistical segment is negative,
$\Delta\alpha \sim -3 \times 10^{-24}$ cm^3 (indicating an interaction between the side
chains), in the expanded state it is positive, $\Delta\alpha \sim 0.5 \times 10^{-24}$
cm^3. The dependence of all optical characteristics on the
composition of the mixtures suggests that: (a) in both net-
works we have a transition between two conformational states
of the chain; while for the ionized network the transition is
a discrete one, for the nonionized network it takes place in
the range between ~30 and ~45 vol.% acetone in the mixture;
(b) in both networks the gels are optically homogeneous
throughout the whole range of compositions of the mixtures
(and thus also in the close vicinity of the collapse of the
ionized network).

Introduction

For loosely crosslinked polyacrylamide (PAAm) networks
with a low amount (~1-5 mol.%) of charges on the chain, phase
transition was observed on passing from the good (water) into
the poor (acetone) solvent, reflected in a distinct jumpwise
change in the macroscopic dimensions of the network (the
volume varies from ten to hundred times) following an in-
finitesimal change in the composition of the solvent (1-4).
While the increasing charge concentration stresses the extent
of the transition (2), both the increasing network density (5)
and decreasing dilution at network formation (6) reduce the
extent of the transition. The jumpwise change in volume was
reflected in a discontinuous change in the equilibrium modulus
of the gel. It may be expected that phase transition will also
be reflected in optical characteristics, viz., in the defor-
mational birefringence, stress-optical coefficient, or in the

refractive index of the gel. An investigation of changes in the deformational birefringence in the collapse range is also interesting because its value is dependent on the optical anisotropy of the statistical segment, and thus also on the detailed structure of the monomer unit, on the short-range interaction between the monomers, on the orientation of the solvent towards the monomer units and on the overall homogeneity of the gels (e.g., microphase separation markedly raises the birefringence value (7,8)). Moreover, the question regarding the homogeneity of PAAm networks is important because of a view (9,10) that it is the assumed heterogeneous structure of these gels (due to large dilution at formation of PAAm networks) that is responsible for the existence of the collapse and the change in physical properties.

In this study we examine the photoelastic behaviour of both non-ionized and ionized network in acetone-water mixtures; the ionized network was prepared by the copolymerization of acrylamide with a small amount of sodium methacrylate.

Experimental Part

Sample preparation: The networks were prepared from 100 ml of a mixture which contained 7 g acrylamide (AAm), 0.135 g N,N´-methylenebisacrylamide (the crosslinking agent), 150 µl tetramethylenediamine and 20 mg ammonium persulfate. To prepare the ionized network, sodium methacrylate (MNa) was added to the mixture in such an amount that the molar fraction of MNa related to the total amount of the monomers was $x_{MNa} = 0.05$. All components with the exception of ammonium persulfate were dissolved in redistilled water, and the solution was bubbled with nitrogen. After that, an aqueous solution of persulfate was added, the mixture was stirred and dosed into glass moulds, 10x10x0.1 cm^3 or 10x10x0.2 cm^3 in size. The polymerization proceeded at room temperature for 3 h; after that, the plates were cut into specimens, size 3x0.8x0.1 cm^3 or 6x1.5x0.2 cm^3, respectively. The specimens were extracted 48 h in redistilled water. After the extraction one part of the samples having the original thickness 0.2 cm was predried.

Swelling and photoelastic characteristics: The specimens after extraction were swollen in 500 ml water-acetone mixtures (20 mixtures in the range 0-80 vol.% acetone). After swelling in mixtures for 20 days, the swelling ratio X related to the network formation state was determined:

$$X = (t^*/t)^3 = V^*/V \tag{1}$$

where t^* is the thickness or width of specimens measured after network formation, t is the thickness or width of specimens after swelling in mixtures, and V^* and V respectively is the specimen volume after preparation and swelling in acetone-water mixtures. The X values in Fig.1 are the average from at least three measurements of the specimen thickness and width. From these values, the volume fraction of the polymer in the swollen state, $v_2 = v^O X$, can be calculated, v^O being the volume fraction of the polymer at network formation ($v^O = 0.052$).

