# Elastic and Swelling Behavior of 2-Hydroxyethyl Methacrylate, Diethylene Glycol Methacrylate, and Methacrylic Acid Copolymers

IVAN KRAKOVSKÝ, MIROSLAVA JELÍNKOVÁ, JIŘÍ VACÍK

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

**ABSTRACT:** The elastic and swelling behavior of copolymers of 2-hydroxyethyl methacrylate, diethylene glycol methacrylate, and methacrylic acid crosslinked with ethylene glycol dimethacrylate has been studied. In the range of copolymer composition studied, Young's modulus of the swollen networks increases with the content of methacrylic acid, and its dependence on the content of diethylene glycol methacrylate passes through a maximum. The concentrations of the elastic network chains determined from Young's moduli of swollen networks are much higher than those calculated from stoichiometry. This effect is attributed to the presence of additional physical crosslinks due to water-induced ordering of the hydrophobic backbone chains. Both the elastic and swelling behavior of the polymers mentioned above are decisive for their application in the preparation of soft contact lenses. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2141–2148, 1997

**Key words:** elasticity; swelling behavior; 2-hydroxyethyl methacrylate copolymers

## INTRODUCTION

The crosslinked copolymers of 2-hydroxyethyl methacrylate (HEMA), diethylene glycol methacrylate (DEGMA), and methacrylic acid (MAA) proved to be very useful in many biomedical applications.[1] Mechanical properties of the swollen gels of these copolymers play an important role. Therefore, the understanding of the relation between the structure and mechanical behavior of the gels is highly desirable.

A small amount of sodium methacrylate added to the starting monomers has a significant impact on swelling equilibria of final polymers. These materials are suitable for disposable contact lenses because 55–70% of water is an appropriate amount for increased transport of oxygen to cornea as well as for drawing off metabolites as lactic acid and carbon dioxide. We assume ionization of —COONa groups at the physiological pH (7.2) of the tear film and hence the influence of the negative charge of this network on positively charged proteins in the tear film. This is why this material is suitable for disposable contact lenses; their cleaning from firmly sorbed proteins is both mechanically and enzymatically quite difficult, so these lenses are not suitable for long-term wearing. The amount of water in the equilibrium swelling stage of the polymers guarantees an excellent biocompatibility of this material with the cornea surface.

Similar homopolymers and copolymers were studied by various authors. Ilavský and Prins[2] and Warren and Prins[3] investigated the structure of poly-HEMA networks in dependence on the crosslinking density, content of the diluent during network formation and swelling solvent

by fotoelasticity, calorimetry, and light scattering. Janáček and Hasa[4,5] studied mechanical and swelling behavior of poly-HEMA and poly-DEGMA, as well as the HEMA–DEGMA copolymers. Ilavský et al.[6,7] studied the structure and properties of HEMA–MAA copolymers in dependence on the copolymer composition and degree of ionization.

In this work, the elastic and swelling behavior of copolymers of HEMA, DEGMA, and MAA crosslinked with ethylene glycol dimethacrylate and swollen to equilibrium with water was studied.

## EXPERIMENTAL

### Materials

The samples were prepared by the radical polymerization of a mixture of HEMA, DEGMA, and MAA with 0.3 wt % of crosslinking agent (ethylene glycol dimethacrylate, EGDMA). The polymerization was performed in a square mold formed by two aluminium plates, $10 \times 10$ cm in size, with a polypropylene film on their surface, and provided with a system of channels for the heating medium (water) running through. The plates were separated with a seal made of silicone rubber and provided with an opening for a syringe used for insertion of the reaction mixture. The thickness of the seal corresponded to the required thickness of sample sheets. The oxygen dissolved in the polymerization mixture was removed by bubbling with nitrogen for 10 min. The polymerization mixture was filled in by a syringe, and the whole system was heated to 70°C for 8 h. After the polymerization, the sheet was cooled, washed with methanol, methanol–water (1 : 1 v/v), and water. The sheets were kept in 0.1% solution of sodium azide, which prevented the growth of microorganisms.

### Methods

As both HEMA and DEGMA contain a small amount of ethylene glycol dimethacrylate as impurity, its contents were determined by chromatography as follows: 0.20 wt % (in HEMA) and 0.17 wt % (in DEGMA).

