The Photoelastic Behaviour of the Ionized Poly(Acrylic Acid) Network
Comparison with Crosslinked Poly(Methacrylic Acid)

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Summary
     In loosely crosslinked networks of poly(acrylic acid) the degree of swelling passes through a pronounced minimum at a neutralization of about 15% obviously as a result of the formation of hydrogen bonds between ionized and nonionized carboxyl groups. In the same range the equilibrium modulus reaches a maximum, but the modulus related to the dry state is constant, as required by the theory of Gaussian networks. The sign of the stress-optical coefficient changes three times with increasing neutralization, which may be interpreted by the varying degree of orientation of the side group. In spite of this, however, the photoelastic behaviour of poly(acrylic acid) networks is simpler than that of poly(methacrylic acid) networks, and its interpretation does not require an assumption of the existence of correlated structures.

Introduction
     The presence and neutralization of ionizable groups on the chain makes possible a considerable change in the swelling equilibrium in polyelectrolyte gels, and thus also a change in the physical properties. Neutralization (ILAVSKÝ et al. 1980 b) or the decreasing NaCl concentration in an aqueous solution (ILAVSKÝ et al. 1980 a) leads to an increase in the degree of swelling of poly(methacrylic acid) gels (PMAA), accompanied by a decrease in the equilibrium modulus G_e. The decrease in G_e with neutralization may be described in terms of a modified kinetic theory, including the electrostatic and non-Gaussian contribution (HASA et al. 1975) and assuming that the statistical segment increases with ionization. However, the stress-optical coefficient passes through a pronounced maximum which has been interpreted as a consequence of the form contribution to birefringence of correlated structures in a lightly crosslinked PMAA network and in copolymers of MAA with 2-hydroxyethyl methacrylate; these domains are probably related with hydrophobic interactions (similar to the "globule-coil" transition in PMAA so-

lutions (cf. CRESCENZI 1968, LANDO et al. 1973). The heterogeneous structure of these gels has also been evidenced by direct measurement of the small-angle X-ray scattering (ILAVSKÝ et al. 1980 b).

This paper reports an investigation of the photo-elastic behaviour of loosely crosslinked poly(acrylic acid) network (PAA), which is compared with the behaviour of loosely crosslinked PMAA networks (ILAVSKÝ et al. 1980 b). It is known that aqueous PAA solutions do not exhibit anomalies which for PMAA are explained by the transition already mentioned. It has been observed earlier that the flow birefringence of PMAA solutions is much higher than that of PAA solutions (TSVET-KOV et al. 1963).

Experimental

The PAA network was obtained by the radical copolymerization of acrylic acid with a low amount (1 wt.-%) of ethylene dimethacrylate in the presence of 45 wt.-% of the mixed solvent water-dioxan (3.7 : 1 by volume) and 0.16 wt.-% azobisisobutyronitrile as initiator. After repeated extraction with water (six months) the individual samples were swollen in 1 M NaCl solution; the degree of swelling of these initial samples was determined by extraction and drying, and also by titration. Neutralization to the required degrees was carried out with concentrated NaOH. The internal degree of neutralization of the gel α_g was calculated from the stoichiometric degree of neutralization α with a correction to the exchange of H^+ and Na^+ ions (BRAUD and SELEGNY 1973),

$$\alpha_g = \alpha + [([H^+] - [OH])/C_H^- \cdot m_o]V \qquad (1)$$

where [ ] denote the molar ion concentration in the external solution, V is the volume of external solution and C_H^- is the concentration of ionizable groups (mol/g) and m_o the mass of the dry gel. The volume fraction of the polymer in the gel, v_2, was determined from the weight of the dry and swollen samples assuming additivity of the polymer and solvent volumes. The value of pH in the external solvent, pH_e, was checked before and after the deformation measurement. The refractive index of the gel, $\bar{n}$, was determined with an Abbe refractometer.

The photoelastic characteristics of swollen gels at 298 K were determined using an apparatus described earlier (ILAVSKÝ and DUŠEK 1977). The modulus G and deformation-optical function A were determined from measurements of the force f and extinction angle ϕ at various elongations of the sample λ ($1 < \lambda \leq 1.1$), using the equations

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

$$A = \mathcal{H}_o \phi / 2\pi d \ (\lambda^2 - \lambda^{-1}) \tag{3}$$

where S and d respectively are the deformed cross-section and thickness of the sample, and $\mathcal{H}_o$ = 546 nm. The stress-optical coefficient C=A/G was also determined (Table I).

