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Synthesis and properties of poly(β-acryloxypropionic acid) hydrogels*

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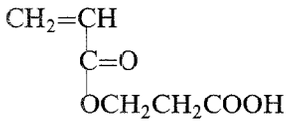
Poly(β-acryloxypropionic acid) (PAOPA) hydrogels crosslinked by ethylene glycol dimethacrylate (EDMA) have been prepared by using both a chemical initiator and by γ-irradiation. Polymerizations were conducted in bulk and also in the presence of water. Characterizations were made by swelling, compression–strain measurements and differential scanning calorimetry (d.s.c.). The findings show the following: (a) that γ-irradiation is the preferred preparative procedure, (b) the equilibrium water content is affected by the concentration of crosslinker, but not by the content of water in the feed mixture, (c) the equilibrium water content increases with increase in the swelling temperature, and (d) there is considerable heterogeneity of crosslinking, as evidenced by calculated curves of instantaneous copolymer composition vs. fractional conversion during the crosslinking copolymerization. Similarities with and significant differences from the properties of poly(2-hydroxyethyl methacrylate) hydrogels are indicated and discussed.

(Keywords: poly(β-acryloxypropionic acid); ethylene glycol dimethacrylate; hydrogel)

INTRODUCTION

Synthetic polymer hydrogels are very useful materials for both biomedical and agricultural applications. Hydrogels where 2-hydroxyethyl methacrylate (HEMA) is a principal component have been so widely studied as to not require specific referencing here. There have been fewer reports[1–3] relating to the hydrogels based on 2-hydroxyethyl acrylate (HEA) which has a similar structure to HEMA.

β-Acryloxypropionic acid (AOPA), also called 2-carboxyethyl acrylate, has long been known[4,5] as a by-product of acrylic acid manufacture or storage. Its formula is as follows:



Like acrylic acid, AOPA is easily polymerizable and can provide polymer chains with a carboxyl group which has many chemical reaction abilities. Recently there have been a few reports on the properties of AOPA and its esters[4,5] and on its copolymerization reactivity ratios[6,7], but there do not appear to have been any reports on the hydrogels of AOPA polymers or copolymers.

This paper presents the preparation of PAOPA hydrogel crosslinked by ethylene glycol dimethacrylate (EDMA). The polymerizations were initiated by γ-radiation or by chemical initiator, i.e. α,α′-azoisobutyronitrile (AIBN). The swelling and mechanical properties were studied and compared with the PHEMA hydrogel.

EXPERIMENTAL

Materials

AOPA (Polysciences) was vacuum distilled twice at 381–385 K/0.3–0.4 mmHg (n_D^{20} = 1.4526). EDMA (BDH) was used as received. AIBN (Fluka) was recrystallized from ethanol/toluene. High-purity deionized water and oxygen-free nitrogen were used in these experiments.

Polymerizations

Glass vials were siliconized inside before use in order to facilitate subsequent removal of the xerogels. Monomer mixtures were made up gravimetrically in these vials and were degassed with N_2 for 10 min. Polymerizations were initiated by either γ-radiation or initiator. In the former case, a total dose of 1.5 Mrad and a dose rate of 0.03 Mrad h^{-1} were used, and the polymerization was carried out at room temperature (ca. 295 K); in the latter case, AIBN at a concentration of 0.25 wt% (based on the mass of AOPA) was used and the polymerization was carried out at 333 K for 24 h. After polymerization, all polymer rods synthesized without water in the monomer mixture were post-cured in an oven at 353 K for one week, the weight loss during the post-curing process being negligible and the apparent conversion being effectively 100%. However, because AOPA is a very-high-boiling-point monomer, there is a very small possibility that any residual monomer may have continued to polymerize during the post-curing in air at 353 K. In any event, the AOPA rods after post-curing should have attained very high conversions. The post-cured rods were lathe cut into discs (thickness 1 mm and

* Dedicated to Professor Ron Koningsveld on the occasion of his 70th birthday
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diameter ~ 9 mm) and into pellets (length ~ 9 mm and diameter ~ 9 mm). If the polymer was made with water in the monomer mixture, then the rods were cut with a scalpel without a post-curing step.

