

Deformational, Swelling, and Potentiometric Behavior of Ionized Gels of 2-Hydroxyethyl Methacrylate–Methacrylic Acid Copolymers

M. ILAVSKÝ, K. DUŠEK, J. VACÍK, and J. KOPEČEK, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

Synopsis

The deformational, swelling, and potentiometric behavior of ionized water-swollen gels of 2-hydroxyethyl methacrylate (HEMA)–methacrylic acid (MA) copolymers used in biomedical and separation applications was investigated. With increasing degrees of neutralization α , the swelling degree strongly increases and the modulus G_s decreases. For the copolymers with MA content ≥ 30 mole-%, the dependence of G_s on α passes through a minimum. Comparison of the results with the modified theory of rubber elasticity shows that the decrease in G_s at low concentrations of charges on the chain is controlled mainly by the degree of swelling. At higher α , both the finite extensibility of network chains, caused by a high degree of swelling, and electrostatic interactions contribute to G_s . The dependence of the interaction parameter χ on the volume fraction of polymer in the gel, ν_2 , is independent of α and closely resembles the dependence obtained for other hydrophilic polymers.

INTRODUCTION

The increasing number of biomedical applications¹ of poly(2-hydroxyethyl methacrylate) (PHEMA) gels require efficient control of their structure and properties. The introduction of ionizable groups into PHEMA chains makes it possible to modify considerably the physical and application properties of the gels, especially their permeability to metabolites^{2,3} and their biocompatibility.⁴ The presence of ionizable groups is very important in separation processes because they determine the membrane selectivity. In all these applications, the mechanical properties of the gels play an important role. They are dependent not only on the fraction of ionizable groups and the degree of crosslinking, but also on the degree of neutralization, which sometimes plays a decisive role. Therefore, it is highly desirable to understand the relations between the structural parameters and the mechanical behavior of ionizable gels.

Recently, the kinetic theory of rubber elasticity has been modified⁵ to include the polyelectrolyte effect caused by the presence of ionizable groups. A strong contribution due to electrostatic interactions and finite (non-Gaussian) extensibility of network chains (caused by a high degree of swelling) was predicted, and results obtained on poly(methacrylic acid) (PMA) were in agreement with the theory if the length of the statistical segment was assumed to increase with increasing ionization.⁶ This assumption is in agreement with the viscometric behavior of PMA and other polyelectrolytes.^{7,8}

In this paper the deformational, swelling, and potentiometric behavior of crosslinked 2-hydroxyethyl methacrylate (HEMA)–methacrylic acid (MA) co-

polymers important for membrane applications is described, and an attempt is made to find out if the results obey theoretical predictions. Unlike in the case of PMA gels, a dilution of charges by introducing nonionizable (HEMA) groups into the network of these copolymers may favor an agreement between theory and experiment.

EXPERIMENTAL

The samples were prepared by copolymerization of 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MA), and 3 wt-% ethylene dimethacrylate as a crosslinking agent in the presence of 20 vol-% butanol as a diluent. The polymerization initiated with azobisisobutyronitrile (1×10^{-2} mole/l) proceeded in polypropylene molds at 60°C for 8 hr. The plates thus prepared were extracted with distilled water at room temperature for several weeks. After extraction the plates were cut into strips $50 \times 10 \times 1$ mm in size and dried at 90°C over P_2O_5 to constant weight (two to three weeks). The composition of the samples is given in Table I.

Neutralization and Swelling

The dried and weighed samples were swollen in 400 ml 0.5M NaCl solution prepared from redistilled water which contained an amount of NaOH needed for obtaining the degree of neutralization α . The 0.1M NaOH solution used did not contain CO_2 , and swelling occurred in closed vessels in a nitrogen atmosphere at room temperature. The swelling took at least two months; the establishment of the equilibrium was examined by measuring the pH of the solution in a nitrogen atmosphere; the equilibrium pH_e values were used in the calculations of the dissociation constant K_0 . The pH values were measured with a pH-meter (Radiometer PHM-64). After establishment of the equilibrium, the samples were weighed in a closed weighing bottle. The volume fraction of the polymer in the swollen state, v_2 , was calculated from the weight of the dry (w_d) sample and of the sample swollen to equilibrium (w_s) using the following relationship, assuming no volume change on mixing:

$$\frac{1}{v_2} = 1 + \left(\frac{w_s}{w_d} - 1 \right) \frac{\rho}{\rho_s} \quad (1)$$

where ρ and ρ_s are the densities of the dry gel and the swelling solution ($\rho_s = 1.019$ g/cm³). The molar fraction of MA in the copolymers was determined by potentiometric titration of the gels neutralized with an excess of NaOH. The values thus obtained differed by 2% at most from the composition of the polymerization mixture.