Elastic properties of the equilibrium-swollen samples were measured by using an INSTRON 6025 apparatus. Rectangular specimens of about 6 cm in length were cut from the sheets of swollen copolymers. To determine the cross section (ca 1.5 $\times 8$ mm$^2$) of samples, a traveling microscope was used. The samples were mounted in grips 16 mm apart and deformed in uniaxial extension at a rate 100% per minute. During the measurement, the samples were immersed in distilled water and measured at 25°C. Young's moduli were determined by the least-squares fitting of the stress-strain dependences in the initial linear region. The stress relaxation of one swollen sample was also measured in the same arrangement. To determine the densities of dried samples, the flotation method was used. As a flotation medium, a mixture of chloroform and diethyl ether was used.

The volume fraction of the polymer in the swollen network $v_2$ was calculated from the weight of the dry ($\omega_d$) and equilibrium-swollen ($\omega_{sw}$) sample according to the following equation:

$$\frac{1}{v_2} = 1 + \left( \frac{\omega_{sw}}{\omega_d} - 1 \right) \frac{\varrho_d}{\varrho}$$

where $\varrho$ is the density of the swelling agent. In the equation, the additivity of volumes on mixing is assumed.

## RESULTS AND DISCUSSION

The compositions of the reaction mixtures and the densities of the dry gels obtained are given in Table I.

From these data, the concentrations of the elastic network chains in the dry (reference) state were calculated assuming full conversion of the crosslinking reaction and the formation of network junctions of the same functionality ($\Phi = 4$) as

$$\frac{v}{V^0} = \frac{\Phi}{2} \frac{\omega_J \varrho_d}{M_J} \tag{1}$$

where $\omega_J$ is the weight fraction of the crosslinking agent (EGDMA) of molar mass $M_J$ ($=222$ gmol$^{-1}$) in the reaction mixture, and $\varrho_d$ is the density of the gel in dry state.

The weight fraction of the crosslinking agent was calculated by

$$\omega_J = \omega_{J,0} + \omega_{HEMA}\omega_{J,HEMA} + \omega_{DEGMA}\omega_{J,DEGMA}$$

where $\omega_{J,0}$ is the weight fraction of EGDMA in the reaction mixture (0.003), and $\omega_{J,1}$ and $\omega_{J,2}$ are the weight fractions of EGDMA as impurity

**Table I   Compositions of Reaction Mixtures, Densities of Dry Gels ($\rho_d$), and Concentrations of the Elastically Effective Chains, Determined from Experimental Data [$\nu/V^o$ (exp)], and Calculated from Stoichiometry [$\nu/V^o$ (calc)]**

| Sample | HEMA (wt %) | DEGMA (wt %) | MAA (wt %) | $\rho_d$ (g/cm$^{-3}$) | $\chi$ | $\nu'/V^o \times 10^5$ (exp) (mol/cm$^{-3}$) | $\nu/V^o \times 10^5$ (calc) (mol/cm$^{-3}$) |
|---|---|---|---|---|---|---|---|
| A1-0 | 95 | 5 | 0 | 1.277 | 0.816 | 8.44 ± 0.34 | 6.45 |
| A1-05 | 94.5 | 5 | 0.5 | 1.279 | 0.746 | 9.00 ± 0.17 | 6.43 |
| A1-1 | 94 | 5 | 1 | 1.285 | 0.668 | 9.28 ± 0.67 | 6.42 |
| A1-2 | 93 | 5 | 2 | 1.280 | 0.620 | 11.1 ± 0.40 | 6.39 |
| A1-3 | 92 | 5 | 3 | 1.282 | 0.575 | 12.7 ± 0.91 | 6.37 |
| A2-0 | 90 | 10 | 0 | 1.277 | 0.802 | 9.18 ± 0.26 | 6.43 |
| A2-05 | 89.5 | 10 | 0.5 | 0.702 | 1.278 | 10.4 ± 0.16 | 6.41 |
| A2-1 | 89 | 10 | 1 | 1.278 | 0.663 | 10.4 ± 0.51 | 6.40 |
| A2-2 | 88 | 10 | 2 | 1.279 | 0.593 | 12.4 ± 0.62 | 6.37 |
| A2-3 | 87 | 10 | 3 | 1.279 | 0.572 | 12.7 ± 0.22 | 6.35 |
| A3-0 | 80 | 20 | 0 | 1.274 | 0.771 | 9.62 ± 0.51 | 6.39 |
| A3-05 | 79.5 | 20 | 0.5 | 1.276 | 0.701 | 11.0 ± 0.26 | 6.37 |
| A3-1 | 79 | 20 | 1 | 1.278 | 0.648 | 12.3 ± 0.19 | 6.36 |
| A3-2 | 78 | 20 | 2 | 1.278 | 0.583 | 13.1 ± 0.79 | 6.34 |
| A3-3 | 77 | 20 | 3 | 1.279 | 0.572 | 13.4 ± 0.47 | 6.31 |
| A4-0 | 70 | 30 | 0 | 1.271 | 0.749 | 8.54 ± 0.44 | 6.35 |
| A4-05 | 69.5 | 30 | 0.5 | 1.274 | 0.680 | 10.1 ± 0.23 | 6.34 |
| A4-1 | 69 | 30 | 1 | 1.280 | 0.631 | 9.79 ± 0.50 | 6.32 |
| A4-2 | 68 | 30 | 2 | 1.280 | 0.579 | 11.8 ± 0.26 | 6.30 |
| A4-3 | 67 | 30 | 3 | 1.277 | 0.559 | 11.4 ± 0.40 | 6.27 |

