Hydroxyalkyl methacrylates: hydrogel formation based on the radical copolymerization of 2-hydroxyethylmethacrylate and 2,3-dihydroxypropylmethacrylate

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The synthesis of hydrogels by radical copolymerization of mixtures of 2,3-dihydroxypropylmethacrylate (DHPM) and 2-hydroxyethylmethacrylate (HEMA) has been performed using ethylene dimethacrylate (DME) as crosslinking agent, in the presence of 2,2'-azobisisobutyronitrile (AIBN) or of a redox system as initiator. The hydrophilicity of the obtained materials increases as the proportion of 2,3-dihydroxypropylmethacrylate increases. The maximum swelling degree of poly(HEMA) hydrogels is limited by thermodynamic effects whereas the equilibrium swelling degree of materials with high DHPM unit content is structure dependent. The gels obtained have been characterized by their equilibrium swelling degrees in water or in organic solvents and by the determination of their elastic modulus by uniaxial compression measurements. All the materials are of great interest as potential biomaterials especially for soft contact lens manufacture.

Keywords Hydroxyalkylmethacrylates; hydrogel; radical copolymerization; biomaterials; mechanical properties

INTRODUCTION

The contact lens industry, based on typical materials, has been developed extensively during the last four decades. Classification of contact lenses has been proposed[1]: hard, hydrophobic flexible and hydrogels.

Originally, hard contact lenses have been manufactured with glass; more recently methylmethacrylate crosslinked by bifunctional monomers such as ethylene dimethacrylate (DME) has been used[2]. Such materials are rigid, hydrophobic and they exhibit rather low oxygen permeability. Some experiments have been performed with success using poly(4-methyl-1-pentane) to improve the oxygen permeability[3,4].

In the second class of materials, the hydrophobic flexible contact lenses are obtained from silicone rubber. Due to the flexibility of Si–O–Si bonds, such polymers are highly permeable to oxygen[5,6]. However, they are basically hydrophobic and generally uncomfortable to the wearer.

Between 1950 and 1955, Wichterle postulated the fundamental conditions required for synthetic materials destined to be in direct contact with living tissues[9]:

(i) the material chosen should not contain any free extractable substances of low or high molecular weight such as residual monomers, traces of initiator or plasticizers. The self-diffusion of these impurities may have consequences for the surrounding tissues.

(ii) the mechanical properties of the material—especially concerning the elastic modulus—have to be similar to those of the surrounding tissues.

(iii) the material has to be permeable to water soluble substances (salts, proteins, oxygen...) to help the metabolism of the ambient tissues.

(iv) the material must resist degradation by enzymatic systems. Even if limited, such a process involves consequences for the mechanical properties of the material.

Starting from these ideas, hydrophilic polymer networks have been introduced by Wichterle and Lim[7]. Such hydrogels are potentially useful in the contact lens industry[8], which uses polymers or copolymers of methacrylic esters containing at least one alcohol function in the side chain[9]. The first hydrogel contact lenses were prepared by crosslinking 2-hydroxyethylmethacrylate (HEMA) with dimethacrylate comonomers such as DME. In that case, hydrogel lenses adhere closely to the cornea with only a tear film of capillary thickness between the cornea and the lens[1]. These soft contact lenses exhibit satisfactory biocompatibility and adequate optical properties. However, the use of poly(HEMA) hydrogels is limited by several factors. Depending upon the water concentration, the radical copolymerization of HEMA and DME yields transparent homogeneous networks, if the water content in the reaction medium is $<40\%$. Beyond this limit, phase separation occurs, involving solvent expulsion from the gel formed[10]. A heterogeneous spongy material is obtained, the mechanical properties of which are poor[11]. However, when transparent swollen hydrogels are formed, it has been established[1] that the insufficient permeability to gas does not allow a sufficient amount of oxygen to reach the cornea for epithelial

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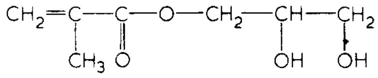
respiration, especially if the eyelids are closed. Moreover, the poly(HEMA) hydrogel lenses of low thickness are fragile and their mechanical properties can be improved. In spite of all the disadvantages poly(HEMA) hydrogels are still the most commonly used materials in the manufacture of soft contact lenses.

