

Hydrophilic Gels Based on Copolymers of 2-Hydroxyethyl Methacrylate with Methacrylamide and Acrylamide

K. DUŠEK and J. JANÁČEK, *Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

Synopsis

Copolymerization of 2-hydroxyethyl methacrylate with methacrylamide or acrylamide and a crosslinking agent in the presence of water or other diluents yielded transparent hydrogels with a varying degree of swelling and varying sorption properties. The equilibrium degree of swelling increases with increasing content of amide groups and exhibits a maximum at ca. 60 wt-% methacrylamide. The temperature dependence of swelling at 25–50°C changes from negative to positive with growing content of methacrylamide in the copolymer. The effect of the introduction of the amide groups can be interpreted by a weakening of the extent of hydrophobic interactions and by an increase in the role played by the hydrogen bonds. At the same time, the swelling-in effect of the salting-in anions decreases and the sensitivity to the sorption of metal cations increases. The increasing content of methacrylamide is reflected in an increase in the modulus, tensile strength, and elongation-at-break in gels swollen to the same degree. In gels swollen in water to equilibrium, the positive effect of methacrylamide units is compensated for by the negative effect of the increasing degree of swelling, so that the mechanical properties of these gels do not depend too much on the composition of the copolymer. The increasing content of acrylamide in the copolymer strongly raises the degree of swelling, which is reflected in poorer mechanical properties compared to poly(2-hydroxyethyl methacrylate).

INTRODUCTION

Hydrophilic 2-hydroxyethyl methacrylate gels were extensively studied in the past and applied in a number of cases in medicine and elsewhere.¹ Poly(2-hydroxyethyl methacrylate) is not too hydrophilic, and homogeneous gels absorb at equilibrium only 42–45% water at the utmost, so that also the content of water as a diluent in the polymerization is limited by this concentration if homogeneous gels are to be obtained. Polymethacrylamide and polyacrylamide are more hydrophilic and in the dry state have a higher glass transition temperature than poly(2-hydroxyethyl methacrylate); it may be expected, therefore, that by copolymerizing 2-hydroxyethyl methacrylate with these amide monomers, one will obtain homogeneous gels with a higher equilibrium water content and different properties. The introduction of the amide group into the gel matrix has both advantages and disadvantages: the amide group is more accessible to chemical transformations,² so that the gel can be readily modified, while at the same time being less stable, especially in an alkaline medium and at elevated temperatures. On the other hand, we have found that a special thermal treatment can raise the stability of the copolymer gels and improve their properties.³

In this paper, we present some basic information about the preparation of gels, their swelling, sorption, and mechanical properties as a function of chemical composition, and conditions of preparation. The results of a study of the low-temperature relaxation behavior of copolymers have been published earlier.⁴

EXPERIMENTAL

The gels were prepared by radical copolymerization of 2-hydroxyethyl methacrylate (containing 0.08% ethylene dimethacrylate) with recrystallized methacrylamide or acrylamide (Merck) and with the crosslinking agent in the presence of a diluent in glass or Teflon molds. Plates 1–2 mm thick were obtained. Ethylene dimethacrylate or methylene diacrylamide prepared from acrylamide and formaldehyde⁵ were used as the crosslinking agent. Water or mixed solvents (e.g., ethylene glycol and its mixtures with water, aqueous solutions of magnesium perchlorate) were used as diluents if homogeneous gels over the whole composition range were required. Either 0.1–0.15% (related to monomers) diisopropyl percarbonates (polymerization at 55–60°C, 6–8 hr) or the redox system ammonium persulfate–potassium pyrosulfite (0.1%, polymerization at room temperature, 24 hr) was used as initiators. With either initiator, no differences in the gel properties could be detected. Before the polymerization the gels were extracted with water at room temperature for 1–2 weeks. Gels for mechanical measurements prepared in presence of ethylene glycol and 1.536M $Mg(ClO_4)_2$ were not extracted after polymerization and were kept in polyethylene bags so that the content and composition of the diluent remained constant.

The weight equilibrium degree of swelling, $W = w/w_d$, was calculated from the weight of the swollen (w) gel and gel dried to constant weight at 60°C at reduced pressure over P_2O_5 (w_d). The densities of dry gels, ρ , were determined in *n*-heptane (Fig. 1) and the weight degree of swelling, W , was recalculated to the volume fraction of the polymer, φ_2 , assuming additivity of the

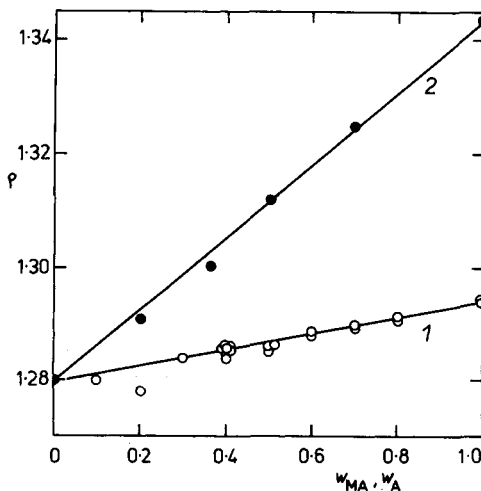


Fig. 1. Dependence of density of dry HEMA-MA and HEMA-A copolymers at 25°C on weight fraction of amide component: (1) HEMA-MA, (2) HEMA-A; copolymers prepared with various amounts of the diluent.

volumes. The volume degree of swelling was measured by means of Abbé's comparator from dimensional changes of the gel strip.⁶ For analysis of the salt content in the gel phase, the gel was first mineralized with sulfuric acid.