The nomenclature of the samples is of the form X/Y/Z where X denotes the mode of initiation, i.e. radiation (R) or chemical (C). Y is the percentage by weight of EDMA in the mixture of (EDMA + AOPA) and Z is the percentage by weight of deionized water contained in the total mixture of (EDMA + AOPA + water). Thus, sample R/1/20 means: (i) radiation initiation; (ii) 100 × weight EDMA/(weight EDMA + weight AOPA) = 1; (iii) 100 × weight water/(weight EMDA + weight AOPA + weight water) = 20.

Swelling

The polymeric discs and pellets were immersed in water inside plastic jars, which were placed in an oven at 323 K for 2 weeks (discs) or 4–6 weeks (pellets) and then left at room temperature for another 2–4 weeks. The water was replaced daily by fresh water to allow removal of any sol fraction. During this process, the weight of a swollen disc usually reached a maximum at a swelling time of 24–48 h. Thereafter, the swollen disc lost weight continuously because of release of sol fraction. Only after 10–14 days did the swollen disc attain its constant weight, i.e. swelling equilibrium. Although no analysis was made of the sol fraction, these findings strongly suggest that the sol fraction contained linear polymer rather than monomer (which can reasonably be assumed to have been removed or polymerized during the post-cure treatment at 353 K for one week). After the necessary measurements were made on the hydrogels, they were dried at 353 K to obtain the weight and dimensions of the xerogels. The dimensions of the swollen gels and xerogels were measured with a calliper. The volume fraction of polymer (ϕ_2) in the hydrogel was obtained as

$$\phi_2 = (D_0/D)^3 \tag{1}$$

where D_0 and D are the diameters of xerogel and hydrogel, respectively. The volume fraction of water in hydrogel, ϕ_1, is simply $(1 - \phi_2)$. At swelling equilibrium the discs were lightly surface-dried with filter paper and weighed to yield the gravimetric equilibrium water content (EWC) as follows:

$$\text{EWC} = \frac{W - W_0}{W} \times 100\% \tag{2}$$

where W_0 and W are the weights of xerogel (after removal of sol fraction) and hydrogel, respectively. The measured dimensions and weights of the xerogel pellets were used to calculate the densities of the xerogels.

Uniaxial compression

Elastic moduli of the hydrogels were determined by stress(compression)–strain experiments at 298 K. Full experimental details for the assembly used are given elsewhere[8].

Differential scanning calorimetry

A Mettler TA3000 system was employed. The sample was placed in a sealed pan in the calorimeter and scanned from 203 to 323 K at a heating rate of 5 K min^{-1}. The built-in 'integration' function was used to obtain the enthalpy ΔH (in J per gram of hydrogel) of the endothermic peak around 273 K. Using pure deionized water a value of $\Delta H_f = 330.0$ J g^{-1} was obtained for the enthalpy of fusion of water. Thus, the freezing water content (W_f) of the hydrogel, expressed as a percentage, was calculated from the following:

$$W_f = \frac{\Delta H}{330.0} \times 100\% \tag{3}$$

and the non-freezing water content (W_{nf}) was simply the difference between EWC and W_f.

RESULTS AND DISCUSSION

General properties of as-reacted polymers

Polymers prepared in the absence of water. All radiation-initiated PAOPA rods appeared optically clear, homogeneous, and free from air bubbles. For AIBN initiated polymerizations, the polymer rods always contained some air bubbles which were too numerous to allow the rods to be used for any measurements when the EMDA content was less than 1%. However, when the EDMA content was high, macroscopic heterogeneity was exhibited. Sample C/3/0 broke into many pieces when swollen in water, while sample C/4/0 broke even before swelling. Hence, for AIBN-initiated PAOPA rods, only the samples containing either 1 or 2% EDMA could be used.

Polymers prepared with water in monomer mixture. These PAOPA hydrogels were polymerized by radiation only. The hydrogels were colourless and optically clear when prepared with less than 40% water in the monomer mixture, white and opaque when prepared with more than 40% water, while a clear shell with an opaque core was obtained when prepared with 40% water. This is similar to the situation for PHEMA hydrogels[9].