More recently, the synthesis of other types of hydrogels with improved properties has been achieved using vinylpyrollidone as a comonomer. Crosslinked copolymers of vinylpyrollidone and HEMA have been obtained[12] as well as graft copolymers of poly(HEMA) onto polyvinylpyrollidine[13]. Other attractive synthetic networks have been prepared by graft copolymerization of vinylpyrollidone onto silicone rubber[5]. Such materials exhibit both hydrophilicity, high oxygen permeability and improved wettability.

In this work, the aim of our project was to prepare and characterize hydrogels of high hydrophilicity, exhibiting improved mechanical properties and a biocompatibility comparable to those obtained for poly(HEMA) hydrogels. We have chosen to copolymerize DME (crosslinking agent) and mixtures of HEMA and 2,3-dihydroxypropylmethacrylate (DHPM):



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH_2}}$$

which is more hydrophilic than any other methacrylic monomer because it contains two hydroxy groups in the side chain.

In a previous paper[14], an efficient method was described for quantitative purification of 2-hydroxyethylmethacrylate. Commercially, this monomer contains impurities such as ethylene glycol, methacrylic acid and chiefly ethylene dimethacrylate. A similar purification procedure has been performed on 2,3-dihydroxypropylmethacrylate. Thereafter no trace of crosslinking agent remains detectable (by g.l.c.) in these two monomers.

Linear poly(HEMA) and poly(DHPM) have been prepared[14] and the kinetic investigation showed that the radical copolymerization of an equimolecular DHPM–HEMA mixture yields an 'ideal' copolymerization system, the product of the radical reactivity ratios of these two monomers being close to unity.

In this work, each pure monomer (and their mixtures) has been copolymerized in the presence of known amounts of ethylene dimethacrylate. In some cases, impure monomers containing some trace of residual DME have also been used. Whatever the experimental conditions, the process should lead to hydrophilic polymer networks with improved hydrophilicity. The materials obtained have been characterized by their water content at equilibrium (swelling degrees) and by their elastic moduli (uniaxial compression).

EXPERIMENTAL

Monomers

Commercial 2-hydroxyethylmethacrylate (HEMA) from Aldrich Co. was quantitatively purified by preparation absorption chromatography on silica columns as described previously[14].

2,3-Dihydroxypropylmethacrylate (DHPM) was prepared by mild acidic hydrolysis of either 2,3-epoxypropylmethacrylate[21] or (2,2-dimethyl-1,3-dioxolan-4-yl) methylmethacrylate[22]. As for HEMA, an adequate procedure for purification was used, which yields the quantitative separation between DHPM and the methacrylic diester present as impurity[14].

Ethylene dimethacrylate (DME) was distilled on calcium hydride under high vacuum before its use.

Initiation

2,2-Azobisisobutyronitrile (AIBN) from Merck Co. was purified by recrystallization from methanol. A redox system was used as well: this initiator is formed by mixing aqueous solutions of ammonium persulphate (12% by weight) and of sodium metabisulphite (6%).

Hydrogels

If AIBN is used as initiator, monomers, crosslinking agent, initiator and solvent are mixed in a glass (or Teflon) tube in well defined proportions. After two degassings under high vacuum, the tube is sealed. The reactions are carried out at 60° ± 0.5°C for given periods of time. The gels obtained are placed in an excess of solvent to reach their swelling equilibrium.

When a redox system is used as the initiator, the reaction mixture (monomers, crosslinking agent, solvent) is placed in a glass tube and then the initiator solution is added. The reaction is fast, exothermic and starts at room temperature. Depending upon the concentrations of the reagents the gel point is reached after a period extending from 5 to 25 min. After 24 h, the gel is taken out of the tube and placed in an excess of solvent.