Tensile strength σ_b and strain-at-break ϵ_b related to the unit cross section of the swollen sample were determined with a table-type Instron tester at 25°C and the deformation rate of clamps 2 cm/min on dumbbell-shaped samples with the narrowed working part 4.1 mm wide. The test samples were cut out from films 1 mm thick and swollen with water to equilibrium; the stress-strain tests were also carried out in water. The working part of samples fixed between the clamps was 22.5 mm; since also the wider part of the dumbbells was somewhat deformed in the tests, the ϵ_b values suffer from a certain error: earlier experiments⁷ allow us to assume that the error does not exceed 15%.

The constants C_1 and C_2 of the Mooney-Rivlin equation were determined by calculations from the stress-strain curves obtained by the deformation of rectangular samples (10–12 cm long and 1 cm wide) at the shift rate of the clamps 0.05 cm/min and the temperature of measurement 25°C.

Samples prepared in the presence of a constant concentration of ethylene glycol and 1.536M $\text{Mg}(\text{ClO}_4)_2$ and kept at the same concentration of the diluent were measured in air atmosphere. The determination of ultimate properties was performed within a short time, but a longer time was needed for the determination of equilibrium stress-strain data. Therefore, the weight of the samples was checked before and after the measurement; the weight changes were small enough to be neglected in further treatment of data.

RESULTS AND DISCUSSION

Conditions for Gel Preparation

The copolymerization parameters of 2-hydroxyethyl methacrylate (HEMA)(1) with methacrylamide (MA)(2) $r_1 = 0.67$, $r_2 = 0.50$ and HEMA (1) with acrylamide (A)(2) $r_1 = 1.84$, $r_2 = 0.41$ calculated from the $Q-e$ data⁸ show that the HEMA-MA system does not differ too much from an ideal system and the copolymerization diagram has the azeotropic point at a molar fraction of MA 0.4. The departures in the HEMA-A system are larger.

Our investigation of the copolymer gels was concentrated on transparent gels and rather on the HEMA-MA than on the HEMA-A copolymers, because the HEMA-A gels with a higher content of A swell strongly, and have poor mechanical properties and also a lower hydrolytic stability. The HEMA-MA gels are stable up to 60–65°C, and their degree of swelling does not vary with time. The preparation of transparent homogeneous gels depends on two factors: (a) thermodynamic stability of the polymerizing system, and (b) limited solubility of the amide monomer in the starting polymerization mixture.

Figure 2 shows the dependence of the weight swelling degree W of poly(2-hydroxyethyl methacrylate) (PHEMA), of the copolymer HEMA:MA (1:1 by wt) and polymethacrylamide (PMA) as a function of the reciprocal weight fraction of the monomer in the polymerization mixture. The broken straight line with a unity slope corresponds to a case when the water content in the gel after polymerization is just equal to the water content in the gel swollen to

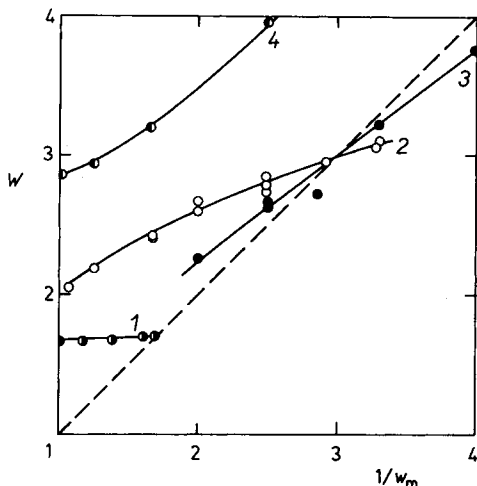


Fig. 2. Dependence of degree of swelling W on reciprocal weight fraction of monomers in starting polymerization mixture, w_m : (1) PHEMA; (2) HEMA:MA 1:1 by wt; (3) PMA; (4) HEMA:A 8:2 by wt; $1.5\text{--}2.5 \times 10^{-5}$ mole/cm³ of crosslinking agent in monomer.

equilibrium. It is evident that the degree of swelling of PHEMA is practically independent of the content of diluent (water) during polymerization and on exceeding a limit of ca. 42% water, phase separation occurs via microsineresis and nonhomogeneous gel are formed.⁹ For the copolymer HEMA:MA 1:1, the increase in W with dilution is already pronounced, and the system ceases to be thermodynamically stable only at 65–70% water. The increase in the degree of swelling is even more pronounced for PMA; transparent gels can be prepared even beyond the limit of ca. 65% water because the excess of the latter is removed by macrosineresis (deswelling). It should be pointed out, however, that PMA is not unlimitedly miscible with water.^{10,11} A is a much more hydrophilic comonomer than MA, so that, e.g., for the copolymer HEMA:A 8:2 by wt the system is thermodynamically stable independently of dilution (Fig. 2).