in HEMA and DEGMA (0.002 and 0.0017), respectively. $\omega_{HEMA}$ and $\omega_{DEGMA}$ are the weight fractions of HEMA and DEGMA in the reaction mixture. The calculated concentrations of elastic network chains are given in Table I.

In Figures 1 and 2, the dependences of the volume fraction of the polymer in swollen network $v_2$ on the weight fraction of MAA and DEGMA in the reaction mixture are shown. As the solvent used was distilled water and due to low ionization constant of MAA, the networks studied in these conditions are in the nonionized state.

The presence of either MAA or DEGMA in the copolymer chain is manifested by the decrease in the value of $v_2$ (increase in the degree of swelling). From these results, the interaction parameter of the copolymers with water was calculated using the equation[8] describing the swelling equilibrium of the polymer network according to the Flory constraint junction model[9]:

$$\chi = -\frac{\ln(1 - v_2) + v_2 + V_1(v/V^0)v_2^{1/3}(1 - K(v_2))}{v_2^2} \quad (2)$$

where $V_1$ is the molar volume of the solvent (wa-

ter), $K = 0$ for the network with free junction fluctuations (phantom network), and $K = v_2^{2/3}$ for the network with fully suppressed junction fluctuations (affine network). However, because the concentration of elastic network chains is small in the system studied, the value of the interaction parameter is given mainly by first two terms in the denominator in eq. (2). The values calculated are given in Table I. It can be seen that the interaction parameter of the copolymer with water also decreases with increasing amount of both MAA and DEGMA. This effect is more pronounced in the case of MAA due to higher polarity of the carboxyl group. The dependence of the interaction parameter on the copolymer composition (in the region studied) was found to be described successfully by the following equation:

