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Swelling and photoelastic behaviour of ionized hydrogels of poly(acrylic acid)

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Summary

The photoelastic and swelling behaviour of poly(acrylic acid) gels swollen in 1 M NaCl aqueous solution was studied as a function of crosslinking degree (1–5 wt.% ethylene glycol dimethacrylate) and degree of ionization $\alpha_g = 0 - 1$. The degree of swelling passes through a minimum at $\alpha_g \doteq 0.15$ regardless of the degree of crosslinking, probably due to the formation of hydrogen bonds between ionized and nonionized carboxyl groups. In the same neutralization region, the equilibrium modulus reaches a maximum; on the other hand, the modulus related to the dry state is independent of α_g for all crosslinker concentrations. Thus the mechanical behaviour of poly(acrylic acid) gels is in accord with the Gaussian theory and no contribution of permanent physical interactions to the modulus is observed. The optical behaviour is more complex – the sign of the stress-optical coefficient C_e changes three times with increasing α_g due to the orientation of the side groups. The analysis of the optical data shows that the C_e value is controlled by the degree of swelling and by the ionization.

Introduction

Polyelectrolyte gels exhibit a special physical behaviour for which the electrostatic interactions of ionized groups are predominantly responsible (1–4). The long-range character of Coulomb interactions and the effect of counterions, which ensure the electroneutrality, are main reasons for their complex behaviour. Several theoretical models have been suggested for interpreting thermodynamic properties of charged gels in which the effect of the repulsion of charges on the chain and finite chain extensibility were included (4–7). The strong inter- or intramolecular interactions may lead even to the formation of a secondary structure found in aqueous solutions and gels of ionized poly(methacrylic acid) (PMAc) (8–11). It was shown (12) that in particular stress-optical coefficient is sensitive to the secondary structure of PMAc gels, due to the form contribution of domains to the total birefringence. Heterogeneous structure of PMAc gels, probably formed by the hydrophobic interactions, was proved by the SAXS experiments (12). It is also known (13, 14) that aqueous poly(acrylic acid) (PAAc) solutions and gels do not exhibit anomalies which for PMAc are explained by the

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"globule-coil" transition. It was found (14) that the increasing neutralization and/or the decreasing salt (NaCl) concentration in aqueous solution leads to an increase in the swelling degree of PAAc gels, accompanied by a decrease in the shear modulus.

This paper reports an experimental investigation of the photoelastic behaviour of ionized, lightly crosslined poly(acrylic acid) gels swollen in 1 M NaCl aqueous solution. The results are compared with those obtained for ionized PMAc hydrogels (11, 12).

Experimental

Sample preparation

The five PAAc networks, S1, S2, S3, S4, and S5, were prepared by the radical copolymerization of acrylic acid with a low amount of crosslinker – ethylene glycol dimethacrylate (EDMA, $c = 1, 2, 3, 4$ and 5 wt.%) in the presence of 45 wt.% of water as diluent and 0.16 wt.% of azobisisobutyronitrile as initiator. The polymerization proceeded in Teflon moulds at 60°C for 8 h. After repeated extraction of the plates with water and drying, the individual samples ($\approx 0.1 \times 1 \times 5$ cm) were swollen in 50 ml of a carbonate-free 1 M NaCl solutions. Neutralization to required degrees was carried out with concentrated NaOH. The internal degree of ionization 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 (15)

$$\alpha_g = \alpha + V([H^+] - [OH^-])/(c'_H m_d) \tag{1}$$

where [ ] denote the molar ion concentration in the external solution, V is the volume of external solution, c'_H is the concentration of ionizable groups (mmol/g) and m_d is the weight of the dry gel. The correction for the ion exchange does not exceed 5% of the value of α.

Swelling and Cl^- ion determination

The volume fraction of the polymer in the gel, v_2, was determined from the weight of the dry (m_d) and swollen (m_s) sample assuming additivity of the volumes of the polymer and solvent from the equation

$$1/v_2 = 1 + (m_s/m_d - 1)(\rho_d/\rho_s) \tag{2}$$

where ρ_d and ρ_s, respectively, are densities of the dry gel and of the NaCl solution ($\rho_d = 1.3$ g cm^{-3} and $\rho_s = 1.038$ g cm^{-3}). The Cl^- co-ions, c_{Cl}, in the gel were determined by repeated extraction of the gel with water followed by potentiometric titration of Cl^- in the extract with 0.02 M $AgNO_3$. The pH values of NaCl external solutions were checked before and after the photoelastic measurements. The refractive index of the gel, n_g, was determined with an Abbe refractometer.

