Hydroxyalkyl methacrylates: Kinetic investigations of radical polymerizations of pure 2-hydroxyethyl methacrylate and 2, 3-dihydroxypropyl methacrylate and the radical copolymerization of their mixtures

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Hydroxyalkyl methacrylates such as 2-hydroxyethyl methacrylate (HEMA) and 2, 3-dihydroxypropyl methacrylate (DHPM) have been prepared. An efficient method has been developed yielding a quantitative purification in order to eliminate any trace of crosslinking agent in these monomers. Kinetic investigations of the radical polymerization and of the radical copolymerization of their mixtures have been performed by measuring, at various times, the monomer consumptions, using gas-liquid chromatography (g.l.c.). It has been established that the radical copolymerization of DHPM–HEMA couple works efficiently without excessive fluctuations in the composition of the formed chains. The corresponding radical copolymerization ratios have been precisely determined and the obtained results to demonstrate that DHPM–HEMA system leads to an ideal copolymerization.

Keywords Polymerization; kinetics; purification; gas–liquid chromatography; methacrylate; monomer

INTRODUCTION

Hydrophilic polymer networks (or hydrogels) have been the subject of much interest for a number of years because of their potential biomedical applications (i.e. orthopedic surgery, plastic implants, soft contact lenses, etc.).

Recently, the hydrogels derived from polymers or copolymers of methacrylic esters containing, at least, one hydroxy group in their side chain, have been of particular interest for their applications. The basic monomer used is 2-hydroxyethyl methacrylate (HEMA). The first synthesis of this monomer was carried out around 1925; however, its use in the synthesis of hydrophilic crosslinked networks was only described in 1960 by O. Wichterle and D. Lim[1]. The results obtained have been applied with great success to the manufacture of soft contact lenses[2].

At present, HEMA is a commercially available monomer and the properties of the corresponding hydrophilic crosslinked networks have been widely studied in many papers[3-5]. Curiously enough, little work has been published in the literature[6-8] on the synthesis and the properties of linear poly(HEMA).

However, attention should be drawn to the following facts:

- The linear homopolymer, in which one alcohol group is present in each repeat unit, exhibits a limited compatibility with water, but it is not soluble in water[9].

—It has been clearly established that the permeability of poly(HEMA) hydrogels is related to the amount of water it contains[10]. Moreover, it is known that, depending upon the concentration of water in the reaction mixture (HEMA, crosslinking agent, initiator, water), the copolymerization process yields either a homogeneous network (when the water content is 40% or less) whatever the crosslinking degree may be, or a heterogeneous material[11]. In the latter case, owing to the fact that water is a thermodynamically poor solvent for the polymer formed, phase separation occurs during the copolymerization process: the so-called 'syneresis' phenomenon takes place, involving solvent expulsion out of the crosslinked material formed[12]. As a consequence, the gel is opaque and its mechanical properties are poor. Such a material obviously does not fit in with the desired applications in the domain of soft contact lenses.

The commercial HEMA monomer always contains impurities such as ethylene glycol, methacrylic acid and chiefly ethylene dimethacrylate (DME). No efficient method has been proposed in the literature[6,7] to quantitatively eliminate the ethylene dimethacrylate. This impurity is responsible for HEMA crosslinking in absence of any addition of crosslinker. This explains why it is not easy to prepare linear poly(HEMA) and to study its properties in solution.

The final aim of our work concerns the synthesis and the characterization of new types of hydrogels with improved hydrophilicity and exhibiting a biocompatibility and mechanical properties comparable to those of poly(HEMA) hydrogels. We developed an efficient method to obtain a quantitative purification of HEMA and of a second monomer containing two alcohol functions in the side chain: 2,3-dihydroxypropyl methacrylate, in order to eliminate any trace of crosslinking agent (i.e. DME) in these monomers. Radical copolymerization of this monomer mixture should yield hydrogels with improved hydrophilicity.