The second limiting factor—solubility of the amide monomer—is also more important for MA. Thus, for instance, for dilution with 40% water, it is possible to prepare, at the polymerization temperature 60°C, homogeneous gels up to the ratio HEMA:MA 2:8. If the water content is increased to 60%, the composition range can be extended up to 100% MA; but at such dilution, gels with 0–20% MA are nonhomogeneous owing to thermodynamically induced microsineresis. Homogeneous gels over the whole range of copolymer composition can be obtained by using solvents other than water, such as aqueous solutions of magnesium perchlorate or glycol–water mixtures, etc., which safeguard thermodynamic stability of the systems over the whole range of copolymer composition and dilution.

Equilibrium Swelling

The weight equilibrium degree of swelling of the HEMA–MA and HEMA–A gels as a function of copolymer composition and at a constant concentration of the crosslinking agent and dilution is given in Figure 3. It is obvious that the degree of swelling is not an additive function of composition, which

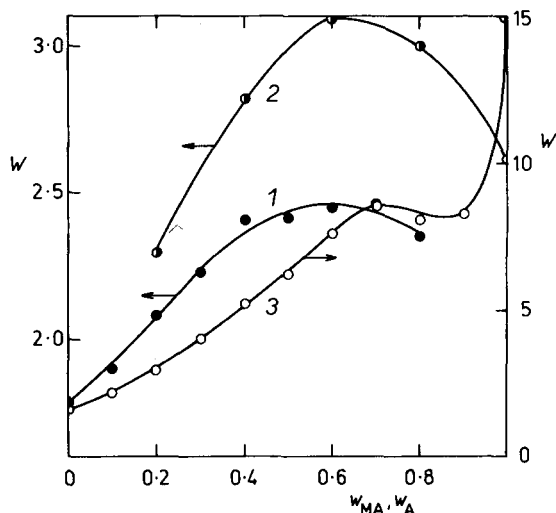


Fig. 3. Dependence of degree of swelling in water of HEMA-MA and HEMA-A gels on weight fraction of MA (w_{MA}) and A (w_A) in the copolymer: (1) HEMA:MA gel prepared in presence of 40 wt-% water; (2) HEMA:MA prepared in presence of 65% water; (3) HEMA:A prepared in presence of 40% water; 0.3% ethylene dimethacrylate in monomer; swelling at 25°C.

indicates that specific interactions between the functional side groups become operative. The swelling of the HEMA-MA gels exhibits a maximum at a weight fraction of MA, w_{MA} , of about 0.6. Also, on the swelling curve of the HEMA-A gels there appears a plateau or even a maximum. The introduction of more hydrophilic groups into the HEMA chain obviously initially brings about destruction of the hydrophobic associates which (as follows from thermodynamic reasonings) are the main cause of the low swelling of PHEMA.¹² The overall effect of the methacrylamide group is greater than would correspond to its capacity of binding more water molecules. The fact that the introduction of the HEMA group into the PMA chain leads also to an increase in swelling cannot be explained by a change in hydrophobic interactions. It is quite likely, however, that the swelling of PMA is also limited by the existence of dimeric associates between neighboring amide groups held by hydrogen bonds, and that the possibility of such association is disturbed by the incorporation of a foreign unit (HEMA).

An analysis of the equilibrium degree of swelling (while using equilibrium moduli obtained by extrapolation to infinite time¹²) shows that the Flory-Huggins interaction parameter χ is comparatively high (Table I) and that the

TABLE I
The Flory-Huggins Interaction Parameter χ of HEMA:MA Copolymers and Water at 25°C^a

[MA]	20	40	60	80	100
χ	0.677	0.627	0.613	0.619	0.640
φ_2	0.375	0.300	0.269	0.280	0.324

^a [MA] = wt-% MA in the copolymer; gels prepared in the presence of 65 vol-% water and crosslinked with 0.5 wt-% methylene diacrylamide; φ_2 = volume fraction of the copolymer in the swollen gel.

contribution of the elongation of elastically active chains is very small. The parameter also depends on concentration; if this dependence is approximated within the given narrow range of volume fractions of the polymer by a linear dependence, we obtain for PMA $\chi = 0.464 + 0.54 \varphi_2$ ($\varphi_2 = 0.30-0.35$), while for PHEMA it was found that $\chi = 0.32 + 0.90 \varphi_2$ ($\varphi_2 = 0.51-0.56$).¹³ However, owing to the small elastic contribution to the chemical potential of the solvent, the concentration dependence rather approaches $\chi \rightarrow -[\ln(1 - \varphi_2) + \varphi_2]/\varphi_2^2$.