TABLE I

Photoelastic and potentiometric characteristics of ionized PAA samples

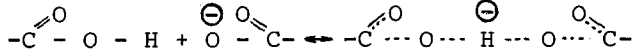| pH_e	α_g	$G \times 10^1$ MPa	$A \times 10^5$	$C \times 10^4$ MPa^{-1}	v_2
1.54	0.0	0.183	0.630	3.60	0.1567
2.57	0.013	0.173	0.530	3.05	0.1867
2.88	0.035	0.235	0.271	1.16	0.2345
3.14	0.072	0.295	-0.350	-1.18	0.2775
3.43	0.159	0.302	-0.590	-1.95	0.2883
4.01	0.256	0.177	0.055	0.31	0.1651
4.43	0.401	0.092	0.174	1.89	0.0573
4.98	0.595	0.082	0.019	0.23	0.0375
5.69	0.789	0.071	-0.123	-1.72	0.0347
7.59	0.983	0.063	-0.270	-4.29	0.0396

Earlier photoelastic data on the ionized loosely crosslinked PMAA network swollen in a 0.5 M NaCl solution (ILAVSKÝ et al. 1980 b) were used for comparison.

Results and discussion
Swelling and mechanical characteristics

In the range of higher degrees of neutralization ($pH_e > 4$) the volume fractions of polymer in the swollen state, v_2, decrease quickly both for the PAA and PMAA networks[2] (Fig.1). In both networks the degree of swelling passes through a maximum in the range of the highest pH_e. The main difference between the behaviour of the PMAA and PAA networks has been found at low degrees of neutralization, where for the PAA network a pronounced minimum of the swelling degree can be observed. This unexpected phenomenon has been observed earlier for the copolymer of acrylic acid with isoprene and divinylbenzene (BRAUD and SELEGNY 1973); also in the sorption of water vapours the water content in polyacrylic acid is almost constant up to the degree of neutralization 0.33, and increases steeply only with neutralization beyond this value (HIRAOKA and YOKOYAMA 1980). At lower degrees of neutralization there obviously is an increased interaction between the ionized

and nonionized carboxy groups mediated by the hydrogen
bond

$$-\overset{\displaystyle O}{\underset{\displaystyle}{C}} - O - H + \overset{\ominus}{O} - \overset{\displaystyle O}{\underset{\displaystyle}{C}} - \rightleftharpoons -\overset{\displaystyle O}{\underset{\displaystyle}{C}} \cdots O \cdots \overset{\ominus}{H} \cdots O \cdots \overset{\displaystyle O}{\underset{\displaystyle}{C}} -$$

which strengthens the polymer-polymer contacts and re-
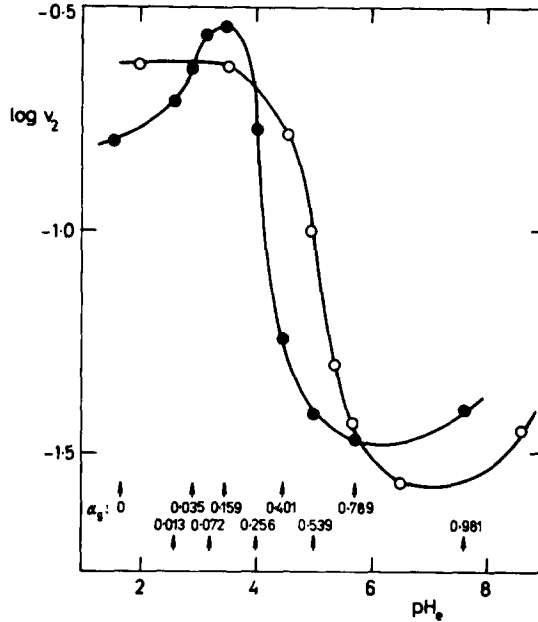duces the degree of swelling. Such an advantageous

Figure 1.   Dependence of the volume fraction of the gel
in the swollen state, v_2, on pH_e or on the
degree of neutralization of the gel, α_g
○ PMAA network, ● PAA network (α_g scale
related to PAA)

interaction may also be provided by a water molecule
incorporated between the ionized and nonionized carbo-
xyl groups. HIRAOKA and YOKOYAMA (1980) assume that co-
ordination of three carboxyl groups (six oxygen atoms)
around the cation is operative in this case; the form-
ation of a complex corresponds to a 33% neutralization.

   The dependence of the modulus G on the degree of
neutralization also differs for the PAA and PMAA net-
works (Fig.2). While for the PMAA network G is constant
at low pH_e, in the PAA network the dependence of G on
pH_e passes through a pronounced maximum which corres-
ponds to the minimum of the degree of swelling. A dif-
ferent behaviour is also exhibited by the modulus re-
lated to the dry state G_d ($=Gv_2^{-1/3}$) depending on v_2
(Fig.3), which according to the theory of ideal Gaus-

sian networks (DUŠEK and PRINS 1969) ought to be cons-
tant. While for PMAA the decrease in G_d with v_2 is very
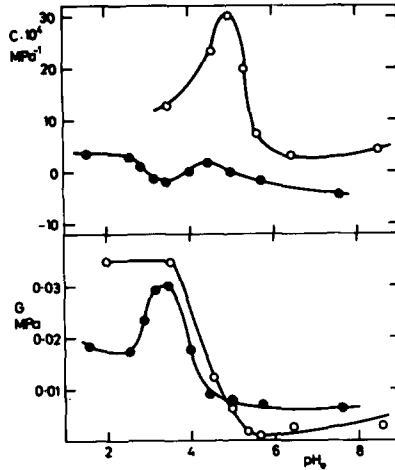