Equilibrium swelling degree

The method of determination of equilibrium volume swelling degree Q of the networks has already been described in detail in our previous work[11,22]. The Q values can be calculated from the experimental determination of the weight degree of swelling G by the relation:

$$Q = 1 + (G-1)\frac{\bar{v}_s}{\bar{v}_0}$$

where $\bar{v}_s$ and $\bar{v}_0$ are the specific volumes of the solvent and of the dry gel, respectively. Sometimes, it is useful to express the solvent content T of the swollen material[23]:

$$T(\%) = \left(\frac{P_{sw} - P_d}{P_{sw}}\right)100 = \left(\frac{G-1}{G}\right)100$$

where P_{sw} and P_d are the weights of the sample, in the swollen and in the dry state, respectively.

Modulus

The determination of the elastic modulus E_G in the swollen state has been performed by uniaxial compression measurements using an apparatus similar to those described by Van De Kraafts[24] and by Donkersloot *et al.*[25]. The cylindrically shaped hydrogel sample (about 1 cm in length and in diameter) is placed in a cell containing an excess of solvent, the temperature being kept constant at 25° ± 0.5°C. The gel cylinder is located between two parallel Teflon discs: the upper one is attached to a pressure transducer which can be moved by means of a

Table 1 Poly(HEMA) hydrogels: influence of swelling

	Initial concentrations (%)			Weight equilibrium swelling degree *G*			
Samples	HEMA	DME	MeOEtOH	MeOEtOH (a)	MeOEtOH/H_2O (b)	MeOEtOH/H_2O (c)	H_2O (d)
MG 102	69.5	0.5	30	4.28	4.23	2.32	1.62
MG 103	49.5	0.5	50	5.60	5.66	2.79	1.65
MG 104	29.5	0.5	70	7.40	–	–	–
MG 105	65	5	30	2.25	2.27	1.66	–
MG 106	45	5	50	2.85	2.82	1.88	–
MG 107	25	5	70	4.15	4.15	2.35	–

(a): 100%, (b): 66/33, (c): 33/66, (d): 100%

$G_{MeOEtOH}$ and G_{H_2O} are the equilibrium swelling degree in 2-methoxyethanol and in water respectively

$G_{66/33}$ and $G_{33/66}$ are the equilibrium swelling degree in 2-methoxyethanol–water in volume proportions 66/33 and 33/66, respectively

Table 2 Poly(HEMA) hydrogels: swelling degree and elastic modulus at the 'native' state and at equilibrium in water and in 2-methoxyethanol

Samples	HEMA (%)	DME (%)	Solvent nature	(%)	G_0	$E_{G_0} \times 10^{-6}$ (dyne cm^{-2})	G	$E_{G_0} \times 10^{-6}$ (dyne cm^{-2})
MG 108	66	0.5	H_2O	33.5	1.5	2.45	1.65	2.14
MG 109	66	0.5	MeOEtOH	33.5	1.5	2.44	4.40	1.53

G_0 and E_{G_0} are the swelling degree and elastic modulus at the 'native' state, respectively
G and E_G are the equilibrium swelling degree and the elastic modulus, respectively

micrometer screw; the lower one, in a fixed position, constitutes the bottom of the cell. The corresponding force F exerted on the sample by turning the micrometer screw is given by the transducer.

If A_G is the base area of the gel cylinder in swollen state it has been established[22,26] that the reduced force is given by:

$$\sigma = \frac{F}{A_G} = ART\nu^* Q^{-1/3} h^{2/3} (\Lambda - \Lambda^{-2})$$

where A is a constant, ν^* is the number of elastic chains per unit volume of dry gel, Λ is the compression ratio and h is the so-called 'memory-term' introduced by Dusek and Prins[26].

The experimental measurements of F, A_G, Q and Λ yield the elastic modulus:

$$E_G = \frac{\sigma}{\Lambda - \Lambda^{-2}} = ART\, h^{2/3} Q^{-1/3}$$

which is the slope of the line corresponding to the variation of σ *versus* $(\Lambda - \Lambda^{-2})$.

All of our experiments have been performed by 'instantaneous' measurements of the force F: they take into account neither possible volume variation, nor relaxation phenomena during the process.