The temperature dependence of swelling (Fig. 4) of the PHEMA and PMA gels differs from each other, even though the effect of temperature is small: for PHEMA, the equilibrium degree of swelling passes through a minimum at 55°C; for PMA, it increases with temperature; and for HEMA:MA (1:1), it remains almost unchanged. If the changes in the interaction are expressed by

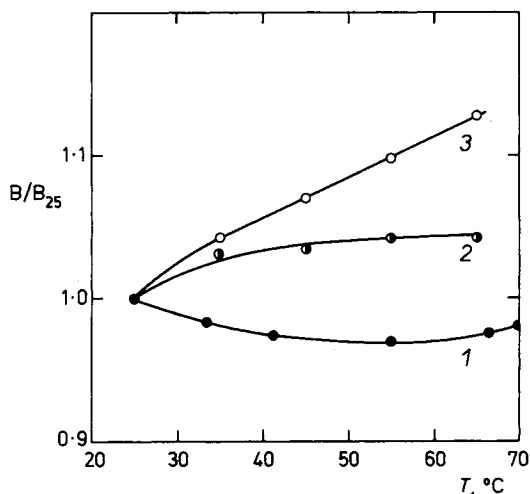


Fig. 4. Temperature dependence of relative degree of swelling in water: (1) PHEMA prepared in presence of 40% water; (2) HEMA:MA 1:1 by wt in presence of 65% water; (3) PMA in presence of 65% water; 0.3% methylene diacrylamide in monomers; B/B_{25} volume degree of swelling at the given temperature related to volume degree of swelling at 25°C.

means of the entropic (χ_S) and enthalpic (χ_H) component of the interaction parameter $\chi = \chi_S + \chi_H$, when $\chi_H = [\partial\chi/\partial(1/T)]_{\varphi_2}$, then for PHEMA at 25°C, we obtain $\chi_S = 0.86$, $\chi_H = -0.03$ (cf. ref. 14; in this case, however, the correction for the degree of swelling with concentration was not taken into account); and for PMA, we get $\chi_S = 0.63$, $\chi_H = 0.03$. It is obvious that the entropic term strongly predominates in both cases, but the higher value for PHEMA indicates a stronger formation of hydrophobic associates during mixing. The negative χ_H of PHEMA can be interpreted by the formation of new hydrogen bonds during mixing with water, while for PMA, it seems that a part of hydrogen bonds disappears. The amide groups in PMA are thus more bonded via hydrogen bond than the hydroxyl groups in PHEMA, which is in accordance with the interpretation of the effect of the change in the copolymer composition. The differences between PHEMA and PMA cannot be explained only by a different degree of swelling: in principle, the PHEMA gel swells in 6M urea similarly to the PMA gel in water; but in spite of this,

the temperature dependence of swelling in the former case is negative.¹⁴ The dependence of the equilibrium swelling of the HEMA-A gels on composition differs by the fact that during the transition to the PA gel the degree of swelling steeply increases.

The dependence of the degree of swelling on the concentration of the crosslinking agent for the PHEMA-MA and PHEMA-A gels proceeds as expected

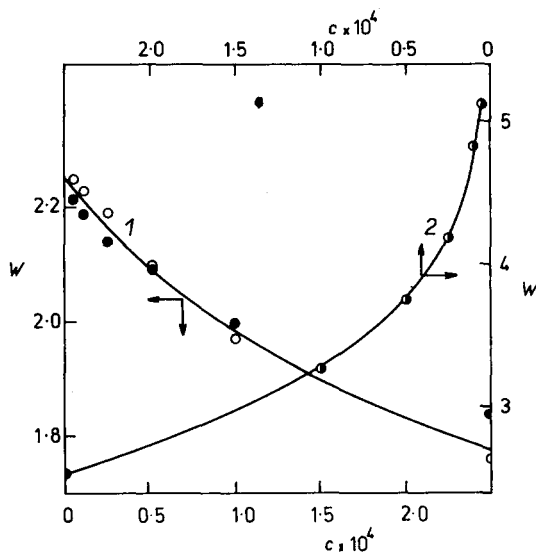


Fig. 5. Dependence of degree of swelling in water on concentration of crosslinking agent, c ; c in mole/cm³ related to monomers; copolymers HEMA-MA (1) and HEMA-A (2) in molar ratio 1:1; (O) ethylene dimethacrylate; (●) methylene diacrylamide, 25°C.

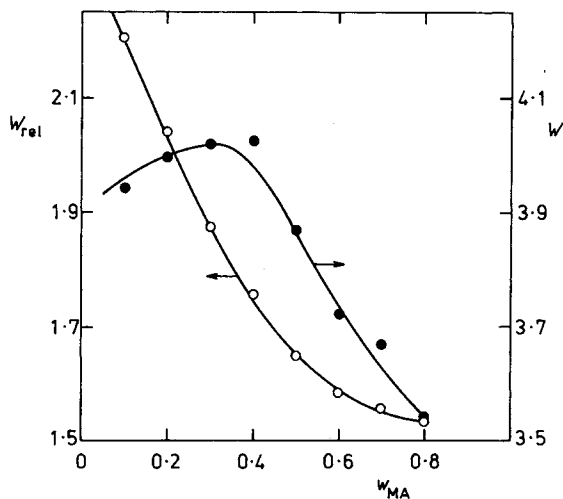
(Fig. 5); no significant differences have been found between both crosslinking agents (ethylene dimethacrylate and methylene diacrylamide) at the same molar concentration. The number of bonds of both crosslinking agents is almost the same, so that almost the same extent of the cyclization (which could affect the swelling) could be expected anyway.