Figure 2.   Dependence of the stress-optical coefficient
            C and of the modulus G on pH_e
            O PMAA network, ● PAA network

pronounced (the slope of the log G_d vs log v_2 dependence
is q = 1.2), the same decrease for PAA is very small
(q=0.2). Moreover, in the case of PAA the dependence
of G_d on v_2 is monotonic, which suggests that the maxi-
mum on the dependence of G on pH_e is fully determined
by the degree of swelling, in agreement with the kine-
tic theory of rubber elasticity (volume effect of the
swelling agent on G). Thus, the mechanical behaviour of
the PAA network is closer to the ideal behaviour than
the behaviour of the PMAA network, where the high q has
been interpreted through the destruction of a correla-
ted structures (ILAVSKÝ et al. 1980 a,b). However,
a direct application of the theory of equilibrium be-
haviour of polyelectrolyte networks (HASA et al. 1975)
in the case of PAA leads to a physically improbable
increase in the number of units in the statistical seg-
ment up to 120 in the range of α_g in which G passes
through a maximum, thus indicating the complexity of
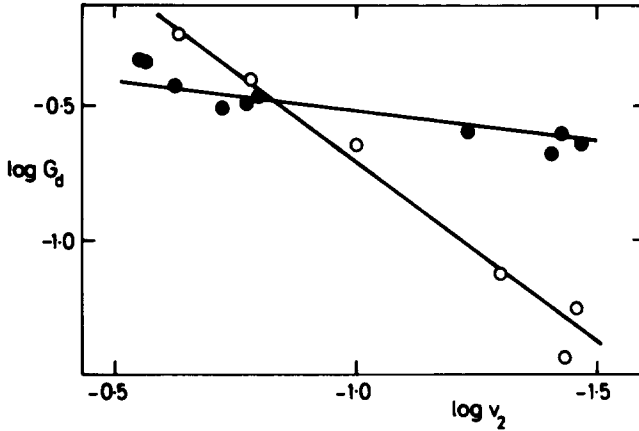interactions.

Figure 3. Dependence of the modulus related to the
dry state G_d (MPa) on v_2
○ PMAA network, ● PAA network

Optical characteristics

Still more pronounced differences than those bet-
ween mechanical characteristics can be observed bet-
ween the deformational birefringence of PMAA and PAA
networks. The stress-optical coefficient C of PAA chan-
ges its sign three times depending on pH_e (Fig.2);
a change in C from a positive to a negative value has
been observed earlier (KUHN 1953, TSVETKOV et al. 1963)
in the flow birefringence of PAA solutions. The C va-
lues of the PMAA network are positive and in the maxi-
mum of the dependence of C on pH_e reach values higher
by an order of magnitude than those obtained for the
PAA network (Fig.2).

The optical anisotropy of the statistical segment
calculated from the equation (TRELOAR 1958)

$$\Delta\alpha \quad = \quad (45kT)\bar{n}\ C/(\bar{n}^2+2)^2 2\pi \qquad (4)$$

(k is the Boltzmann constant) changes for the PAA net-
work from $\Delta\alpha = 0.95 \times 10^{-24} cm^3$ (for the nonionized
sample with $C = 3.6 \times 10^{-4} MPa^{-1}$) to $\Delta\alpha = -1.15 \times 10^{-24} cm^3$
(for the most ionized sample with $C = -4.3 \times 10^{-4} MPa^{-1}$).
In the case of the most ionized sample the negative $\Delta\alpha$
value is in accordance with the flow birefringence
measurement of PAA solutions (KUHN 1953, TSVETKOV et al.
1963) and poly(methyl acrylate) networks (ILAVSKÝ et al.

1975). A comparison of $\Delta\alpha$ with theoretical values of the intrinsic optical anisotropy of a monomeric unit $\Delta\beta$ for methyl acrylate (ILAVSKÝ et al. 1975) with partially relaxed rotations of the side group leads to the view of a fully released motion of the side group of the nonionized sample ($\Delta\beta = 0.74 \times 10^{-24}cm^3$) and of the side group orientation perpendicular to the main chain in the case of the most ionized sample $\Delta\beta = -0.9 \times 10^{-24}cm^3$). The initial neutralization of PAA gels first leads to the preferential orientation of the side chain in a direction perpendicular to the main one (C decreases to negative values), obviously due to the assumed role of hydrogen bond reflected in the minimum of the degree of swelling. Since with proceeding neutralization of gels the degree of swelling quickly increases, the orientation of side groups is weakened and the coefficients C and $\Delta\alpha$ again assume positive values. Owing to the high charge density on the chain at the highest degrees of neutralization the side groups again lose their mobility and assume an orientation perpendicular to the main chain.

Since no major change in the intrinsic anisotropy can be expected on transition from methyl acrylate to methyl methacrylate, the high positive values of the coefficient C of the PMAA network can be explained by the decisive form contribution of the assumed structural domains (ILAVSKÝ et al. 1980 b).

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