TABLE I
Characteristics of Un-ionized Samples of the Copolymer HEMA-MA

Sample	MA, mole-%	HEMA, mole-%	$G_{s,0}$, MPa	$v_{2,0}$	$v_d \times 10^4$, mole-cm ³	χ	ρ , g/cm ³
A	5	95	0.510	0.645	2.71	0.933	1.280
B	15	85	0.520	0.665	2.74	0.963	1.285
C	30	70	0.660	0.691	3.43	1.006	1.295
D	50	50	0.490	0.690	2.55	1.006	1.305

Measurement of Deformational Characteristics

Prior to the deformation measurement, the pH_e was determined and the cross section of the sample in the swollen state was assessed. The deformation measurements were performed with a simple relaxometer in which the sample length was ascertained by a centesimal indicator and the force on the sample was measured by means of a force transducer and a bridge (Hottinger-Baldwin-Messtechnik, FRG). Measurements were carried out on samples immersed in the swelling solution (0.5M NaCl) in a nitrogen atmosphere at 298°K. The initial modulus G_s was determined within the deformation range $\lambda = L/L_0 = 1.0$ –1.1, where L and L_0 are, respectively, the deformed and initial lengths of the sample in the swollen state. Starting with the smallest deformation, at least ten values of deformed lengths L_i were used, and the force f_i was determined each time after 2 min of relaxation. The modulus G_s was calculated by the least-squares method using the relation (Tables I and II)

$$\frac{f_i L_i^2}{A_s} = \frac{G_s L_i^3}{L_0} - G_s L_0^2$$

The swollen cross section A_s was determined by combining measurements with a micrometer and calculations using the weight and density of the sample. The time interval of 2 min was sufficiently short so that no change in swelling with deformation for samples with higher α values was observed.⁶

After the measurement had been completed, pH_e value was measured again; the difference between the two values was lower than 0.1 in all cases. With

TABLE II
Deformational, Swelling, and Potentiometric Characteristics of Gels in the Ionized State

Sample	α	ν_2	G_s , MPa	c_+ , mole/l	pH_e	χ	pK_0
A	0.10	0.585	0.503	0.113	5.30	0.853	7.50
	0.20	0.557	0.486	0.122	5.65	0.821	7.48
	0.35	0.520	0.450	0.133	6.20	0.783	7.70
	0.50	0.503	0.461	0.136	6.25	0.767	7.52
	0.75	0.475	0.480	0.149	6.35	0.742	7.35
	1.00	0.421	0.455	0.174	—	0.697	—
B	0.10	0.495	0.485	0.114	5.05	0.758	6.64
	0.20	0.433	0.491	0.140	5.50	0.705	6.66
	0.35	0.388	0.474	0.163	5.60	0.672	6.37
	0.50	0.338	0.458	0.174	5.95	0.637	6.44
	0.75	0.289	0.406	0.191	6.35	0.605	6.47
	1.00	0.260	0.360	0.220	—	0.585	—
C	0.10	0.523	0.604	0.090	4.64	0.786	5.62
	0.20	0.435	0.563	0.125	5.02	0.709	5.61
	0.35	0.324	0.544	0.170	5.30	0.628	5.46
	0.50	0.265	0.493	0.190	5.54	0.587	5.35
	0.75	0.230	0.535	0.210	6.08	0.562	5.41
	1.00	0.211	0.561	0.225	—	0.542	—
D	0.10	0.447	0.455	0.108	4.75	0.722	5.53
	0.20	0.344	0.451	0.152	5.15	0.641	5.49
	0.35	0.251	0.461	0.184	5.55	0.596	5.50
	0.50	0.202	0.480	0.206	5.80	0.563	5.49
	0.75	0.173	0.553	0.196	6.45	0.553	5.56
	1.00	0.171	0.648	0.220	—	0.565	—

sample C, containing 30% MA in the un-ionized and ionized states to $\alpha = 0.35$, the temperature dependences of the initial moduli $G_{s,0}$ and G_s were determined. The measurements were performed at constant temperatures increasing from 25 to 85°C each time after thermostating for 1 hr. We also determined in this temperature range the change in the volume fraction values of the polymer in the swollen state, v_2 , for the same samples (sample C); and the relaxation of the force $f(t)$ at constant extension $\lambda = 1.05$ and at 298°K was followed in the time interval of 1 to 400 min.