It is necessary, however, to know the distribution of the units of each type along the elastic chains of the network,

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and the amplitude of the fluctuations in composition that affects the system. Preliminary experiments were meant to establish the best conditions for a detailed kinetic investigation by measuring at various times the monomer consumptions using gas-liquid chromatography (g.l.c.).

The present paper gives an account on kinetic investigations of the radical homopolymerization of HEMA and DHPM and of the radical copolymerization of their mixtures. Thus, the values of the radical reactivity ratios of the two monomers involved can be calculated.

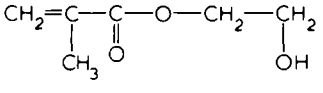
In a second paper[25], equilibrium swelling degrees and mechanical properties of the corresponding hydrophilic networks will be examined as a function of their average composition.

SYNTHESIS AND PURIFICATION OF THE HYDROXYALKYL METHACRYLATES

Principle of the synthesis and the purification of the monomers

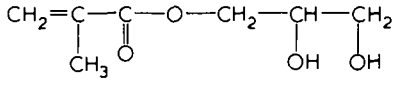
The present study is carried out using three basic monomers:

. 2-hydroxyethylmethacrylate (HEMA)



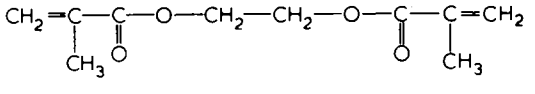
(1)

. 2,3-hydroxypropylmethacrylate (DHPM)



(2)

. ethylene dimethacrylate (DME), a bifunctional monomer used as crosslinking agent:

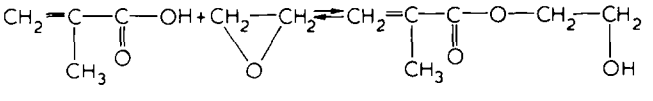


(3)

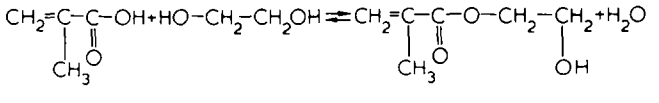
HEMA and DME are commercially available monomers, DHPM was synthesized in the laboratory.

2-Hydroxyethylmethacrylate. The synthesis of HEMA is well known and widely described in the literature[13]. We can recall the methods commonly used:

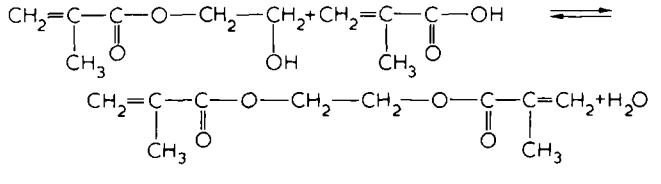
. Reaction of methacrylic acid with ethylene oxide:



. Esterification of methacrylic acid with a large excess of ethylene glycol:

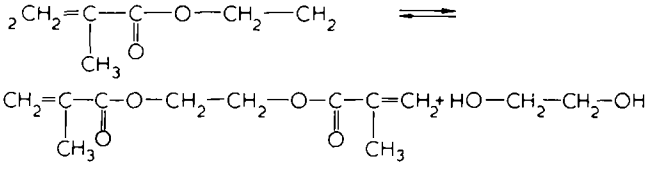


In both cases, a side reaction occurs yielding ethylene dimethacrylate (DME):



The latter reaction clearly shows why the commercial HEMA contains always some DME as impurity.

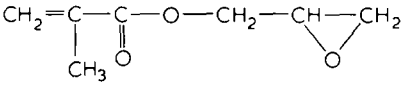
We have performed a quantitative separation of HEMA and DME using preparative absorption chromatography. However, it had to be checked first whether starting form pure HEMA, the dismutation reaction can be disregarded:



If such a reaction took place, the HEMA purification attempts would be elusive.