The photoelastic measurements were carried out at room temperature using an apparatus described earlier (11), by which the relaxation of both force, $f(t)$, and optical retardation $\delta(t)$ could be determined (hence also the relaxation of bire-fringence $\Delta n(t) = \lambda_0 \delta(t)/2t_1$, where t_1 is the thickness of the deformed specimen and $\lambda_0 = 546.1$ nm is the wavelength of light). The measurements were performed with specimens immersed into the corresponding acetone-water mixtures; the force and retardation values were read off each time after 30 s of relaxation which in most cases was sufficient for reaching the equilibrium (with the exception of the least swollen specimens in the collapsed state). From the dependence of stress, $\sigma = f/S$ (S is the deformed cross-section of the specimen) and of birefringence, Δn on elongation Λ (in the range $1 < \Lambda < 1.2$), the initial modulus G, the deformational-optical function A and the stress-optical coefficient $C = A/G$ were determined, using the equations

$$\sigma = G(\Lambda^2 - \Lambda^{-1}) \qquad\qquad (2)$$

$$\Delta n = A(\Lambda^2 - \Lambda^{-1}) \qquad\qquad (3)$$

The refractive index n_g of swollen gels was recorded with an Abbe refractometer at room temperature.

Results and Discussion

Swelling and refractive index of gels

While the nonionized network shows a continuous dependence of the swelling ratio X on the acetone content in the mixture, a, a network with $x_{MNa} = 0.05$ has a pronounced discontinuity at a = 54 vol.%, corresponding to phase transition (Fig.1). A change in volume at gel collapse, $\Delta \log X \doteq 1.4$, roughly corresponds to the extent of the collapse of the PAAm network aged in the polymerization solution for 24 days (4).
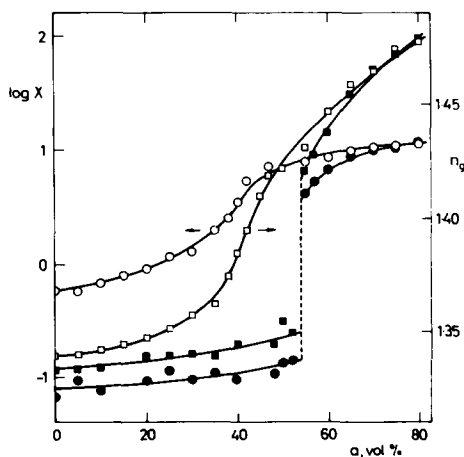

Fig.1. Dependence of the swelling ratio X ($\bigcirc$) and of the refractive index of swollen gel n_g ($\square$) on the acetone content a
$\bigcirc$, $\square$ nonionized network;
$\bullet$, $\blacksquare$ ionized network.

Due to phase transition, the ionized network undergoes a jump-
wise change also in the refractive index of the gel n_g at the
concentration a = 54 vol.%; the nonionized network displays
a continuous dependence of n_g on a (Fig.1). Even though the
refractive index of the solvent acetone-water varies somewhat
with composition (passes through a maximum in the range 75
vol.% acetone), it may be said that in the first approximation
n_g of the gel is determined by the swelling degree (dependence
of n_g on v_2 is roughly the same for both networks).

Photoelastic characteristics
        Similarly to the swelling ratio, the dependence of shear
modulus on the acetone concentration is continuous for the
PAAm network, while for the network with x_{MNa} = 0.05 a dis-
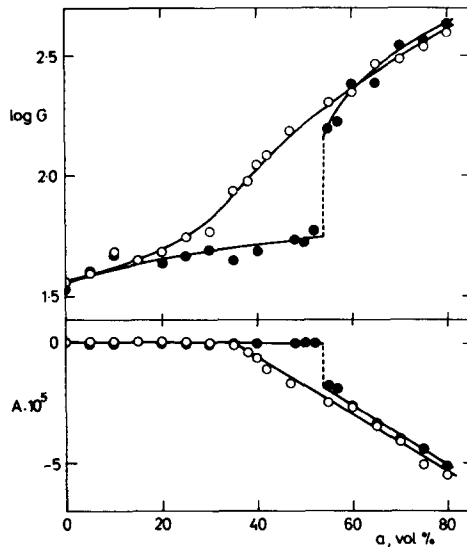continuity appears (Fig.2). The dependence of log G on log X