Chloride Ion Concentration in the Gel

On completion of the deformation measurements, the samples were extracted with distilled water at room temperature; after extraction, the chloride ion content in the gel was determined by potentiometric titration with a 0.02M AgNO_3 solution.

RESULTS AND DISCUSSION

Time and Temperature Dependence of Mechanical Properties

The time dependence of the force $f(t)$ obtained with the sample containing 30 mole-% MA and having the lowest degree of swelling is shown in Figure 1. After 2 min of relaxation, $f(2)$ is only 10% above the equilibrium value obtained for the un-ionized sample, and the same conclusion follows from the temperature dependence of the modulus (Fig. 2). For other samples with a higher degree of swelling, faster relaxation is expected. Such a small time dependence, which is close to that observed with PHEMA gels,⁹ can be explained by the relatively high content of the crosslinking agent, which was, however, suitable for membrane applications. Neutralization of the carboxyl groups accelerates the stress relaxation even more (Figs. 1 and 2), which can be explained primarily by an increase in the degree of swelling.

The reduced moduli $\log [G_{s,0}/v_{2,0}^{1/3}T]$ of un-ionized samples (the subscript 0 refers to un-ionized samples) decrease almost linearly with increasing temperature (Fig. 2), most probably as a result of a decrease in the unperturbed di-

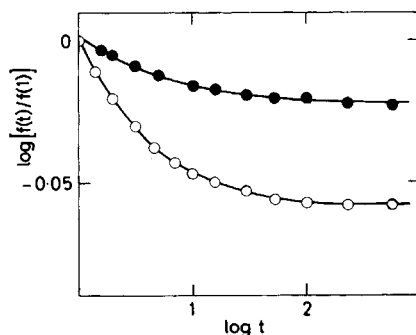


Fig. 1. Dependence of force ratio $f(t)/f(1)$ on time t (min). Sample C with 30 mole-% MA: (O) $\alpha = 0$; (●) $\alpha = 0.35$.

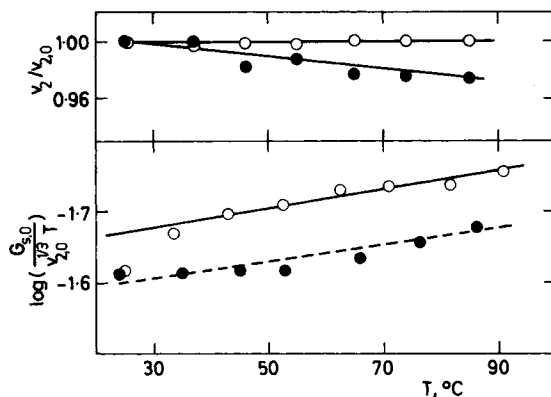


Fig. 2. Dependence of reduced modulus and volume fraction of polymer in gel, v_2 , on temperature T . Symbols same as in Fig. 1.

mensions of network chains r_0^2 with temperature. The value of the factor $k = d \ln r_0^2/dT = (2.5 \pm 0.5) \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ is slightly higher than that for PHEMA,¹⁰ $k = (1.6 \pm 0.3) \times 10^{-3} \text{ }^\circ\text{K}^{-1}$. No marked dependence of k on the degree of ionization and swelling has been observed (Fig. 2).

Dependence of Deformational Behavior on Neutralization

Considering first the un-ionized samples, one observes that the modulus $G_{s,0}$ and the volume fraction of the polymer in the gel, $v_{2,0}$, pass through a maximum (Table I) with increasing MA fraction in the copolymer at 30 to 50 mole-% MA. Such an effect is primarily due to a strong interaction between carboxyl and hydroxyl groups¹¹ increasing the number of polymer-polymer contacts and thus reducing the degree of swelling. The maximum in the modulus $G_{s,0}$ is also influenced to a small extent by the viscoelastic effect.

It is clear from Table II that the modulus G_s decreases with increasing degree of neutralization α and that the decrease (at a low MA content) is accelerated by increasing MA content in the copolymer. At an MA content ≥ 30 mole-%, the dependence of G_s on α passes through a minimum; similar results were obtained earlier for gels of pure PMA.⁶ The volume fraction of the polymer in the swollen gel, v_2 , decreases within the whole neutralization region; the decrease becomes larger with increasing MA content in the copolymer (Table II).