$$\chi = 0.808 - 0.17\omega_{DEGMA} - 15.1\omega_{MAA} + 270\omega_{MAA}^2$$

where $\omega_{MAA}$ is the weight fraction of MAA. The constants of the above expression were found by the least-squares polynomial regression. The value of the interaction parameter of HEMA with water found by extrapolation ($\chi = 0.808$) corre-
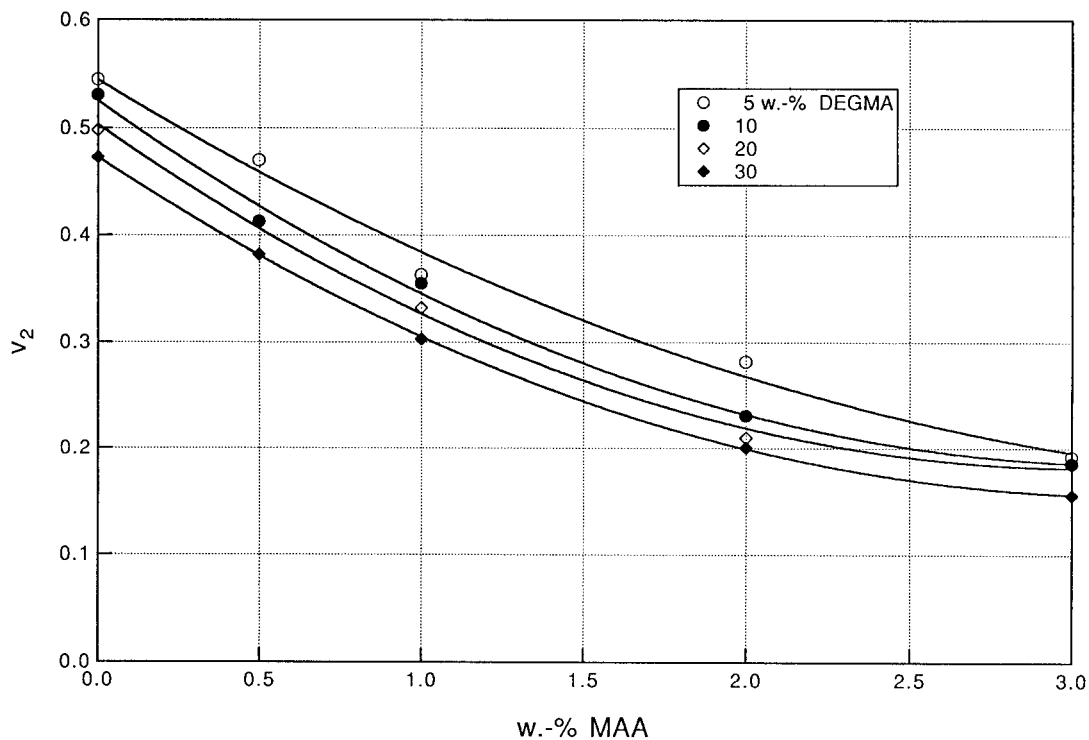
**Figure 1**    Dependence of the polymer volume fraction in swollen samples $v_2$ on the weight fraction of MAA in the reaction mixture.
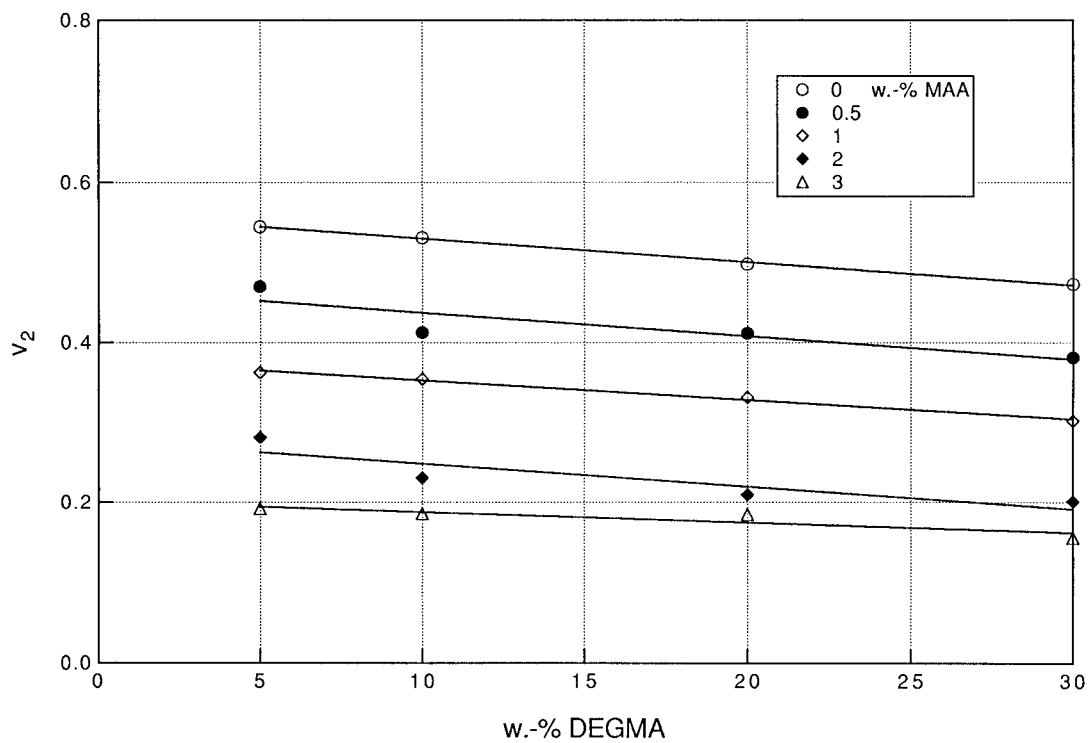