Photoelastic measurements

The strain-stress and strain-birefringence measurements of swollen samples were carried out at 25°C on an earlier described apparatus (16). The equilibrium shear modulus G_e and deformation-optical function A_e were determined from measurements of the force f and extinction angle ϕ (in a de-Senarmont's compensator) at various elongations of the sample $\lambda (1 < \lambda \leq 1.1)$ using the equations (16)

$$G_e = f/[S(\lambda^2 - \lambda^{-1})] \tag{3}$$

$$A_e = \kappa_o \phi/[2\pi d(\lambda^2 - \lambda^{-1})] \tag{4}$$

where S and d, respectively, are deformed cross-section and thickness of the sample, and $\kappa_o = 546$ nm is the wavelength. The stress-optical coefficient $C_e = A_e/G_e$ was also determined (Table 1).

Table 1: Photoelastic, swelling and potentiometric characterictics of PAAc hydrogels

Sample	α_g	pH	$G_e \times 10^1$ MPa	$A_e \times 10^5$	$C_e \times 10^4$ MPa^{-1}	v_2	c_{Cl} mol.l^{-1}	n_g
S1	0.000	1.54	0.183	0.630	3.60	0.1567	0.755	1.368
	0.013	2.57	0.173	0.530	3.05	0.1867	0.617	1.372
	0.035	2.88	0.235	0.271	1.16	0.2345	0.604	1.386
	0.072	3.14	0.295	-0.350	-1.18	0.2775	0.412	1.396
	0.159	3.43	0.302	-0.590	-1.95	0.2883	0.358	1.398
	0.256	4.01	0.177	0.055	0.31	0.1651	0.671	1.374
	0.401	4.43	0.092	0.174	1.89	0.0573	0.963	1.353
	0.595	4.98	0.082	0.019	0.23	0.0375	0.967	1.350
	0.789	5.69	0.071	-0.123	-1.72	0.0347	0.954	1.349
	0.983	7.59	0.063	-0.270	-4.29	0.0396	0.950	1.350
S2	0.000	1.54	0.492	0.920	1.85	0.1812	0.751	1.376
	0.014	2.54	0.500	0.610	1.29	0.2082	0.542	1.382
	0.037	2.91	0.605	-0.290	-0.48	0.2600	0.444	1.391
	0.082	3.17	0.730	-1.060	-1.45	0.2861	0.355	1.396
	0.180	3.65	0.590	-1.310	-2.22	0.2754	0.528	1.397
	0.286	4.05	0.480	-0.400	-0.83	0.1773	0.784	1.377
	0.445	4.46	0.393	-0.070	-0.18	0.0810	0.900	1.357
	0.661	5.01	0.315	-0.272	-0.86	0.0550	0.963	1.352
	0.877	5.65	0.280	-0.690	-2.46	0.0513	0.963	1.352
	1.000	7.33	0.252	-1.214	-4.82	0.0577	0.963	1.354
S3	0.000	1.51	0.735	0.620	1.44	0.1955	0.676	1.380
	0.015	2.50	0.700	1.060	0.88	0.2205	0.543	1.384
	0.038	2.85	0.830	-0.360	-0.44	0.2744	0.530	1.394
	0.079	3.13	0.970	-1.390	-1.43	0.2952	0.439	1.402
	0.178	3.69	0.870	-1.830	-2.11	0.2796	0.393	1.399
	0.277	4.03	0.750	-0.850	-1.13	0.1955	0.515	1.380
	0.435	4.38	0.550	-0.290	-0.52	0.1041	0.731	1.363
	0.645	4.99	0.500	-0.470	-0.95	0.0656	0.806	1.357
	0.855	5.66	0.480	-1.170	-2.43	0.0603	0.845	1.354
	1.000	7.33	0.400	-1.890	-4.74	0.0638	0.808	1.354

Table 1 (continued)