In our preceding paper⁵ the kinetic theory of rubber elasticity has been modified to include the polyelectrolyte effect caused by the presence of ionizable groups. In deriving the equilibrium stress-strain relation, the Debye-Hückel-type electrostatic interaction of ionized groups on a Gaussian chain was assumed. It implies that the ionic strength should not be too low and the ion atmosphere too small compared to the chain dimensions. By employing the three-chain model for network chains of finite extensibility, also the non-Gaussian contribution to the configurational free energy was obtained. The theory predicts an equilibrium stress σ per unit swollen initial crosssection in the form (see eq. (14) in reference 5)

$$\sigma = G_s(\lambda - \lambda^{-2}) = G_{s,0}(1 + \phi_E + \phi_N)(\lambda - \lambda^{-2}) \quad (2)$$

where $G_{s,0} = \langle \alpha_s^2 \rangle \nu_d v_{2,0}^{1/3} RT$ and electrostatic ϕ_E and non-Gaussian ϕ_N contri-

butions are given by eqs. (15) and (16) in reference 5; $\langle \alpha_s^2 \rangle$ is the dilatation factor given¹² by $\langle \alpha_s^2 \rangle = (v_0/v_{2,0})^{2/3}$, $v_0 = 0.8$ being the polymer volume fraction at network formation; ν_d is the concentration of the elastically active network chains (EANC) in the dry state; and R is the gas constant.

In order to compare the effect of the degree of neutralization on G_s with that predicted by eq. (2) in more detail, we use the experimental factor

$$\varphi_e = G_s v_2^{-1/3} / G_{s,0} v_{2,0}^{-1/3}$$

The theoretical value

$$\varphi_t = (1 + \phi_E + \phi_N) / (1 + \phi_{N,0})$$

was calculated from eqs. (15) and (16) in reference 5 using experimental values of v_2 , c_{-} , and ν_d and a procedure explained in reference 6. The degree of neutralization α' used in the calculation was related to the total number of monomer units in the chain, i.e., $\alpha' = \alpha x_A$, x_A being the MA fraction. The mean molecular weight of monomer unit M_0 is given by

$$M_0 = M_A x_A + M_B (1 - x_A)$$

where M_A and M_B , respectively, are the molecular weights of MA and HEMA. All other parameters used for the calculation were the same as before.⁶ For the calculation of $\phi_{N,0}$ (corresponding to the un-ionized state), the number of monomer units in the statistical segment, s , was put equal to 4.^{13,14} In comparing theory with experiment, such a value of s was sought for the calculation of ϕ_E and ϕ_N in order to reach $\varphi_t/\varphi_e = 1$ for all degrees of neutralizations. These s values of the individual copolymers together with s values found earlier⁶ for PMA are plotted in Figure 3.

A comparison of the electrostatic (ϕ_E) and non-Gaussian (ϕ_N) contribution, calculated by the procedure explained above for a constant value of s ($s = 4$), shows that they are of opposite sign and compensate each other to a certain extent

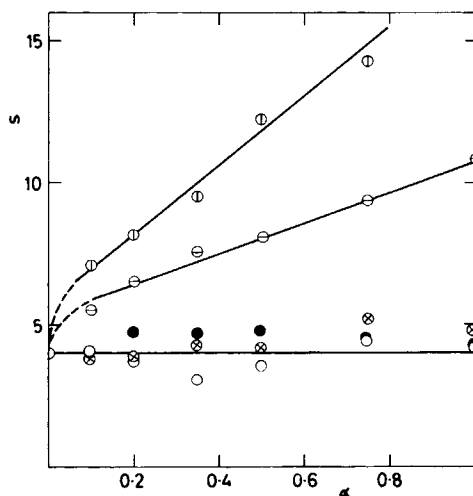


Fig. 3. Dependence of number of monomer units s in the statistical segment on degree of neutralization α . Molar ratio MA:HEMA: (O) 5:95; (●) 15:85; (⊗) 30:70; (⊖) 50:50; (⊕) 100:0. Published data.⁶

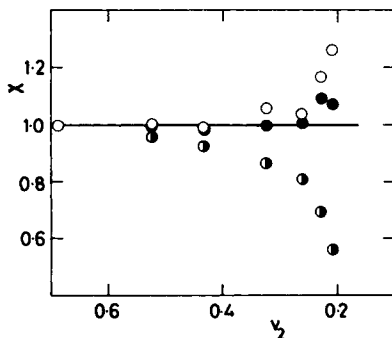


Fig. 4. Dependence of factor $X = \varphi_e/\varphi_t$ on polymer volume fraction in gel, v_2 . Sample C with 30 mole-% MA: (O) in $X\phi_E = \phi_N = \phi_{N,0} = 0$; (◐) in $X\phi_E = 0, \phi_N \neq \phi_{N,0} \neq 0$ ($s = 4$); (●) in $X\phi_E \neq \phi_N \neq \phi_{N,0} \neq 0$ ($s = 4$).