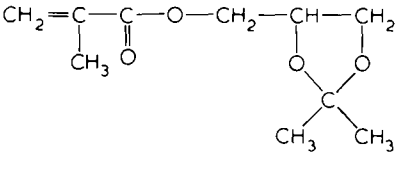
2,3-Dihydroxypropyl methacrylate. The preparation of 2,3-dihydroxypropyl methacrylate (glyceryl methacrylate) has been carried out by mild acidic hydrolysis of the following monomers[14,15]:

. 2,3- epoxypropyl methacrylate (glycidyl methacrylate):



(4)

. (2,2-dimethyl-1,3 dioxolan-4 yl) methyl methacrylate:



(5)

Monomer (4) is commercially available. Monomer (5) has been synthesized in our laboratory as described previously[14,15]. A mixture of methacrylic acid and thionyl chloride is reacted with 2,3-isopropylidene glycerol in HMPT/ether medium.

The opening of the epoxy or the acetal group by acidic hydrolysis yields the formation of DHPM. The reaction is carried out using dilute acids to prevent the attack of the ester function of monomers (4) and (5). At the beginning the reaction medium is heterogeneous, the monomers (4) and (5) being insoluble in water. A few additional days are necessary for the reaction to go to completion.

Quantitative purification of HEMA and of DHPM

The purity of the monomers involved has been characterized by g.l.c. It was shown that commercial HEMA contains up to 4% or 5% of bifunctional monomers. In the case of DHPM, it is even worse as the proportions of difunctional monomer (probably, glyceryl dimethacrylate), originating (as DME) from the esterification of the second alcohol function of DHPM, is present in higher proportions.

Several methods have been attempted to purify accurately the monomers used:

- Classical distillation, even with efficient columns, is inoperative as is shown for HEMA (*Figure 1a*) and for DHPM (*Figure 2a*). The impurities are still present, even after two successive distillations.

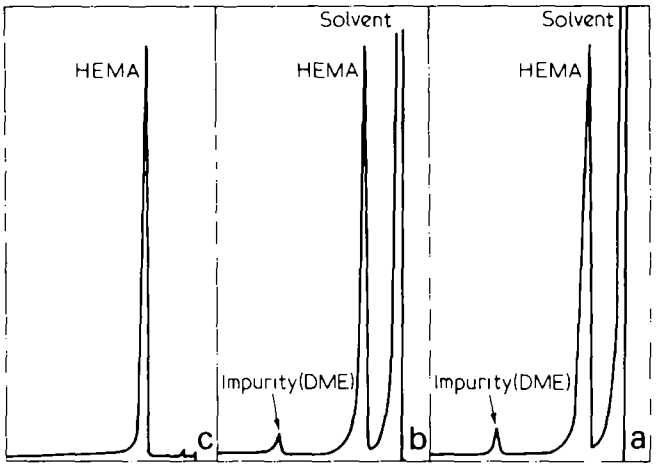


Figure 1 Purification of 2-hydroxyethylmethacrylate: (a) chromatogram of distilled HEMA; (b) chromatogram of HEMA after extraction with hexane; (c) chromatogram of HEMA after preparative absorption chromatography on silica column

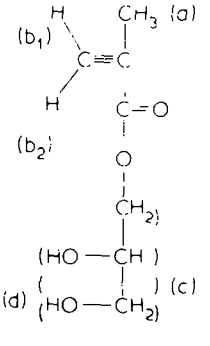
—A continuous liquid–liquid extraction apparatus has been used to try to separate HEMA and DME as described in the literature[7]. An aqueous solution of predistilled commercial HEMA is submitted to a continuous extraction with hexane for 10 h (hexane being a good solvent for DME and a non-solvent for HEMA). The monomer was then isolated by salting out with sodium chloride and the whole extraction procedure was repeated over 10 h. After separation of methacrylic acid, the chromatographic control showed clearly (*Figure 1b*) that ethylene dimethacrylate was still present in HEMA. In the case of DHPM (*Figure 2b*), the results are the same.