Sample	α_g	pH	$G_e \times 10^1$ MPa	$A_e \times 10^5$	$C_e \times 10^4$ MPa^{-1}	v_2	c_{Cl} mol.l^{-1}	n_g
S4	0.000	1.49	0.970	1.240	1.26	0.2186	0.665	1.384
	0.016	2.47	0.970	0.740	0.76	0.2390	0.511	1.388
	0.040	2.87	1.120	-0.820	-0.73	0.2952	0.430	1.400
	0.082	3.05	1.190	-1.620	-1.36	0.2906	0.356	1.401
	0.174	3.61	1.260	-3.200	-2.55	0.2872	0.302	1.404
	0.273	4.01	1.030	-1.880	-1.82	0.2142	0.507	1.385
	0.427	4.42	0.920	-0.700	-0.75	0.1156	0.665	1.366
	0.632	5.02	0.800	-0.930	-1.17	0.0771	0.740	1.357
	0.838	5.63	0.810	-1.650	-2.03	0.0715	0.749	1.356
	1.000	7.42	0.650	-2.670	-4.11	0.0743	0.720	1.350
S5	0.000	1.52	1.44	1.30	0.90	0.2390	0.726	1.386
	0.012	2.59	1.46	0.27	0.19	0.2704	0.471	1.394
	0.034	2.88	1.60	-1.66	-1.04	0.3126	0.360	1.402
	0.070	3.16	1.49	-2.93	-1.96	0.3322	0.367	1.410
	0.160	3.67	1.46	-3.70	-2.54	0.3139	0.359	1.404
	0.253	4.06	1.41	-2.67	-1.89	0.2339	0.456	1.386
	0.395	4.47	1.24	-1.01	-0.82	0.1312	0.641	1.366
	0.587	5.03	1.20	-1.36	-1.14	0.0924	0.706	1.359
	0.778	5.71	1.12	-2.52	-2.25	0.0853	0.723	1.358
	0.970	7.36	1.07	-4.46	-4.17	0.0898	0.720	1.359

Results and Discussion

Swelling and ionization of networks

As it follows from Figure 1 a roughly universal correlation between the α_g and pH exists for all networks. The swelling degree of the gels, $Q = 1/v_2$, is controlled by

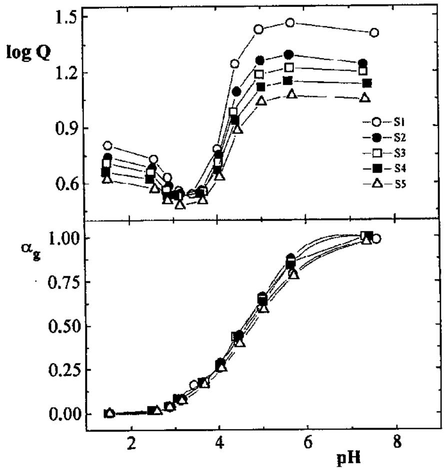
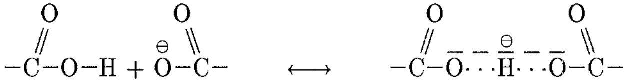


Figure 1: The dependence of the swelling degree Q and of the internal degree of ionization α_g on the pH of the solution

the content of the crosslinker (c) and neutralization (pH). As expected, increasing c decreases Q values for all pH values; this effect is highest at highest pH values. On the other hand a pronounced minimum of the swelling degree with increasing pH, located at $\alpha_g \approx 0.15$, can be observed for all samples. This unexpected phenomenon was observed earlier (15) for the copolymers of acrylic acid with isoprene crosslinked by divinylbenzene and can be explained by increased interaction between the ionized and nonionized carboxy groups mediated by the hydrogen bond



$$-\overset{\overset{\displaystyle O}{/\!/}}{C}-O-H+\overset{\ominus}{O}-\overset{\overset{\displaystyle O}{\backslash\backslash}}{C}- \quad\longleftrightarrow\quad -\overset{\overset{\displaystyle O}{/\!/}}{C}-O\cdots\overset{\ominus}{H}\cdots O-\overset{\overset{\displaystyle O}{\backslash\backslash}}{C}-$$

which strengthens the polymer–polymer contacts and reduces the swelling degree. Also a water molecule incorporated between the ionized and nonionized carboxyl groups may prefer such an advantageous interaction. As was pointed out by Hiraoka and Yokoyama (17) also the formation of a complex corresponding to a 33% neutralization (coordination of three carboxyl groups – six oxygen atoms) is probable.