(an example is given in Fig. 4). At low α' , $\phi_E \doteq -\phi_N$ and the initial step decrease in G_s is caused practically only by an increase in the degree of swelling; whereas at higher α' , the correction of the modulus by the factor $v_2^{-1/3}$ is not sufficient, because ϕ_N and ϕ_E do not compensate each other fully (ϕ_E is about -0.5 for $\alpha' = 0.3$).

The s values of copolymer samples with a MA content ≤ 30 mole-% (samples A, B, and C, Table II) are virtually independent of α , s lying between 4 and 5 (Fig. 3). For sample D, with 50 mole-% MA, s increases with increasing α , but the increase is smaller than for the PMA gels⁶ (Fig. 3). The relationship for ϕ_E was derived under the assumption that all charge pairs contributed to the interaction energy to the same extent.¹⁵ It may be expected, however, that the interaction of adjacent or very close charges along the chain may be different from that of more distant ones.¹⁶ It may be inferred, using our results, that the model used adequately describes the effect of charge at constant s on the deformational behavior if the charge distance is larger than three monomer units (one charge in one statistical segment at the most). At a higher charge density, interactions inside the statistical segment become operative which may lead to a change in its length.

It has been assumed that the counterions present in the gel enjoy free mobility. If the degree of neutralization α' were higher than the degree of ionization i , the conclusions would remain qualitatively the same, as follows from the introduction of the osmotic coefficient ϕ ($i = \alpha'\phi$).^{5,6}

Swelling and Potentiometric Equilibria

As has been stated, the introduction of ionizable groups into the polymer chains is a convenient, important method in practice for modifying the swelling properties of gels. The condition of swelling equilibrium can be written as⁵

$$\Delta F_1 + \Delta F_2 + \Delta F_3 + \Delta F_4 = 0 \quad (3)$$

where ΔF_1 corresponds to the mixing of polymer segments and solvent molecules, ΔF_2 to the difference between the osmotic pressures in gel and solution, ΔF_3 to the change in the conformational elasticity of the chains, and ΔF_4 to the electrostatic interactions of charges on the chains. The contributions are given as

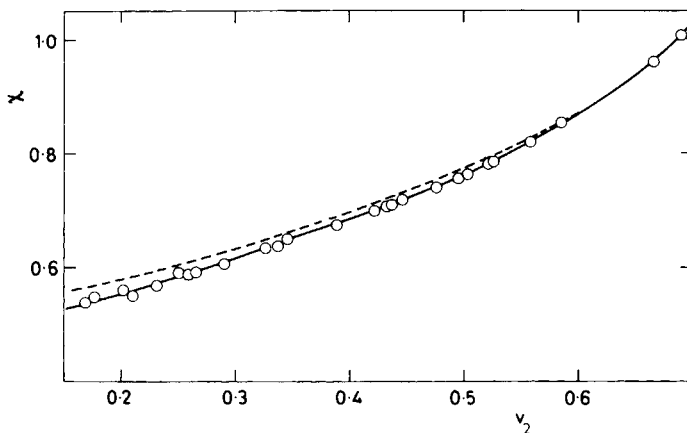


Fig. 5. Dependence of interaction parameter χ on polymer volume fraction in gel, v_2 . (O) χ calculated from eq. (3); (---) χ calculated from relation $[\ln(1 - v_2) + v_2 + \chi v_2^2] = 0$.