Equilibrium water content

Table 1 gives the sol fractions and water contents at 298 K for PAOPA hydrogels prepared without water in the feed mixture. Rather unusually, the sol fraction is affected only slightly by the concentration of crosslinker. The effects of an increasing content of crosslinker are twofold, namely (a) to yield a reduced water content in the hydrogel and (b) to increase the density of the xerogel. With regard to (a) the decrease in EWC is very significant when comparing samples of zero and 0.5 wt% EDMA, but is smaller at higher contents of crosslinker, with the EWC tending to a value of ca. 36 wt%. With regard to (b) the high densities of the polymer are the main contributory factor for the volumetric water contents ($100\phi_1$) being higher than the gravimetric ones (EWC). It is also seen that, at comparable crosslinker concentrations, the densities of radiation-initiated samples are higher than those of the chemically initiated ones (e.g. 1.372 and 1.335 kg dm^{-3} for R/1/0 and C/1/0, respectively). This effect must certainly be due primarily to the effect of the γ-irradiation, in addition to EDMA, in inducing crosslinking (PAOPA is an acrylic polymer rather than a methacrylic one and hence is susceptible to radiation crosslinking). It is possible that a minor contributory factor may be the existence of tiny bubbles

Table 1 Swelling properties at 298 K of PAOPA hydrogels polymerized without water

Sample	Sol fraction (wt %)	Density of xerogel (kg dm^{-3})	*EWC* (wt%)	$100\phi_1$
R/0/0	9.1	1.351	45.8	48.1
R/0.5/0	8.1	1.359	39.8	45.6
R/1/0	7.0	1.372	38.6	45.5
R/2/0	7.8	1.393	37.2	44.5
R/3/0	7.1	1.392	36.0	44.2
R/4/0	7.4	1.390	35.7	43.9
C/1/0	7.4	1.335	39.2	44.5
C/2/0	8.0	1.346	37.6	43.7

Table 2 The effect of swelling temperature on the EWC of PAOPA hydrogels

	Gel					
T (K)	C/1/0	C/2/0	R/0.5/0	R/1/0	R/2/0	R/4/0
293	38.8	36.8	38.4	37.4	35.9	34.7
298	39.1	37.4	39.8	38.6	37.2	35.7
303	40.5	38.0	40.2	39.3	38.4	36.0
313	43.1	39.5	42.8	40.8	40.5	37.7
323	45.9	41.6	45.6	43.4	43.0	39.7
333	49.0	44.5	49.1	46.1	45.2	40.8
343	52.5	47.2	53.1	50.3	48.7	43.3
351	55.6	49.9	56.8	54.6	50.8	45.7

of gas (probably nitrogen) within the AIBN-initiated samples. In this connection, although sample discs and pellets used in the measurements were cut from what appeared to be the most uniform parts of the solid rods, it is possible that even these samples contained minute gas bubbles.

Table 2 shows the effect of swelling temperature on the EWC of PAOPA hydrogels prepared without water in the monomer mixture. It can be seen that, within the temperature range studied, the EWC always increases with increasing temperature, indicating that the swelling is an endothermic process. This is different from the behaviour of PHEMA hydrogels, in which a minimum EWC at about 328 K was reported by Dušek *et al.*[10]. In the equilibrium swelling state at each temperature, all PAOPA hydrogels are clear, but if the gel is first swollen at a high temperature, e.g. 323 K, to an equilibrium state and then allowed to cool down to room temperature, all hydrogels become opaque because they contain an excess amount of water with respect to the quantity required at room temperature. When such opaque hydrogels swell at room temperature for a very long time, the excess water is able to be released from the hydrogels, which then become clear again. The time needed for release of this surplus water is much longer than the time needed for swelling the corresponding xerogels to the equilibrium state, and it was observed that the lower the crosslinker content, then the longer is the time needed for release of surplus water and attainment of clarity.

Table 3 shows the effect of water content in the monomer mixture on the EWC of the hydrogels for swelling at 298 K. After polymerization, the gel was swollen in water at room temperature for 4–6 weeks in order to reach its constant weight. Then the gel was dried and weighed. The equilibrium water content thereby obtained is denoted as EWC1. The dried gel was reswollen in water to equilibrium and dried again, to give an equilibrium water content denoted by EWC2.