—Finally, preparative absorption chromatography on silica columns has been attempted. The choice of this hydrophilic support is justified by the difference of affinity it exhibits for HEMA and for DME. Knowing that HEMA contains one alcohol function, it should be eluted more slowly than DME. Preliminary experiments on thin layer chromatography demonstrated the validity of this hypothesis. The choice and the composition of the eluting mixture are of major importance and the best results have been obtained using a benzene-ethyl acetate mixture (see experimental data). The efficiency of our method is demonstrated by a chromatogram of pure HEMA without any trace of DME (*Figure 1c*). Similar results have been obtained in the purification of DHPM (*Figure 2c*) using the same method. In that case, the affinity of DHPM (with its two alcohol functions) for the silica filling is better than that of HEMA. Similarly, the methacrylic diester is more hydrophilic than ethylene dimethacrylate. From these considerations, it results that the most efficient separation of DHPM from its impurities is obtained with an eluting mixture composed of benzene and acetone (see experimental data).

Experimental

Materials. 2-hydroxyethylmethacrylate (1) is a commercial monomer from Aldrich Co. Its purification has been performed by preparative absorption chromatography on silica columns. It has been established that the best composition of the eluting mixture corresponds to 70% of ethylacetate and 30% benzene (by volume). After careful distillation, the characteristics of pure HEMA are: $Bp_{0.5} = 64°C$. Elemental analysis: % C, 55.25; H, 7.73; O, 37.03. By g.l.c. (*Figure 1c*), DME cannot be detected. The pure HEMA obtained by the proposed method is stable and can be kept indefinitely in a refrigerator. Repeated chromatographic analyses demonstrate that the possible dismutation reaction does not occur, even when the pure monomer is heated to 60°C. Such a monomer was used for the kinetic investigation without further purification.

2,3-Dihydroxypropylmethacrylate (2) has been prepared by acidic hydrolysis either of 2,3-epoxypropylmethacrylate (4) or of (2,2-dimethyl-1,3 dioxolan-4 yl) methyl methacrylate (5) following some preliminary attempts described by M. Refojo[16] for monomer (4) and more recently by G. Hild[14] in the case of monomer (5). We have used the following procedure: a 40:60 mixture of (4) and aqueous solution of H_2SO_4 (3.10^{-1} mol l^{-1}) was efficiently mixed for one week at room temperature. The acidic hydrolysis of (5) was carried out using HCl, as this acid seems more efficient for the hydrolysis of acetal groups. After reaction, the solution was neutralized by a 10% NaOH solution and monomers (4) and (5) were extracted from the water phase by ether. The DHPM was obtained by saturation of the aqueous phase using NaCl followed by ether extraction. The organic phase was dried for one day on anhydrous sodium sulphate. After filtration, the ether was slowly evaporated yielding a colourless viscous liquid (yield: 65%). The crude DHPM has been carefully distilled on CuCl in an apparatus in which the Vigreux column is replaced by copper wire to prevent any spontaneous polymerization. After distillation the total yield is about 50%. However g.l.c. exhibits the presence of the methacrylic diester (*Figure 2b*). Using preparative absorption chromatography on silica columns, an efficient separation was achieved (Figure 2c): the eluting mixture consisted of 90 parts acetone and 10 parts benzene (in volume). The final product has been controlled by i.r., n.m.r. and elemental analysis. The i.r. spectrum shows the existence of a large band near 3400 cm^{-1}, characterizing the HO-function and the absence of absorption at 1265 cm^{-1} due to the epoxy group. Figure 3 shows the n.m.r. spectrum (using HMDS as a reference).



(a) corresponds to a triplet at 1.85 ppm; (b) shows two peaks at 5.5 ppm and 6 ppm corresponding to b_1 and b_2 protons; (c) and (d) present a set of peaks between 3.3 ppm and 4.3 ppm. $Bp_{0.2} = 81°C$–$82°C$. Elemental analysis: %C, 52.30; H, 7.62; O, 40.06.

. Ethylene dimethacrylate (3) is a monomer commercially available from Aldrich Co. Its distillation is carried out under high vacuum over H_2Ca just before use.

. 2,3-Epoxypropylmethacrylate (4) is a commercial product from Aldrich Co., distilled before use.