Effect of Salts

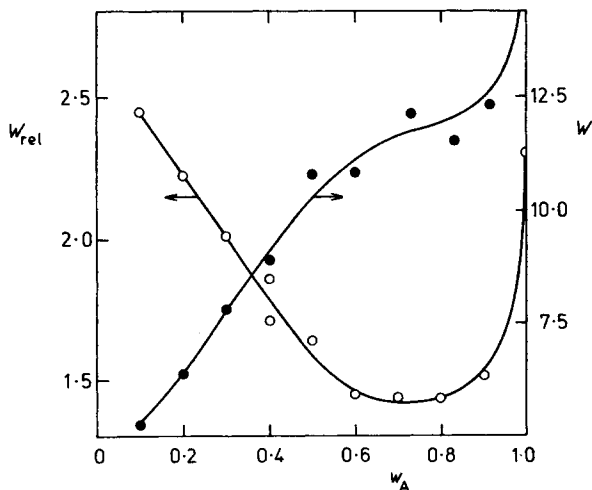
Both inorganic and organic salts can have a considerable influence on the degree of swelling of the PHEMA gels (salting-out and salting-in effects). It was found that for the PHEMA gels, the main role is played by the anion,¹⁵ which roughly agrees with the structure-forming and structure-breaking effects of these salts on water. It can be seen that generally the introduction of the MA units reduces the effect of the anions, while that of the cation (especially of heavier metals) increases. Table II shows some examples of salts having the salting-in and salting-out effect. It can be seen that the effect of the anion on the relative degree of swelling with respect to the degree of swelling of the gel in water is lower for the copolymer gels. LiBr (and other lithium salts, such as LiClO₄, LiCl) is an exception, but it is known that Li⁺ enters into specific interactions with the amide groups.¹⁶ The dependence of the salting-in effect on the copolymer composition is illustrated by magne-

sium perchlorate as an example (Figs. 6a and b). The relative degree of swelling, W_{rel} , decreases steeply with increasing content of MA, in agreement with the assumption of the decreasing effect of hydrophobic interactions. A similar trend is found for the dependence of W_{rel} for the HEMA-A copolymers. The fact that W_{rel} increases again at a high content of A could be explained by the effect of salt on the splitting of hydrogen bonds.

An anomalous behavior was found for sodium thiocyanate which is known by its salting-in effect and which also raises the degree of swelling of the PHEMA, PMA, and PA homopolymers, but "salts out" the HEMA-MA copolymers within a concentration range of MA of 25-70% (Fig. 6). It seems that the SCN^- anion could specifically interact with the $-OH$ and $-CONH_2$

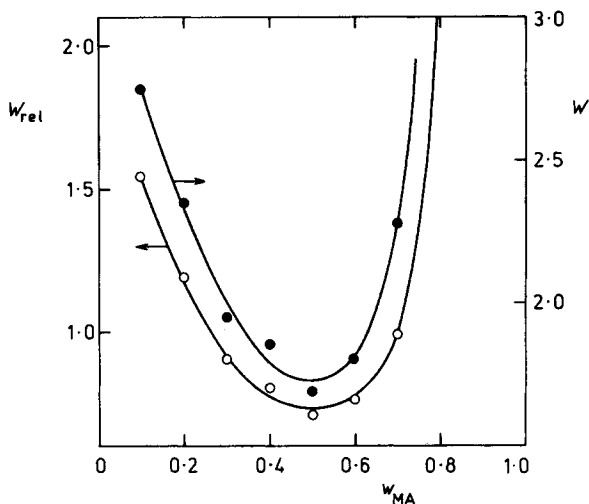


(a)



(b)

Fig. 6 (continued)



(c)

Fig. 6. Swelling of HEMA-MA and HEMA-A gels in aqueous salt solutions. (a) copolymers HEMA-MA in 0.855M $Mg(ClO_4)_2$; (b) copolymers HEMA-A in 0.855M $Mg(ClO_4)_2$; (c) copolymers HEMA-MA in 1M NaSCN; copolymers prepared in presence of 40% water, 0.3% ethylene dimethacrylate in monomers; $W_{rel} = W(\text{salt soln.})/W(\text{water})$; w_{MA} and w_A are weight fractions of methacrylamide and acrylamide, respectively, in copolymer; 25°C.

groups, thus building physical bonds between them. W_{rel} of the HEMA-A copolymers has a similar course with the difference that at the minimum of W_{rel} NaSCN still has a mild salting-in effect ($W_{rel} = 1.3$); in this case, however, the volume concentration of the functional groups is considerably lower because of the high degree of swelling.

The effect of cations was studied on a number of nitrates of some bi- and trivalent cations (Table III). It is obvious that the relative degree of swelling increases with increasing content of the amide units, which suggests more specific interactions of these cations with the amide group.

TABLE II
Effect of 1M Salts on Swelling at 25°C of HEMA-MA Copolymers and PHEMA^a

	HEMA-MA 1:1				PHEMA	
	W	W_{rel}	$w_s(s)$	$w_s(g)$	W	W_{rel}
NaCl	2.16	0.92	0.057	0.039	1.49	0.91
Na_2SO_4	1.28	0.54	0.128	0.054	1.31	0.80
LiBr	2.64	1.12	0.082	0.099	1.76	1.07
KI	3.28	1.39	0.148	0.130	2.35	1.43
NaSCN	2.03	0.87	0.078	0.094	2.68	1.63
$Mg(ClO_4)_2$	3.97	1.69	0.192	0.100	4.09	2.50
$(C_2H_5)_4NBr$	2.79	1.19	0.202	0.157	2.32	1.41

^a The HEMA-MA 1:1 by wt gel was prepared in the presence of 40 wt-% water and crosslinked with 0.3% ethylene dimethacrylate; the PHEMA gel in the absence of water was crosslinked with 0.3% ethylene dimethacrylate; $W_{rel} = W(1M \text{ salt})/W(\text{water})$, $w_s(s)$ and $w_s(g)$ are the weight fractions of salt in the outer and gel phase solutions, respectively.