Table 3 The effect of water content in the monomer mixture on the equilibrium water content of resultant hydrogels at 298 K[a]

Sample	EWC1 (wt %)	EWC2 (wt %)
R/1/0	38.3	38.9
R/1/5	38.1	38.4
R/1/10	38.9	39.1
R/1/20	38.0	38.2
R/1/30	38.8	38.5
R/1/40	38.3	38.0
R/1/50	41.2	39.1
R/1/60	41.9	39.0

[a] See text for meaning of EWC1 and EWC2

From *Table 3* it may be seen that the EWC1 water contents remained unchanged and independent of water content in the feed mixture, provided that the values of the latter were ≤ 40 wt%. However, for samples prepared in the presence of greater concentrations of water there was an increase of EWC1. This is similar, qualitatively, to the situation obtained in PHEMA hydrogels. Especially noteworthy is the finding that, within experimental uncertainty, the values of EWC2 were constant regardless of the water content of the original feed mixture.

At the first time of swelling equilibrium, the materials may be referred to as virgin hydrogels. They retained their original appearance, i.e. the opaque ones remained opaque and the clear ones remained clear. However, when these hydrogels were dried, all of the resultant xerogels became clear; when these xerogels were reswollen in water to the new equilibrium state, the hydrogels remained clear regardless of their original appearance. This is different from the behaviour of PHEMA hydrogels in which the hydrogels prepared with more than 40% water in the monomer mixture were always opaque no matter whether they were virgin gels or reswollen gels. In connection with the EWC data in *Table 3*, it can be concluded that, at the first time of swelling, the hydrogels prepared with more than 40% water in the monomer mixture did not reach their true equilibrium states.

However, the reswollen clear hydrogels R/1/50 and R/1/60 readily become translucent if the temperature is lowered after swelling equilibrium is reached. Even a very small temperature difference is able to cause such translucency. For example, for a swelling temperature of 298 K (in a water bath) and room temperature of 293 K, when samples R/1/50 and R/1/60 were surface dried, they changed from clear to translucent gels in seconds, and the original colourless gels became iridescent (light blue). Such changes were more significant for R/1/60 than R/1/50.

The virgin hydrogels of R/1/50 can also become clear after prolonged swelling. After 8 weeks for swelling at room temperature the hydrogel disc of thickness ~ 1 mm and diameter ~ 10 mm became completely clear and the shell (the thickness of this shell is ~ 1 mm) of the pellet having a length and diameter of ~ 8 mm and ~ 10 mm, respectively, also became clear, whereas the interior core remained opaque. However, the virgin hydrogel R/1/60 did not display any optical changes after 8 weeks of swelling.

Table 4 Freezing and non-freezing water contents of PAOPA hydrogels at 25 °C

Sample	W_f (wt %)	W_{nf} (wt %)
R/0/0	33.3	12.5
R/0.5/0	27.6	12.1
R/1/0	26.3	12.2
R/2/0	25.2	12.0
R/4/0	22.4	13.3
C/1/0	27.7	11.4
C/2/0	26.3	11.1

Freezing and non-freezing water

Table 4 gives the freezing and non-freezing water contents of PAOPA hydrogels prepared in the absence of water in the feed mixture. It is seen that the incorporation of 0.5 wt% EDMA causes a reduction in the freezable water content of the hydrogel, and there is only a small, but discernible reduction in W_f on incorporating higher contents of EDMA. This trend parallels the effect of EDMA on EWC (see *Table 1*) and, as a consequence, the values of W_{nf} remain sensibly constant. No meaningful difference is apparent between the values of W_f and W_{nf} for radiation-produced samples and chemically initiated ones of the same crosslinker content.

Network parameters

Values for the Young's modulus (E) of the PAOPA hydrogels were obtained as the slopes of the linear plots of stress (τ) vs. strain ($\lambda - 1$), as follows:

$$\tau = E(\lambda - 1) \quad (4)$$

where τ is the applied force per unit area of the swollen gel and λ is the ratio of deformed length to undeformed length of the hydrogel. Values for the effective crosslinking density (ν_e) were derived from the slopes of the linear plots of stress (τ) vs. ($\lambda - \lambda^{-2}$) according to equation (5)[11]:

$$\tau = RT\phi_2^{1/3}\nu_e(\lambda - \lambda^{-2}) \quad (5)$$

Over the range of λ examined, i.e. from 0.93 to 1, the plots based on equations (4) and (5) were found to be linear.