. (2,2-Dimethyl-1,3 dioxolan-4 yl) methyl metha-

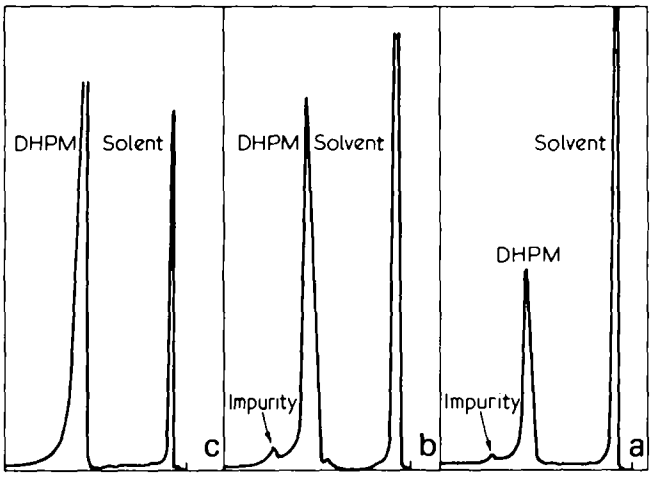


Figure 2 Purification of 2-3 dihydroxypropylmethacrylate: (a) chromatogram of DHPM after its preparation; (b) chromatogram of DHPM after extraction with hexane; (c) chromatogram of DHPM after preparative absorption chromatography on silica column

crylate: the synthesis and the characteristics of this monomer have been described in recent publications[14,15].

Apparatus. Gas-liquid chromatography (g.l.c.) was carried out using a Girdel apparatus, equipped with flame ionization detection, the driving vector being nitrogen. The column (length 2 m) is filled with a stationary phase OV 17 at 3% on G 100–120 mesh chromosorb. The temperature of the chromatographic column was programmed:
$T_1 = 140°C$ during 60 s. The rate of increase of temperature is about 10°C per min until 250°C. ^{1}H-n.m.r. spectra have been performed using a Hitachi Perkin–Elmer R 24 A (60 MHz) apparatus. A Perkin-Elmer 125 apparatus has been used for the i.r. characterization of the monomers.

KINETIC INVESTIGATIONS

Kinetic investigations of the radical polymerization of each monomer (HEMA and DHPM) and of the radical copolymerization of their mixture will be described in this section.

Some general considerations

Basic equations. In all our experiments the kinetic investigations of the homopolymerization of HEMA and DHPM have been carried out during the early stages of the process. Therefore, the initiator concentration [I] can be considered as a constant and the conversion degree $X = \frac{[M]_0 - [M]}{[M]_0}$ is given by the classical expression[17]:

$$\ln\frac{[M]_0}{[M]} = -\ln(1-X) = k_p\left(\frac{k_d f}{k_t}\right)^{1/2}[I]^{1/2} \qquad (1)$$

where k_d, k_p and k_t are the initiation, propagation and termination rate constants, respectively and f is the efficiency factor.

When a mixture of two monomers A and B is submitted to a radical initiator I, the copolymerization equation can be written as[17]:

$$\frac{d[A]}{d[B]} = \frac{[A]r_a[A]+[B]}{[B]r_b[B]+[A]} \qquad (2)$$

where the radical reactivity ratios are defined as usual:

$$r_a = \frac{k_{aa}}{k_{ab}} \qquad r_b = \frac{k_{bb}}{k_{ba}} \qquad (3)$$

By introducing the following parameters:

$$f_a = \frac{[A]}{[A]+[B]}$$

percentage amounts of A of the monomer mixture at time t

$$F_a = \frac{d[A]}{d[A]+d[B]}$$

proportion of A units in the copolymer during time interval $(t, t+dt)$

Equation (2) can be written in a different form:

$$F_a = \frac{r_a f_a^2 + f_a f_b}{r_a f_a^2 + r_b f_b^2 + 2 f_a f_b} \qquad (4)$$