Mechanical behaviour

All networks show a maximum in the dependence of equilibrium modulus G_e on pH which corresponds to the minimum of the degree of swelling Q (Fig. 2). On the other hand, the modulus related to the dry state, G_d, in accord with the theory of Gaussian network ($G_d = G_e v_2^{-1/3}$), is practically constant independent of Q (Fig. 3). Only for the loosest network S1, a small decrease of G_d with Q is found. This fact suggests that the maximum on the dependence of G_e on pH is fully determined by the degree of swelling in agreement with the classical theory of rubber elasticity (1) (the volume effect of the solvent on G). It may be concluded further that the interactions between ionized and nonionized carboxylic groups do not contribute to the equilibrium stress after deformation. On the other hand, a quite pronounced decrease in G_d with Q was observed earlier for PMAc ionized and nonionized networks ($\log G_d$ vs $\log Q$,

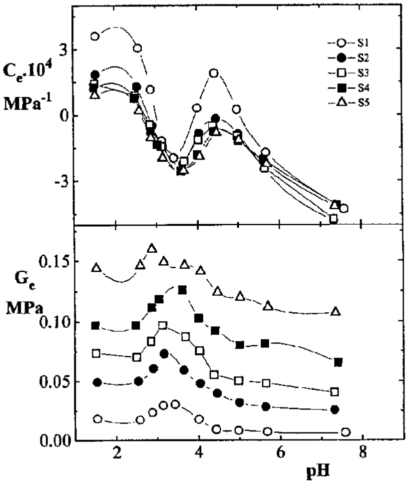


Figure 2: The dependence of the modulus G_e and of the stress-optical coefficient C_e on the pH of the solution

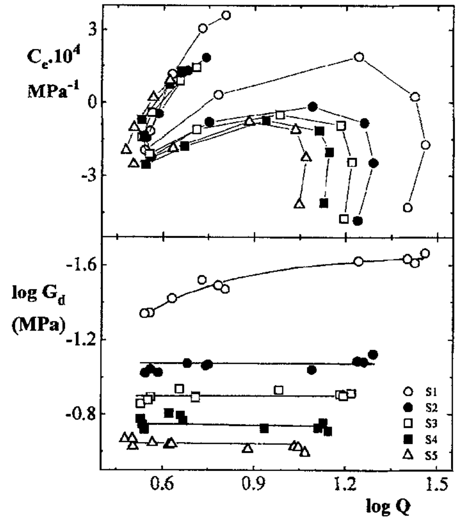


Figure 3: The dependence of the stress-optical coefficient C_e and of the modulus reduced to the dry network G_d on the swelling degree Q

slope $q \doteq 1.0$); this decrease was interpreted by the disappearance of the secondary structure of PMAc chains with increasing swelling (11, 12).

From the equilibrium modulus G_e the concentration of the elastically active chains in dry network ν_d was calculated from (11)

$$\nu_d = G_e v_2^{-1/3}(v^\circ)^{-2/3}/(RT) \tag{5}$$

where $v^\circ = 0.55$ is the volume fraction of the polymer at network formation, R is the gas constant, and T is the temperature. The dependence of ν_d on $2c$ (c is the crosslinker concentration in mol.cm^{-3}) is shown in Figure 4; the value $2c$ represents the ideal chemical concentration of the chains at 100% efficiency of the crosslinking reaction. For comparison, also the data obtained on PMAc gels are included in Figure 4; as in this case ν_d depends on the swelling degree, the values of ν_d obtained for $\log Q = 0.8$ are shown (see Figs 3 and 5 from Ref. (11)). It seems from Figure 4 that the efficiency of the crosslinking reaction, given by the slope of the linear part of the ν_d vs $2c$ dependence ($s \doteq 0.25$) is roughly the same for PAAc and PMAc networks. The low s value suggests a high cyclization accompanying the network