RESULTS AND DISCUSSION

Much interest has been devoted to establish the relation between the structure and the properties of poly(HEMA) hydrogels prepared by radical copolymerization with DME in aqueous medium[15–20]. In the next subsection, comparison of the behaviour of poly(HEMA) hydrogels swollen either in water or in alcohols, has been achieved, in order to get references for the following sections.

Only a few papers have been published on the synthesis and the properties of poly(DHPM) hydrogels[20,21]. From our preliminary attempts using either redox systems or classical initiators (AIBN, benzoyl peroxide...) it results that the DHPM copolymerization with DME is very fast and that some inhomogeneity in the network should result.

The main aim of the present work was to determine whether the use of 2,3-dihydroxypropylmethacrylate as comonomer increases the hydrophilicity of the materials obtained, without basic changes in their mechanical properties (second subsection).

Poly(HEMA) hydrogels

As was described previously[14], water is a 'bad' solvent of the linear poly(HEMA) whereas alcohols, especially 2-methoxyethanol, are good solvents for the same elastic chains.

We have prepared two series of poly(HEMA) gels in 2-methoxyethanol (*Table 1*). Each of these series is characterized by a constant amount of DME (0.5% and 5%, respectively), the concentration of HEMA being variable. The networks obtained are swollen to equilibrium in 2-methoxyethanol–water mixtures of various proportions. The corresponding weight equilibrium swelling degrees G have been measured. It has to be noted that solvent exchange is sometimes difficult (i.e. MG 104) as disaggregation of the material may result, owing to tensile forces corresponding to the difference of affinity of the gel for the two competitive solvents. However, the results obtained show that the elastic chains of poly(HEMA) exhibit a preferential affinity for the best diluent; the values of G start to decrease when the proportion of water in the solvent mixture reaches 2/3.

Two additional gels have been prepared (*Table 2*) in water and in 2-methoxyethanol, respectively, at the same concentration of HEMA (66%) in the presence of the same amount of DME (0.5%). The elastic moduli E_{G_0} have been measured in the 'native' state which means at the swelling degrees G_0 corresponding to the concentration of the

Table 3 Poly(HEMA–DHPM) hydrogels prepared by redox initiation

Sample	HEMA (%)	DHPM (%)	$(H_2O)_i$ (%)	$(H_2O)_{eq}$ (%)	G	$E_G \times 10^{-6}$ (dyne cm^{-2})
ME 10	14	6	80	Syneresis		
ME 11	21	9	70	Syneresis		
ME 12	28	12	60	60	2.51	0.615
ME 13	35	15	50	56	2.28	1.020
ME 14	42	18	40	55	2.20	1.250
ME 15	49	21	30	52	2.08	1.500
ME 16	56	24	20	50	2.00	2.110
ME 17	10	10	80	Syneresis		
ME 18	15	15	70	70	3.36	0.392
ME 19	20	20	60	67	3.06	0.745
ME 20	25	25	50	63	2.67	0.975
ME 21	30	30	40	60	2.51	1.400
ME 22	35	35	30	58	2.36	1.570
ME 23	40	40	20	52	2.08	4.270
ME 24	6	14	80	84	6.35	0.135
ME 25	9	21	70	76	4.11	0.436
ME 26	12	28	60	71	3.44	0.846
ME 27	15	35	50	65	2.86	1.320
ME 28	18	42	40	62	2.61	1.660
ME 29	21	49	30	62	2.61	1.800
ME 30	24	56	20	60	2.51	1.870
MG 93	0	10	90	–	–	–
MG 94	0	20	80	92.2	12.85	0.040
MG 95	0	30	70	87.5	8.12	0.100
MG 96	0	40	60	83.5	6.02	0.293
MG 97	0	50	50	81.2	5.55	0.399
MG 98	0	60	40	76.5	4.24	0.801
MG 99	0	70	30	72.0	3.54	1.280
MG 100	0	80	20	67.0	3.01	2.050

% $(H_2O)_i$ and % $(H_2O)_{eq}$ are the volume proportions of water in the reaction medium and at equilibrium swelling degree, respectively
G is the weight equilibrium swelling degree
E_G is the elastic modulus at equilibrium

reaction mixtures. These two gels are placed in each of the two solvents: the moduli E_G and the equilibrium swelling degrees G have been determined. From these basic experiments, it results that whatever the swelling solvent, at identical swelling degrees, the gels exhibit similar mechanical properties. The nature of the swelling solvents influences the mechanical behaviour of the materials only when it affects their swelling degree.