TABLE III
Effect of 0.5M Metal Nitrates on Swelling of Gels at 25°C^a

	W_{rel}		
	PHEMA	HEMA:MA 1:1	PMA
Ni(NO ₃) ₂	1.13	1.24	1.32
Co(NO ₃) ₂	1.18	1.31	1.44
Cu(NO ₃) ₂	1.15	1.25	1.35
Cd(NO ₃) ₂	1.17	1.32	1.46
Mn(NO ₃) ₂	1.18	1.31	1.38
Fe(NO ₃) ₃	1.21	1.46	1.58
Cr(NO ₃) ₃	1.29	1.50	1.61
Al(NO ₃) ₃	1.25	1.37	1.66

^a Conditions for preparation of gels: PHEMA and HEMA-MA 1:1 by wt in presence of 40% water, 0.3% ethylene dimethacrylate; PMA in presence of 60% water, 0.3% methylene diacrylamide; $W_{rel} = W(0.5M \text{ salt})/W(\text{water})$.

Mechanical Behavior

Our investigation of the mechanical behavior of the HEMA-MA and HEMA-A gels was predominantly concentrated on a comparison with the results obtained for the PHEMA gels.¹⁷⁻²⁰

The tensile strength σ_b of the HEMA-MA samples swollen with water to equilibrium related to the swollen cross section decreased with increasing concentration of MA in the copolymer, but within the range $w_{MA} = 0-0.7$ was not too sensitive to the concentration of MA if recalculated to the dry cross

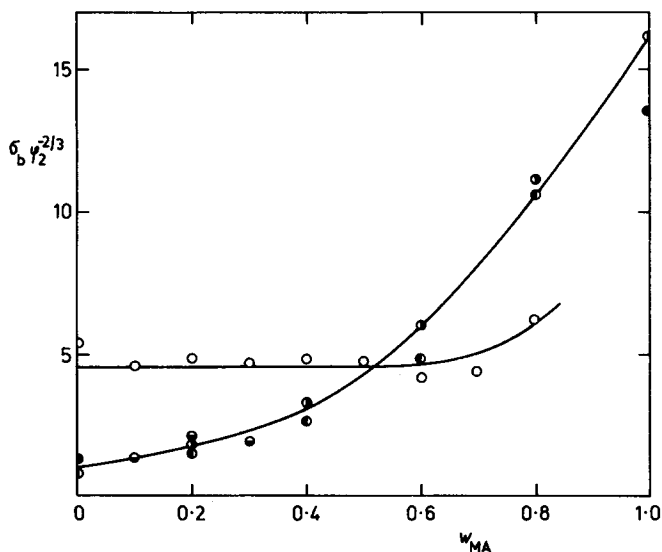


Fig. 7. Dependence of $\sigma_b \phi_2^{-2/3}$ on weight fraction of methacrylamide w_{MA} in HEMA-MA copolymers: (O, ●) prepared in presence of water ($w_m = 0.6$) and swollen with water to equilibrium; (●) prepared in presence of ethylene glycol ($w_m = 0.4$) and measured at the same concentration; (●) prepared in presence of 1.536M Mg(ClO₄)₂ ($w_m = 0.4$) and measured at the same concentration; for comparison's sake, HEMA-A copolymers (●) prepared in presence of water are given ($w_m = 0.6$); σ_b in kg/cm².

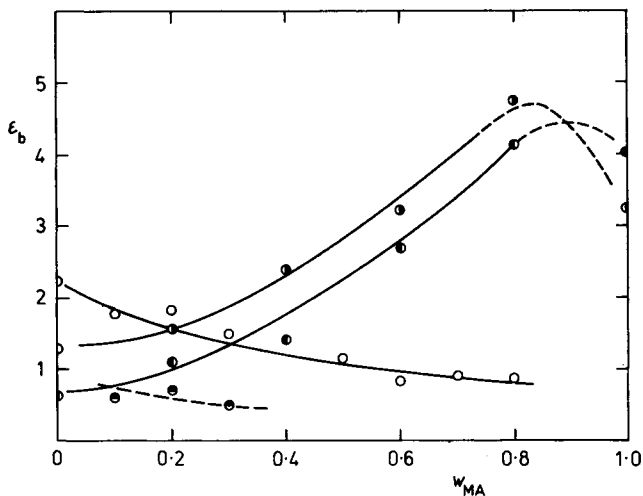


Fig. 8. Dependence of elongation-at-break ϵ_b on weight fraction of MA, w_{MA} , for HEMA-MA copolymers. Designation of points as in Fig. 7.