The theoretical crosslinking density (ν_t) was calculated from the following relationship:

$$\nu_t = Cf/2 \quad (6)$$

In equation (6), C (mol dm^{-3}) is the concentration of crosslinker and f is its functionality; for EDMA, $f = 4$.

The polymer–water interaction parameter χ was calculated from the following relationship[12]:

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \quad (7)$$

where V_1 is the molar volume of water (18.05 dm^3 mol^{-1} at 298 K).

From ν_e the effective molecular mass between crosslinks (M_c) was calculated via equation (8), in which ρ is the density of the xerogel:

$$M_c = \rho/\nu_e \quad (8)$$

The values of ν_t, ν_e, E, M_c, and χ are listed in *Table 5*.

Table 5 Parameters obtained from compression–strain measurements on PAOPA hydrogels at 298 K

Sample	ν_t (mol dm^{-3})	E (kPa)	ν_e (mol dm^{-3})	M_c (kg mol^{-1})	χ
R/0/0	0.000	35	0.005	282	0.791
R/0.5/0	0.069	258	0.037	36.9	0.814
R/1/0	0.138	500	0.073	18.8	0.814
R/2/0	0.281	670	0.099	14.1	0.824
R/3/0	0.421	955	0.140	9.9	0.826
R/4/0	0.561	1269	0.187	7.4	0.828
C/1/0	0.132	289	0.040	33.1	0.825
C/2/0	0.269	551	0.078	17.0	0.833

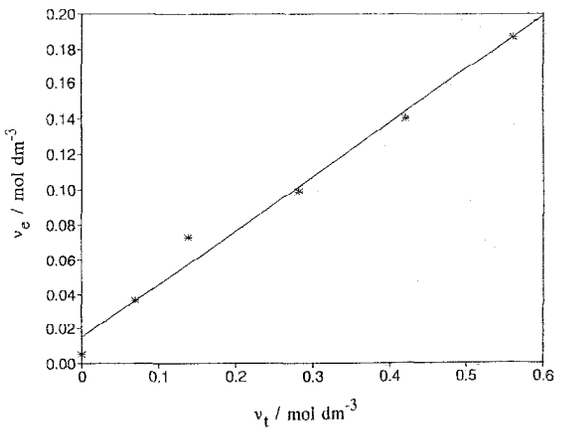

Figure 1 Dependence of the effective crosslinking density on the theoretical crosslinking density for the γ-ray initiated copolymerization of AOPA with the crosslinking comonomer EDMA

Table 6 Q–e values of EDMA, AOPA, and HEMA obtained from the literature

Monomer	Q	e	Ref.
EDMA	0.88	0.24	14
AOPA	1.09	1.26	7
HEMA	0.80	0.20	14

It can be seen that, although the EWC of PAOPA hydrogel is almost equal to that of PHEMA hydrogel, the Young's moduli are significantly smaller, and the M_c is much bigger than that of PHEMA hydrogel. This can be explained at least in part by the more flexible chain of PAOPA (without the methyl group in the backbone) when compared with PHEMA. Decreasing polymer–water interaction with increasing crosslinking density is shown by the small increase in χ.

The variation of ν_e with ν_t follows a linear relationship, as follows:

$$\nu_e = \alpha + \beta\nu_t \quad (9)$$

From *Figure 1*, values of $\alpha = 0.015$ mol dm^{-3} and $\beta = 0.31$ can be derived.