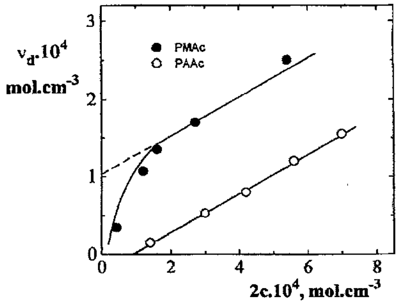


Figure 4: The dependence of the elastically active chains concentration, ν_d on the crosslinker concentration $2c$

formation, which is a consequence of the dilution in the system. On the other hand, at constant $2c$ the ν_d values of PMAc networks are always much larger than those of PAAc ones. This difference is probably associated with much stronger intermolecular interactions in PMAc gels. Thus, the mechanical behaviour of PAAc gels is simpler than that of PMAc ones and closer to the behaviour of Gaussian networks.

Optical behaviour

As follows from Table 1, the refractive index n_g of all networks is predominantly given by the degree of swelling; n_g decreases with increasing Q. With increasing Q also the concentration of the Cl^- co-ions, c_{Cl}, in the gel increases; analysis of the data shows that at the constant Q the value c_{Cl} decreases with increasing crosslinking agent concentration.

A more complex neutralization behaviour than in the modulus G_e and in the degree of swelling Q can be observed in the dependence of the stress-optical coefficient C_e on pH (Fig. 2). The C_e changes its sign three times depending on pH; a change in C_e from a positive to a negative value was observed in the flow birefringence experiments of PAAc solutions earlier (18). From the coefficient C_e, the value of the optical anisotropy of the statistical segment, $\Delta\alpha$, can be calculated using the equation (16)

$$\Delta\alpha = 45kTn_gC_e/[2\pi(n_g+2)^2] \tag{6}$$

where k is the Boltzmann constant. The values of $\Delta\alpha$ change from $\Delta\alpha = 0.95 \times 10^{-24}$ cm^3 (for the nonionized network S1 with the highest C_e value, Table 1) to $\Delta\alpha = -1.30 \times 10^{-24}$ cm^3 (for the most ionized sample of networks S2 with the lowest C_e value). In the case of the most ionized samples of all networks S1–S5 the negative $\Delta\alpha$ values are in accordance with the measurements of the flow birefringence of PAAc solutions (18) and poly(methyl acrylate) networks in the dry state (19). A theoretical calculation of the intrinsic optical anisotropy of the monomeric unit $\Delta\beta$ for methyl acrylate (19, 20) with a fully free rotation of the side group has given a positive $\Delta\beta$ (0.74×10^{-24} cm^3); on the other hand, if the side group is oriented perpendicular to the main chain the calculation has led to a negative $\Delta\beta$ (-0.9×10^{-24} cm^3). These values correlate well with experimental $\Delta\alpha$ values and lead to the view of a fully free motion of the side group in nonionized samples and of the perpedicular side group orientation to the main chain of the most ionized samples. The initial neutralization first leads to the preferential orientation of the side chains in a perpendicular direction to the main chain (C_e decreases to negative values), obviously due to the assumed hydrogen bond interactions reflected in the minimum of the swelling degree. Since with further neutralization of gels Q rapidly increases, the orientation of the side group is weakened and C_e and $\Delta\alpha$ increase up to pH $\doteq 4.5$. The value corresponds to a $\sim 50\%$ ionization of the chain and further neutralization does not change much the swelling degree (Fig. 1). On the other hand, with increasing charge concentration α_g at these highest pH, the side groups again lose their mobility and assume a perpendicular orientation to the main chain. Since at constant swelling degree Q both the positive and negative C_e values were observed (Fig. 3), one can conclude that the orientation of the side group (given by its freedom of rotation) is controlled not only by the Q value (as in the case of equilibrium modulus G_e) but also by the degree of ionization α_g.

For the ionized and nonionized PMAc gels, the high positive values of C_e (from 30×10^4 MPa^{-1} to 5×10^4 MPa^{-1}) were observed (11, 12). Since no major change in the values of the intrinsic anisotropy can be expected in transition from methyl acrylate to methyl methacrylate, these high positive C_e values were interpreted in terms of a decisive contribution of the form birefringence of the assumed structural domains in PMAc gels to the total birefringence. Thus we can conclude that also optical behaviour of PAAc gels is simpler than that of PMAc gels (similarly to the equilibrium mechanical behaviour) and its interpretation does not require an assumption of the existence of correlated regions.

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