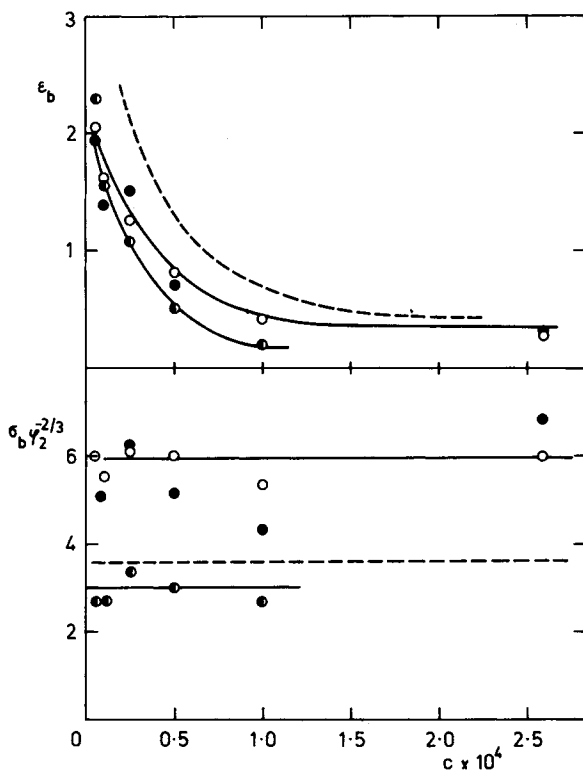


Fig. 9. Dependence of tensile strength $\sigma_b \phi_2^{-2/3}$ and elongation-at-break ϵ_b of gels swollen to equilibrium on concentration of crosslinking agent c (mole/cm³): HEMA-MA (1:1 by wt) system crosslinked with ethylene dimethacrylate (●) and methylene diacrylamide (○); HEMA-A (1:1 by wt) crosslinked with ethylene diacrylamide (●); broken curve for PHEMA (ref. 7); σ_b in kg/cm².

section ($\sigma_b/\varphi_2^{2/3}$) (φ_2 being the volume fraction of the polymer). Only at $w_{MA} = 0.8$, a greater increase sets in (Fig. 7). To eliminate the effect of the varying degree of swelling on mechanical characteristics, we prepared gels in presence of a constant amount (60 wt-%, i.e., $w_m = 0.4$) of 1.536M $Mg(ClO_4)_2$ and ethylene glycol. In such mixtures, no phase separation occurs during polymerization, so that the gels are homogeneous over the whole composition range. The measurements were carried out at the same concentration of diluent. The tensile strength now increased with increasing concentration of MA over the whole range. The σ_b values of homogeneous PHEMA samples prepared in presence of a higher concentration of diluent than indicated ($w_m = 0.4$) were lower compared to the values of samples prepared in presence of water ($w_m = 0.6$). With increasing MA content, the differences become gradually smoothed.

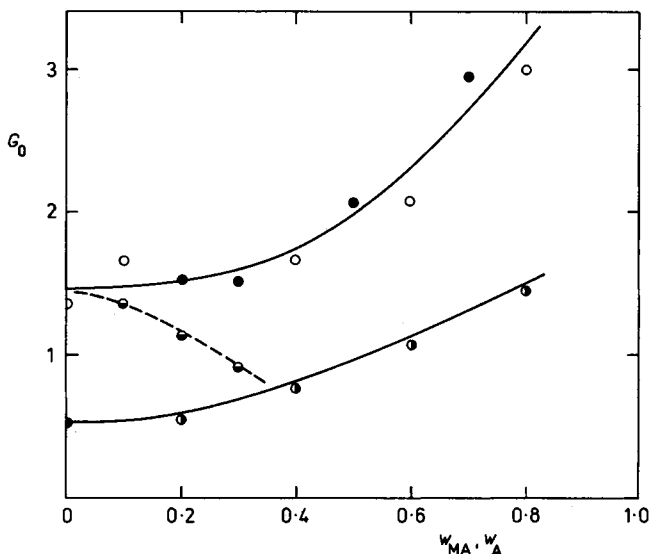


Fig. 10. Dependence of initial modulus related to dry state, G_0 , on w_{MA} of HEMA-MA copolymers. Designation of points as in Fig. 7; G_0 in kg/cm².

Elongation-at-break ϵ_b decreases with increasing MA content for systems swollen to equilibrium, but increases for systems containing a constant amount of ethylene glycol (Fig. 8). Similarly to the strength related to the dry cross section, in systems swollen with water to equilibrium, two effects compensate each other; namely, an increase in ϵ_b with increasing concentration of MA and a decrease in ϵ_b with increasing degree of swelling. It seems that ethylene glycol has a more favorable effect than 1.536M $Mg(ClO_4)_2$, which may be due to the presence of two OH groups in the molecule and to the possibility of formation of physical bridges via hydrogen bonds.