Generally F_a and f_a are quite different. Consequently one of the monomers is consumed more rapidly than the other, and the composition of the monomer feed varies, leading to a continuous shift of the composition. To evaluate the amplitude of these fluctuations with respect to the reaction yield, let us consider that during the time interaval $(t, t+dt)$, $d[M]=d[A]+d[B]$ monomer molecules are converted and the overall amount of the monomer A in the mixture shifts from f_a to $(f_a - d f_a)$. This can be expressed by:

$$f_a d[M] - (f_a - d f_a)([M] - d[M]) = F_a d M$$

which yields Skeist's differential equation[18]:

$$\frac{d[M]}{[M]} = \frac{d f_a}{F_a - f_a} \qquad (5)$$

To integrate this expression, computer calculations are useful[19]. However, analytical expressions have been proposed by several authors, especially by G. C. Lowry[20].

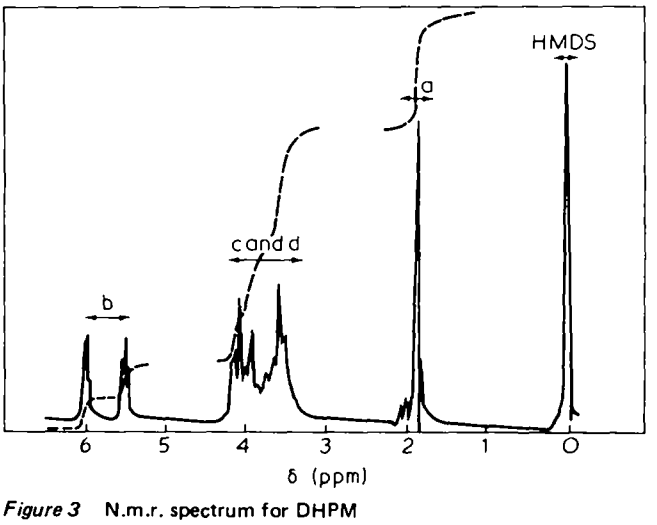


Figure 3 N.m.r. spectrum for DHPM

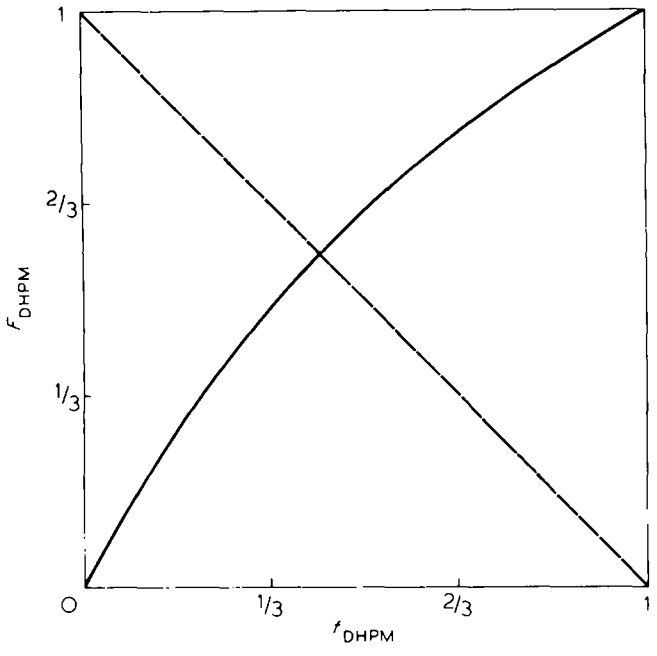


Figure 4 Variation of F_A (DHPM) as function of f_a (DHPM)

Radical reactivity ratios. To determine the values of the radical reactivity ratios r_a and r_b, kinetic investigations have to be carried out at low degrees of conversion. For each experiment, the obtained values of f_a and F_a have to be considered. One can also follow by g.l.c. the concentration of the residual monomer and its derivation with respect to time t. In both cases, the determination of r_a and r_b is obtained by linearization of equation (4). The linearization processes most commonly used are:

The Mayo–Lewis method[21] in which equation (4) is written as:

$$r_b = \frac{f_a^2}{f_b^2}\left(\frac{1-F_a}{F_a}\right) r_a - \frac{f_a}{f_b}\left(\frac{2F_a-1}{F_a}\right) \tag{6}$$

For each couple of experimental values of f_a and F_a, r_a is a linear function of r_a and the best intercept between all the lines gives the real values of r_a and r_b.