Poly(DHPM-HEMA) hydrogels

The synthesis of hydrogels containing various proportions of DHPM and HEMA has been performed in aqueous medium with DME as crosslinking agent. Under well defined experimental conditions, homogeneous crosslinked networks with satisfactory optical properties have been obtained. In this section, the influence of several parameters on the behaviour of the hydrogels has been examined.

Hydrophilicity of the networks. In order to examine the compatibility between water and networks containing DHPM, four series of gels have been prepared by radical copolymerization in the presence of redox initiating system.

In each series, the water content in the reaction medium extends from 20 to 80% (*Table 3*). The first three series are characterized by a volume ratio HEMA/DHPM equal to 30/70, 50/50 and 70/30, respectively. The last set of experiments deals with the crosslinking of DHPM in the absence of HEMA in the reaction mixture (MG 93 to MG 100).

From these experiments, the following conclusions can be drawn:

(i) In the case of poly(HEMA) hydrogels, owing to the fact that water is a thermodynamically poor solvent for linear poly(HEMA), syneresis takes place[10] as soon as the water content reaches 40%. This result means that the maximum swelling degree is strictly limited by thermodynamic effects. The pure poly(HEMA) hydrogels are still homogeneous in the presence of 90% water. These experiments show that the hydrophilicity of poly(DHPM) networks is determined by structural factors. These results are similar to those obtained for polystyrene networks swollen in benzene[27,28].

(ii) The hydrophilicity of the materials obtained increases from 40 to 90% water with increasing DHPM proportion in the reaction medium, the variation being practically linear between these two limits, as shown in *Figure 1*. Below the limit of syneresis, all materials obtained are transparent: swollen to equilibrium in water, they stay transparent. Beyond that limit, the gels are opaque: when such materials are submitted to a deswelling effect, they exhibit satisfactory optical properties. However, if the same gels are replaced in an excess of water, they come back to their initial state. These experiments show that structural inhomogeneities are responsible for the behaviour observed.

(iii) By increasing the DHPM/HEMA ratio one improves the equilibrium swelling G. Moreover, when overall monomer concentration in the reaction medium increases, the values of G decrease whereas the corresponding elastic moduli E increase. The equilibrium water content increases with increasing DHPM content in the medium, the highest water content being obtained with pure DHPM.

Influence of crosslinking agent. The crosslinking degree is directly connected with the amount of crosslinking agent introduced in the reaction mixture. In order to study the influence of the proportions of DME on the properties of the materials obtained, two series of gels have been prepared. In the first, an equimolar mixture of DHPM and HEMA has been copolymerized, using the redox system as initiator, with increasing DME content with a constant amount of water (40%). Under the same experimental conditions, a second set of experiments has been performed using only the DHPM monomer (MG 78 to MG 84). The results are listed in *Table 4*. The two values of the water content at equilibrium and the high elastic moduli obtained are noteworthy. These facts are due to the presence of residual impurities of DHPM monomer (probably glyceryl dimethacrylate). Nevertheless, these results show that the DME content is an important factor. One can observe simultaneously an increase of the elastic modulus and a decrease of the water content at equilibrium when the DME concentration increases. These experiments confirm that the equilibrium swelling degree of poly(DHPM) networks is determined by structural factors and not by thermodynamics, as is the case for poly(HEMA) hydrogels.