**Figure 2**    Dependence of the polymer volume fraction in swollen samples $v_2$ on the weight fraction of DEGMA in the reaction mixture.
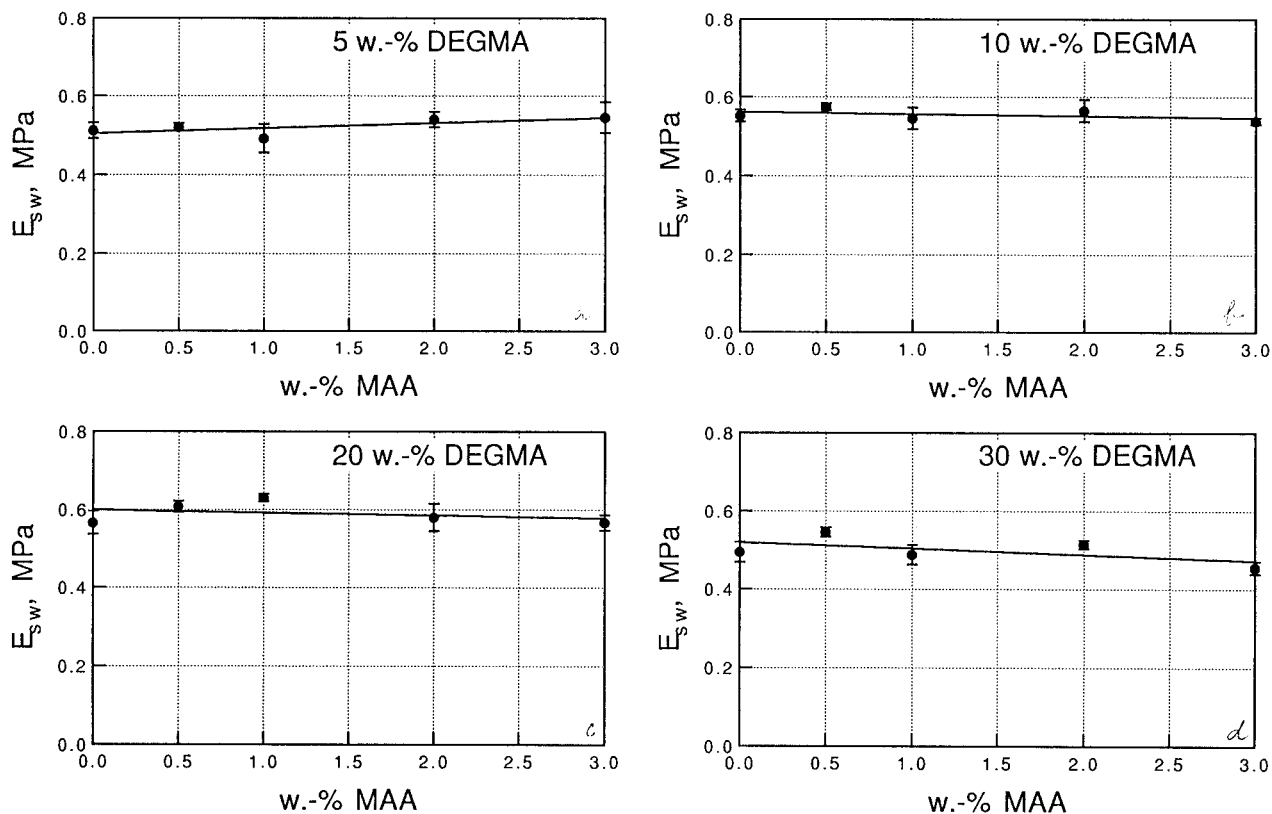
**Figure 3** Dependence of the Young's moduli of swollen samples $E_{sw}$ on the weight fraction of MAA in the reaction mixture.

sponds well to the value found by other authors (see, e.g., Janáček and Hasa[4]).