The value of β for PAOPA gels (0.31) is much smaller than that of the PHEMA hydrogels (0.80) also prepared by using EDMA as crosslinker and by γ-radiation[13]. This indicates strongly that the crosslinking efficiency of the EDMA–AOPA system is much lower than that of the EDMA–HEMA system. From the Q–e values shown in *Table 6*, the reactivity ratios for these two

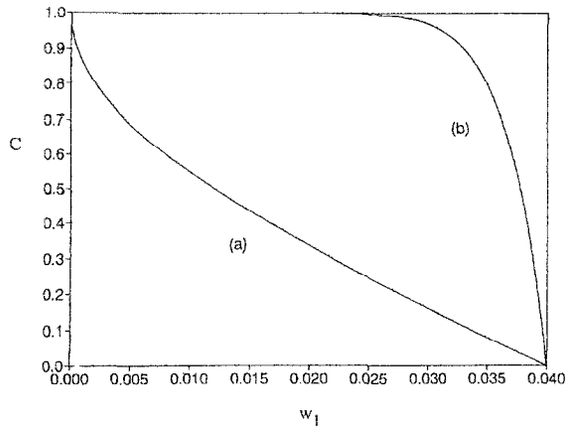

Figure 2 Calculated change in composition of unreacted monomer mixture (expressed as the weight fraction w_1 of EDMA) for various stages of fractional conversion of monomers (C) for the copolymerization of EDMA with (a) AOPA and (b) HEMA

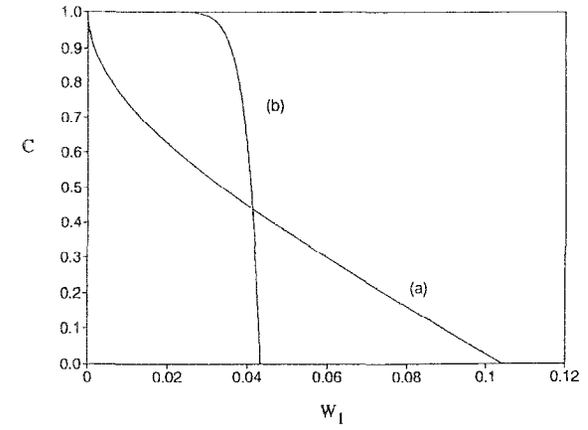

Figure 3 Calculated instantaneous copolymer composition (expressed as the weight fraction W_1 of EDMA) for various stages of fractional conversion of monomers (C) for the copolymerization of EDMA with (a) AOPA and (b) HEMA

systems can be estimated as follows:

$$\text{EDMA–AOPA}, r_1 = 1.03, r_2 = 0.34$$

$$\text{EDMA–HEMA}, r_1 = 1.09, r_2 = 0.92$$

These reactivity ratios were used to calculate the composition of residual monomer mixture (AOPA + EDMA) and the instantaneous copolymer composition at each stage of conversion. The results of such calculations are illustrated in *Figure 2* for sample R/4/0. For comparison, the corresponding calculated curve is also shown for the EDMA–HEMA copolymerization system containing the same amount of crosslinker (4 wt% of EDMA) in the initial monomer feed mixture. It can be seen that the feed composition changes much more significantly in the present system than in the EDMA–HEMA copolymerization system. *Figure 3* shows the calculated instantaneous copolymer composition at various stages of fractional conversion of monomers for the same systems as shown in *Figure 2*. It is very clear that the EDMA–AOPA copolymer is much more heterogeneous in composition than the EDMA–HEMA copolymer. This is likely to be the main reason for the much lower crosslinking efficiency of the EDMA–AOPA system compared with the EDMA–HEMA system, as evidenced by the respective values of the coefficient β, the effective crosslinking density ν_e and Young's modulus E.

CONCLUSIONS

PAOPA hydrogels with similar water contents but smaller moduli when compared with PHEMA hydrogels can be made by γ-radiation or by a chemical initiator. For practical reasons already indicated, γ-radiation is the preferred procedure for this practical synthesis. The swelling of PAOPA in water is an endothermic process as manifested by the increase in EWC with increasing swelling temperature within the temperature interval 293–351 K. The EWC is greatly affected by the crosslinker content, but not affected by the water content in the monomer mixture. The crosslinking efficiency of EDMA in the PAOPA hydrogels is much smaller than that in the PHEMA hydrogels. The heterogeneity of the crosslinking is a parameter to be quantified shortly by means of quasielastic light scattering measurements on the hydrogels, according to a theoretical approach developed by ourselves.

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