The increasing concentration of the crosslinking agent practically left unaffected the tensile strength related to the dry cross section, while elongation-at-break decreased (Fig. 9). No important differences between both crosslinking agents used, i.e., ethylene dimethacrylate and methylene diacrylamide, were detected. All ultimate characteristics of the HEMA-A gels are

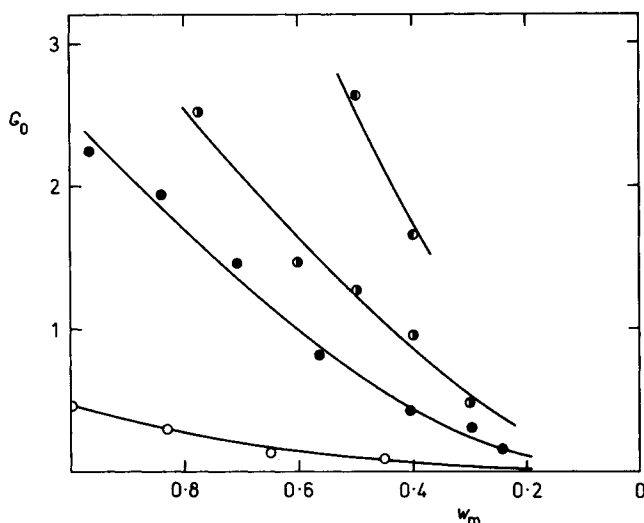


Fig. 11. Dependence of initial modulus related to dry state, G_0 , on weight fraction of monomers in polymerization mixture, w_m : (●) system PHEMA-MA 1:1 by wt, $c = 0.15 \times 10^{-4}$ mole/cm³ of methylene diacrylamide; (◐) PMA, $c = 0.15 \times 10^{-4}$ mole/cm³ of methylene diacrylamide; (●) PHEMA (ref. 22), $c = 0.11 \times 10^{-4}$ mole/cm³ of ethylene dimethacrylate; (○) PHEOEMA (ref. 21), $c = 0.15 \times 10^{-4}$ mole/cm³ ethylene dimethacrylate.

poorer than those of the HEMA-MA gels, probably mainly because of the markedly higher degree of swelling.

The stress-strain dependences measured at a slow deformation rate (and thus close to the equilibrium values) satisfied the two-parameter Mooney-Rivlin equation. The initial modulus G_0 given by the sum of the constants C_1 and C_2 and corrected with $\varphi_2^{1/3}$, $G_0 = 2(C_1 + C_2)\varphi_2^{-1/3}$, i.e., related to the dry state, increases for samples swollen with water to equilibrium with increasing content of MA (Fig. 10). For samples having a constant concentration of ethylene glycol, G_0 also increases with concentration of MA (Fig. 10); for PHEMA under these conditions ($w_m = 0.4$), G_0 is approximately one third compared to the gel prepared in presence of 40% water ($w_m = 0.6$) and in equilibrium with water. On the other hand, for the HEMA-A copolymers, the initial moduli were found to decrease with increasing content of A (Fig. 10). It is noteworthy that the constant C_1 increases with increasing fraction of MA over the whole concentration range, while the change in C_2 is smaller. The initial moduli increased almost linearly with increasing concentration of the crosslinking agent, and the dependences were virtually identical for both crosslinking agents used. It is interesting, however, that the participation of the constant C_1 in G_0 is higher for gels crosslinked with methylene diacrylamide.

The decrease in the initial modulus with increasing dilution during polymerization is considerably greater than would correspond to the factor $\varphi_0^{2/3}$ (φ_0 being the volume factor of the polymer after polymerization) according to the kinetic theory of the rubber elasticity (Fig. 11). The highest G_0 values were found for the MA gels and the lowest for the HEMA gels. For comparison's sake, we also give values for poly(2-hydroxy-2-ethoxyethyl methacrylate) (PHEOEMA),²¹ which are even lower. It should be pointed out that

the MA and HEMA-MA (1:1) gels swell virtually to the same degree, but the degree of swelling of PHEMA is much lower. It seems, therefore, that the high moduli of the MA and HEMA-MA gels at the same degree of crosslinking and dilution at polymerization have their cause in a different type of physical interactions, which influence the time dependences of the decrease in the modulus and establishment of equilibrium. The initial modulus of gels rich in MA could be further from the equilibrium value than in the case of the HEMA gels.¹² It is possible that the slower relaxation is related to the greater role played by the hydrogen bonds.

CONCLUSIONS

By changing the copolymer composition and dilution at polymerization, it is possible to prepare transparent hydrogels with a controlled degree of swelling even at a constant concentration of the crosslinking agent. Methacrylamide and particularly acrylamide increase the hydrophilicity of the gel and the equilibrium degree of swelling in water. The maxima found on the dependence of the degree of swelling on copolymer composition and the temperature dependence of the degree of swelling indicate that with increasing content of the amide component the extent of hydrophobic interactions decreases and the role played by the hydrogen bonds increases. This is in agreement with the decreasing effect of anions of the salting-in salts. The amide groups enter into more specific reactions with polyvalent cations. The degree of swelling of A-rich gels is already very high so that the gels are not too cohesive.

From the viewpoint of mechanical properties, the increasing content of methacrylamide is predominantly reflected in an increase of the modulus, tensile strength, and strain-at-break of gels swollen to the same degree. On the other hand, since the increase in the fraction of methacrylamide units is accompanied by an increase in swelling (which has an opposite effect on the mechanical properties), a certain compensation of the effects of composition and swelling takes place in gels swollen in water to equilibrium and the mechanical properties do not differ too much from the properties of PHEMA, despite the great difference in the degree of swelling. Thus, the introduction of MA into the PHEMA chain makes possible a considerable increase in the swelling capacity of the gel without any impairment of the mechanical properties.

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