Fig.2. Dependence of the modulus G (g cm^{-2}) and of the
deformational-optical function A on the acetone content a
        O nonionized network;   ● ionized network

of the nonionized network in the range log X < 0.8 is linear,
with the slope s ± 0.6; a similar slope has been observed
earlier (2,4). On the other hand, however, a change in the
modulus accompanying the collapse of the ionized network
Δ log G = 0.4 is somewhat smaller than one would expect on
the basis of earlier results (2) obtained with specimens
polymerized in the form of cylinders.
        Also, for the deformational-optical function A (Fig.2)
and stress-optical coefficient C (Fig.3), continuous depen-
dences on the acetone concentration were recorded for the non-
ionized network, along with a discontinuity corresponding to
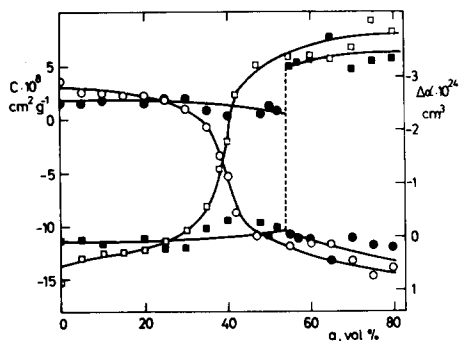phase transition for a network with x_{MNa} = 0.05 at the acetone

Fig.3. Dependence of the stress-optical coefficient C $(cm^2 g^{-1})$ ($\bigcirc$) and of the optical anisotropy of statistical segment (cm^3) ($\square$) on the acetone content in the mixture
$\bigcirc$,$\square$ nonionized network;
●,■   ionized network.

concentration a = 54 vol.%. The dependences of A and C on a are roughly the same for both networks, in the range of both low (expanded state) and high (collapsed state) acetone concentrations. This finding is a consequence of the existence of only a small quantity of sodium methacrylate in the nonionized network (moreover, the structure of MNa resembles that of AAm).

From the C values, the values of optical anisotropy of the statistical segment $\Delta\alpha$ were calculated using the relation (12)

$$\Delta\alpha = (45\ kT/2\pi)\,[n_g/(n_g^2 + 2)^2]\,C \tag{4}$$

where k is the Boltzmann constant and T is temperature. Fig.3 shows that the jumpwise change in the range of phase transition remained also in the dependence of $\Delta\alpha$ on a recorded for the ionized network. While small positive values are characteristic of the expanded state, $\Delta\alpha \sim 0.5 \times 10^{-24}\ cm^3$, the collapsed state is characterized by higher negative values $\Delta\alpha \sim -3 \times 10^{-24}\ cm^3$. Negative $\Delta\alpha$ values are usually found for polymers with side chains in monomer units; they indicate the existence of interactions between side groups in the collapsed state. An increase in swelling cancels these correlations, and the low positive $\Delta\alpha$ in the expanded state suggests a higher mobility of side chains. Such conclusion is in accord with theoretical calculations of the anisotropy values of various models of the monomer units of alkyl acrylates (13) and with photoelastic results obtained with networks of poly(alkyl acrylates) (13), polymethacrylic acid (14), and poly(N,N´-diethylacrylamide) (15).

Also for the nonionized network the change in $\Delta\alpha$ values (the same holds for C) takes place within a relatively narrow concentration range of acetone (from ~30 to ~45 vol.% in the mixture). A similar character of the dependence of the hydrodynamic radius or radius of gyration on the acetone concentration in the mixture acetone-water has been observed earlier (16) for PAAm solutions; in this case too there was a marked change in the radii of gyration in the concentration range $a \doteq 40$ vol.%.