The composition dependences of Young's moduli of swollen networks ($E_{sw}$) are given in Figures 3(a,d) and 4(a,e). In copolymers with small contents of DEGMA, the modulus increases with the content of MAA [see Fig. 3(a)]. In those with higher contents of DEGMA, the Young's modulus is almost constant [at least in the studied range of MAA amounts; Fig. 3(b,c)]; in those with more than 30 wt % of DEGMA, the dependence decreases [Fig. 3(d)]. In the dependences of Young's moduli on the content of DEGMA, maxima at about 15–20 wt % of DEGMA were found [Fig. 4(a,e)].

From the results of the elastic and swelling experiments, the concentrations of the elastic network chains (in dry state) were determined according to the following equation:

$$\frac{\upsilon'}{V^0} = \frac{E_{sw}\upsilon_2^{-1/3}}{3RT} \qquad (3)$$

where $R$ is gas constant and $T$ is temperature.

The results given in Table I show a big differ-

ence between the concentrations of elastic network chains determined experimentally [$\upsilon'/V^0$, eq. (3)] and those calculated from stoichiometry [$\upsilon/V^0$, eq. (1)]. The difference increases with the content of MAA, and its dependence on the content of DEGMA passes through a maximum (at ca. 20 wt % of DEGMA, independently of the MAA content). As the experimental concentrations of elastic network chains are always much higher than theoretical, an additional contribution to the network elasticity has to be considered.

Since the values of Young's moduli used in the calculations were measured at constant strain rates, a question about their proximity to equilibrium values could arise. To estimate the magnitude of the difference between the observed and equilibrium moduli, we measured the stress relaxation of one representative sample (sample A1-2; see Fig. 5) for one value of the relative elongation. It can be seen that the stress after 1 min relaxation differs only by about 10% from its equilibrium value. Therefore, the difference between the observed and equilibrium moduli of the networks should not be large and cannot be the cause
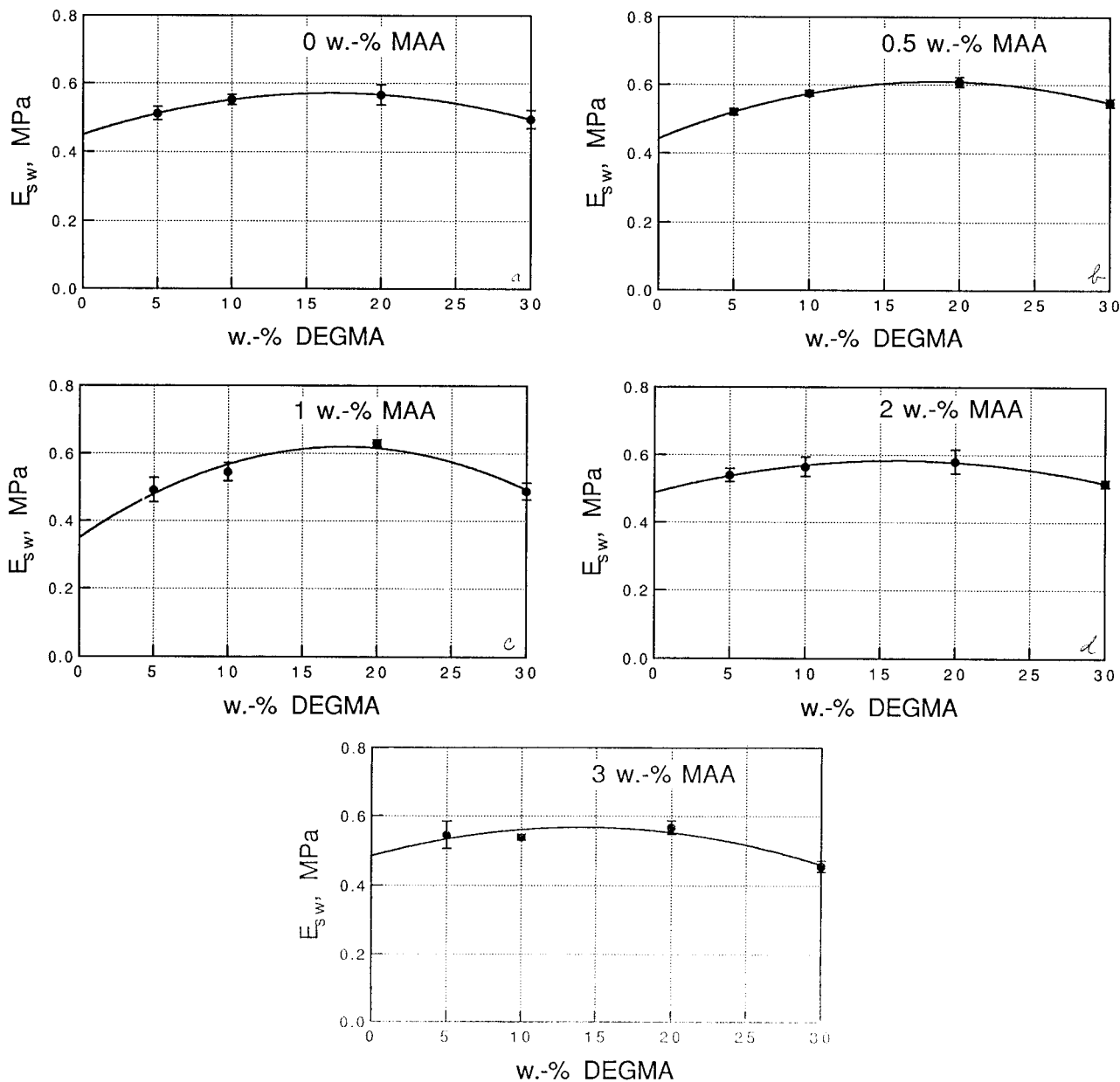
**Figure 4** Dependence of the Young's moduli of swollen samples $E_{sw}$ on the weight fraction of DEGMA in the reaction mixture.