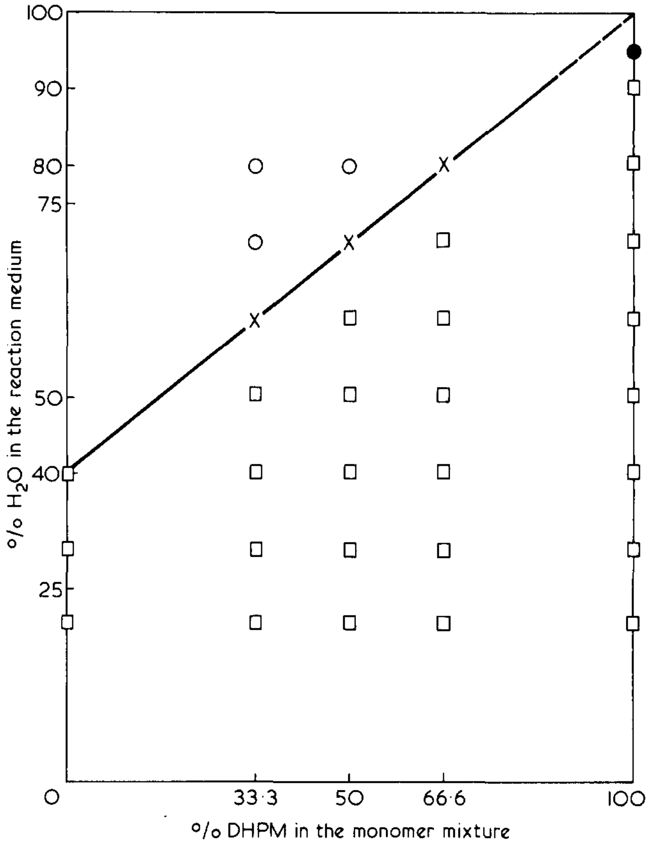


Figure 1 Limit of syneresis for poly(HEMA–DHPM) hydrogels. ●, No gel formation; □, Transparent hydrogels; X, Turbid hydrogels; ○, Opaque hydrogels

CONCLUSION

The radical copolymerization of mixtures of 2,3-dihydroxypropylmethacrylate and 2-hydroxyethylmethacrylate yields hydrogels of high hydrophilicity and exhibiting improved mechanical properties. It can be concluded that the use of 2,3-dihydroxypropylmethacrylate as comonomer removes the limit of syneresis which characterizes the limited affinity of a gel for its swelling solvent. The syneresis phenomenon appears at 40% water in the case of poly(2-hydroxyethylmethacrylate) hydrogels but it is located above 90% water for poly(2,3-dihydroxypropylmethacrylate) networks exhibiting the same crosslinking density.

The influence of various parameters on the behaviour of the networks obtained has been considered: composition of the monomer mixture, swelling solvents and crosslinking degree. At similar equilibrium swelling degrees, materials containing some 2,3-dihydroxypropylmethacrylate exhibit moduli higher than those of poly(2-hydroxyethylmethacrylate) hydrogels[25].

Table 4 Poly(HEMA–DHPM) hydrogels and poly(DHPM) hydrogels prepared by redox initiation with various amounts of DME

Sample	HEMA (%)	DHPM (%)	DME (%)	$(H_2O)_i$ (%)	$(H_2O)_{eq}$ (%)	*G*	$E_G \times 10^{-6}$ (dyne cm^{-2})
MG 65	30	30	0	40	59.6	2.47	1.40
MG 66	29.85	29.90	0.25	40	56.6	2.30	1.74
MG 67	29.75	29.75	0.50	40	55.8	2.26	1.84
MG 68	29.50	29.50	1	40	55.2	2.23	2.29
MG 69	29	29	2	40	53.3	2.14	3.03
MG 70	27.50	27.50	5	40	47.4	1.90	3.44
MG 71	25	25	10	40	43.3	1.76	3.80
MG 78	0	60	0	40	59.7	2.48	3.31
MG 79	0	59.75	0.25	40	57.3	2.34	4.30
MG 80	0	59.50	0.50	40	55.6	2.25	4.33
MG 81	0	59	1	40	54.0	2.20	5.77
MG 82	0	58	2	40	51.4	2.06	7.47
MG 83	0	55	5	40	Syneresis		
MG 84	0	50	10	40	Syneresis		

% (DME) is the proportion of DME added to the reaction medium
% $(H_2O)_i$ and % $(H_2O)_{eq}$ are the volume proportions of water in the reaction medium and at equilibrium swelling degree, respectively
G is the weight equilibrium swelling degree
E_G is the elastic modulus at equilibrium

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