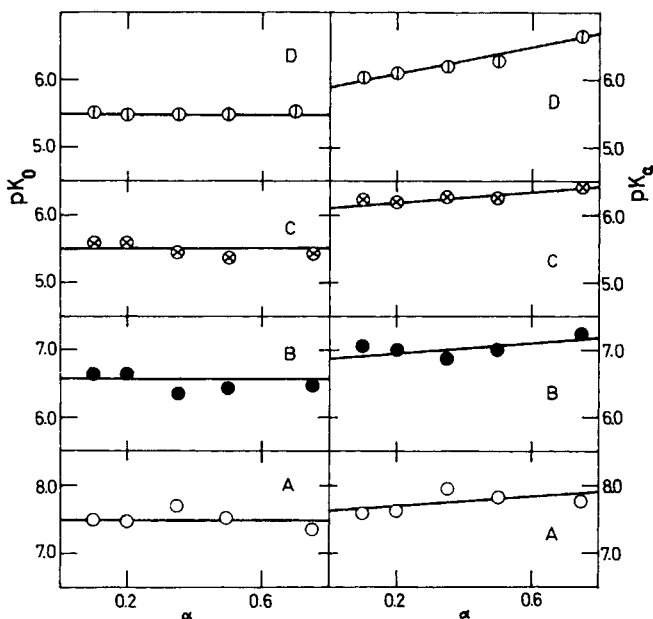


Fig. 6. Dependence of pK_a [eq. (4)] or pK_0 [eq. (31) of ref. 5] values on neutralization α . Symbols same as in Fig. 3.

an explicit function of structural parameters and external variables in eqs. (17) to (25) of reference 5.

The Flory-Huggins interaction parameter χ calculated from eq (3) is free from ionic interactions and is a measure of affinity of the polymer to the solvent as if all charges were fully screened. Figure 5 shows that all samples irrespective of α fit a single curve χ versus v_2 and that their dependence closely resembles that found for un-ionized and weakly ionized PMA gels⁶ and even PHEMA gels.¹⁸ It is worth noting that the χ -versus- v_2 dependence is close to the pseudoideal curve given by $\Delta F_1 = (-RT/V_1) [\ln(1 - v_2) + v_2 + \chi v_2^2] = 0$, where V_1 is the molar volume of the solvent (Fig. 5) which has been found to describe the sorption

equilibria for a number of hydrophilic polymers.¹⁹ From the practical point of view, such result would suggest that the swelling degree would not depend much on the degree of crosslinking, but this is actually not true. In reality, the electrostatic interactions (electrostatic repulsion of charges and hydration of fixed ions) are responsible for an increase in swelling and not the hydration ability of the "uncharged" polymer segments.

Experimental pH_e values were used to determine the apparent dissociation constants $\text{p}K_a$:

$$\text{p}K_a = \text{pH}_e + \frac{\log(1 - \alpha')}{\alpha'} \quad (4)$$

It was found that $\text{p}K_a$ increased with α (Fig. 6) as in other systems,²⁰⁻²² the increase being more pronounced with increasing MA content in the copolymer. Comparison with theory was tested in eq. (31) of reference 5, using the same parameters as in the case of swelling equilibria. The $\text{p}K_0$ values calculated from eq. (31) of reference 5, which should be independent of α , are practically constant for all copolymers (Fig. 6), which indicates that correction in the suggested model acts in the required direction. As expected, the average $\text{p}K_0$ values decrease with increasing MA content in the copolymer. An extrapolation to 100% MA gives a value approaching the $\text{p}K_0$ of PMA in NaNO_3 or NaCl solutions^{23,24} ($\text{p}K_0 \approx 4.3$).

CONCLUSIONS

The analysis shows that the modulus and the interaction parameter are determined mainly by the degree of swelling of the gel, at least at a low concentration of charges on the chain. Such a low concentration can be obtained either at a lower content of MA units or at lower degrees of ionization. The degree of swelling is greatly affected by the presence of ionized groups, and the electrostatic interactions play a predominant role. The hydration ability of the rest of the network remains almost the same; the dependence of the Flory-Huggins χ parameter on the polymer concentration fits a single curve with a number of other hydrophilic polymers and is independent of ionization.

The modified kinetic theory of rubber elasticity is in fair agreement with experimental data using a reasonable assumption about a change in the length of the statistical segment with ionization. (Thus, theoretical prediction of the variation of some mechanical and swelling properties seems possible.) For a majority of gels, the finite extensibility of network chains cannot be neglected, but the respective effect on the modulus is greatly compensated for by the electrostatic effect due to the presence of charges.

We think, however, that these fairly simple conclusions about the experimental behavior of HEMA-MA gels are limited by the comparatively high level of the crosslinking agent used ($\sim 3\%$). There are indications that the behavior is more complex at considerably lower degrees of crosslinking, not only because of a much slower stress relaxation but also because of other features not accounted for in the theory, which could be explained by some kind of cooperative phenomena leading to aggregation and structure formation. The possibility of a cooperative association is greatly reduced by crosslinks; this is why our system is more "ideal" than less crosslinked gels.

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Received November 11, 1977

Revised February 1, 1978