of the difference between the experimental and calculated concentrations of elastic network chains.

Ilavský and Prins[2] and Warren and Prins[3] observed a similar difference between experimental and theoretical concentrations of elastic network chains in the case of crosslinked HEMA polymers in water, while it vanished when water was changed for a less polar solvent (glycol) or temperature was increased. They came to the conclusion

(supported by the rheooptical and light-scattering measurements) that the increase is caused by the solvent-induced ordering of the hydrophobic backbone regions, which act as additional physical crosslinking. We think that the same phenomenon is responsible for the behavior of the system studied here.

The concentration of physical crosslinks grows with the increasing content of MAA, probably due to higher polarity of carboxyl group and increas-
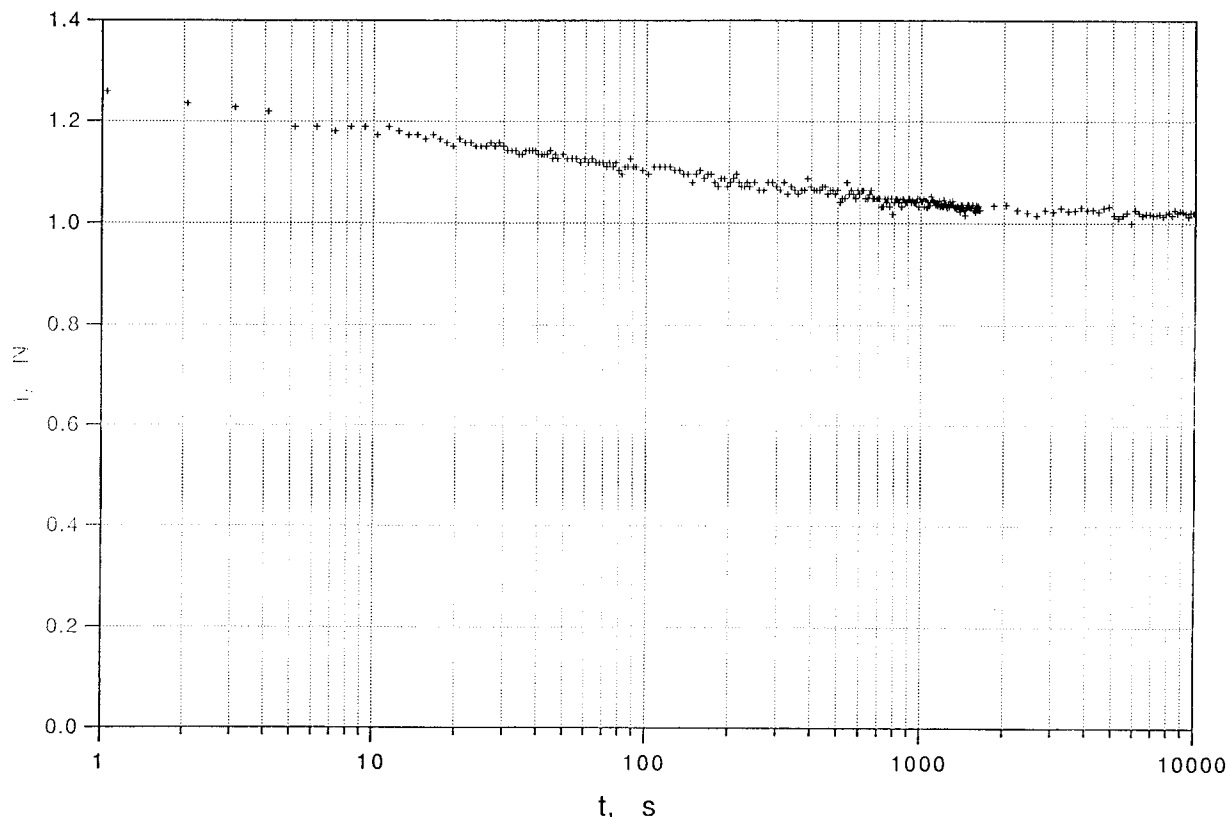
**Figure 5** The time dependence of the force $f$ in the stress relaxation of the sample A1-2. The extension ratio used was 20%.