With increasing n_g (increasing swelling) the stress-optical coefficient C quickly increases, the C vs. n_g depen-

dence remaining the same for both networks (Fig.4). A similar
increase of C with n_g has been observed earlier for ionized
gels of polymethacrylic acid (14). The independence of C vs n_g
on ionization is due to the fact that the introduction of
a small number of MNa does not cause any pronounced change in
$\Delta\alpha$ and that no specific interactions are caused by phase
transition which would lead to an anomalous rise in the C
values. It can also be said that samples of the ionized net-
work remain homogeneous also in the close vicinity of phase
transition (as has been pointed out earlier (7,8), the onset
of phase separation is reflected in a pronounced rise in
anisotropy $\Delta\alpha$). The quadratic increase of C with n_g may be
interpreted semiquantitatively by a contribution from the form
birefringence Δn_f (and thus the form contribution C_f) originat-
ing in the elastic network chain between the junctions for
which we have (14,17): $C_f \sim [(n_p^2 - n_g^2)/n_g]^2$ (where $n_p = 1.5365$
is the refractive index of dry PAAm). The overal value of the
stress-optical coefficient is $C = C_i + C_f$, where the contri-
bution $C_i = -15 \times 10^{-8}$ $cm^2 g^{-1}$ is then given by the intrinsic
anisotropy of the statistical segment. It can be seen in Fig.4
that the experimental dependence of C on n_g is adequately
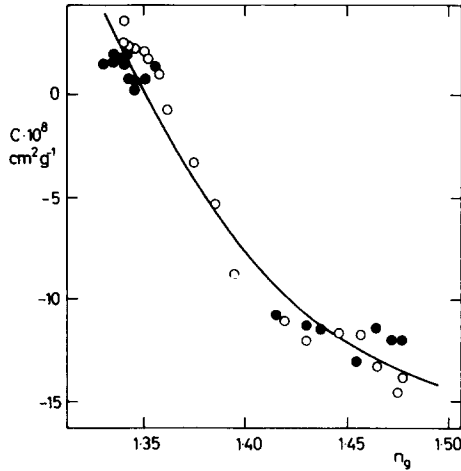described by the form contribution C_f.

Fig.4. Dependence of the stress-optical coefficient C $(cm^2 g^{-1})$
on the refractive index of swollen gel n_g

○ nonionized network, ● ionized network, —— dependence
given by shape contribution C_f ($C_f \sim [(n_p^2 - n_g^2)/n_g]^2$.

References

1. T.Tanaka, D.Fillmore, Shao-Tang Sun, I.Nishio, G.Swislow and A.Shah, Phys.Pev.Lett. $\underline{45}$, 1636 (1980).
2. M.Ilavský, Macromolecules $\underline{15}$, 782 (1982).
3. D.Nicoli, C.Young, T.Tanaka, A.Pollak and G.W.Whitesides, Macromolecules $\underline{16}$, 887 (1983).
4. M.Ilavský, J.Hrouz, J.Stejskal and K.Bouchal, Macromolecules in press.
5. M.Ilavský and J.Hrouz, Polym.Bull. $\underline{8}$, 387 (1982).
6. M.Ilavský and J.Hrouz, Polym.Bull. $\underline{9}$, 159 (1983).
7. M.Ilavský and W.Prins, Macromolecules $\underline{3}$, 415 (1970).
8. M.Ilavský, J.Hrouz and K.Dušek, J.Macromol.Sci.-Phys. $\underline{B19}$, 227 (1981).
9. V.F.Janas, F.Rodriquez and C.Cohen, Macromolecules $\underline{13}$, 977 (1980).
10. Hsu Tsong-Piu, Ma Dong Sung and C.Cohen, Polymer $\underline{24}$, 1273 (1983).
11. M.Ilavský and K.Dušek, Collect.Czech.Chem.Commun. $\underline{36}$, 1569 (1979).
12. L.K.G.Treloar, The Physics of Rubber Elasticity, Clarendon Press, Oxford 1958.
13. M.Ilavský, J.Hasa and K.Dušek, J.Polym.Sci. $\underline{C-53}$, 239 (1975).
14. M.Ilavský, E.Talašová and K.Dušek, Eur.Polym.J. $\underline{16}$, 191 (1980).
15. J.Hrouz, M.Ilavský, K.Ulbrich and J.Kopeček, Eur.Polym.J. $\underline{17}$, 361 (1981).
16. I.Nishio, Shao-Tang Sun, G.Swislow and T.Tanaka, Nature $\underline{281}$, 208 (1979).
17. V.N.Tsvetkov, in Newer Methods of Polymer Characterization, B.Ke, Ed., Wiley, N.Y. 1964, Chap. 14.