ing swelling of the network with water. Consequently, the tendency to the ordering of hydrophobic backbone parts of network chains also increases with swelling.

The dependence of the concentration of physical crosslinks on the content of DEGMA can be explained in the same way for low amounts of DEMA. Longer hydrophilic side chains of DEGMA in comparison with those of HEMA increase the swelling of the network with water. This supports the ordering of hydrophobic backbone parts. However, this increase is not so strong as in the case of MAA. If the amount of DEGMA increases further, hydrophilic side chains become an important part of the swelling ambient, reducing its polarity in this way. This reduces the ordering tendency in the system, as manifested by a lower contribution of physical crosslinks in poly-DEGMA networks in comparison with poly-HEMA networks (cf. Janáček and Hasa[4]). The existence of the maximum on the dependence of the experimental concentration of elastic network chains on DEGMA content can be explained by an interplay of the two effects.

The ordering phenomenon is reduced substantially by ionization of carboxyl groups or by increased network density, as shown in Ilavský et al.[6] However, the conclusions stated above need more experimental evidence for their support.

## CONCLUSIONS

The elastic and swelling behavior of the copolymers of HEMA, DEGMA, and MAA crosslinked with EGDMA has been studied. A big difference between the concentrations of elastic network chains determined experimentally and those calculated from stoichiometry was observed. The difference increases with the content of MAA, and its dependence on the content of DEGMA passes through a maximum. This difference is attributed to the solvent-induced ordering of the hydrophobic backbone chains, which act as additional physical crosslinks. All materials studied proved to be suitable for application as soft contact lenses.

## REFERENCES

1. O. Wichterle and D. Lím, *Nature,* **185,** 117 (1960).
2. M. Ilavský and W. Prins, *Macromolecules,* **3,** 415 (1970).
3. T. C. Warren and W. Prins, *Macromolecules,* **5,** 506 (1972).
4. J. Janáček and J. Hasa, *Collect. Czech. Chem. Commun.,* **31,** 2186 (1966).
5. J. Hasa and J. Janáček, *J. Polym. Sci.,* **C16,** 317 (1967).
6. M. Ilavský, K. Dušek, J. Vacík, and J. Kopeček, *J. Appl. Polym. Sci.,* **23,** 2073 (1979).
7. M. Ilavský, J. Pleštil, and K. Dušek, *Eur. Polym. J.,* **16,** 901 (1980).
8. J. P. Queslel and J. E. Mark, *Adv. Polym. Sci.,* **71,** 229 (1985).
9. P. J. Flory and B. Erman, *Macromolecules,* **15,** 800 (1982).