– The Fineman–Ross linearization process[22] in which:

$$G = \frac{f_a}{f_b}\left(\frac{2F_a-1}{F_a}\right) \text{ is plotted } \textit{versus } H = \frac{f_a^2}{f_b^2}\left(\frac{1-F_a}{F_a}\right) \tag{7}$$

Each experiment yields one point (G,H) and the experimental points define one straight line: $-r_b$ is the intercept and the slope is r_a.

—By introducing the following parameters:

$$x = \frac{[A]}{[B]} \quad \text{and} \quad y = \frac{d[A]}{d[B]}$$

equation (4) becomes:

$$\frac{x}{y}(y-1) = r_a\frac{x}{y} - r_b \tag{8}$$

By plotting $\frac{x}{y}(y-1)$ *versus* $\frac{x^2}{y}$ a straight line is also obtained where r_a corresponds to the slope and $-r_b$ to the intercept.

Ideal copolymerization. When the product of the two radical reactivity ratios $r_a.r_b$ is unity, a so-called 'ideal' copolymerization can be involved[23]. That implies that each of the radicals A^0 and B^0 exhibits the same affinity for the two monomers which means:

$$\frac{k_{aa}}{k_{ab}} = \frac{k_{ba}}{k_{bb}}$$

The composition diagram (f_a *versus* F_a) is symmetric with respect to the second bisector (*Figure 4*).

The composition equation (2) reduces to:

$$\frac{d[A]}{d[B]} = r_a\frac{[A]}{[B]} \tag{9}$$

There is proportionality between the consumption rate of each monomer and its residual concentration. Equation (9) can be written as:

$$\frac{d[A]}{[A]} = r_a\frac{d[B]}{[B]} \tag{9}$$

It follows that if one of the monomers is converted into polymer according to a first order law, the same should be true for the second monomer. These results are comparable to those recently described by G. Hild and P. Rempp[24] in the case of the radical copolymerization of styrene and divinylbenzene.

The distribution of A and B units along a chain obeys Bernouilli statistics: it is governed by one single parameter. The probability for BA and AA diads to be formed are equal and the same is true for BB and AB diads:

$$P_{aa} = \frac{r_a[A]}{r_a[A]+[B]} \qquad P_{ab} = \frac{[B]}{r_a[A]+[B]}$$

$$P_{bb} = \frac{r_b[B]}{r_b[B]+[A]} = \frac{[B]}{r_a[A]+[B]}$$

$$P_{ba} = \frac{[A]}{r_b[B]+[B]} = \frac{r_a[A]}{r_a[A]+[B]}$$

It follows:

$$P_{aa} = P_{ba} = 1 - P_{ab} = 1 - P_{bb} \tag{10}$$

If $r_a r_b = 1$ equation (10) is valid whatever the parameters of instantaneous composition of the mixture may be.

Experimental

Polymerization process. The polymerization and copolymerization reactions have been performed in 2-methoxy-ethanol under dry argon atmosphere, at 60°C using azo-2-2' isobutyronitrile as initiator.

Gas liquid chromatography. The kinetic investigations have been performed by measuring the residual concentrations of the monomers as a function of time. These determinations have been carried out by gas liquid

chromatography (g.l.c.) using dimethylphthalate as an internal standard.

The chromatographic apparatus (Perkin Elmer Sigma 1) is equipped with flame ionization detection. The column is filled with a stationary phase of OV 17 at 20% on G 100–120 mesh chromosorb (length: 2 m), the driving gas being nitrogen (flow: 22 ml/mm).

Homopolymerization of HEMA. Composition of the initial reaction medium: —$[HEMA]_0$: 1.505 mol l^{-1} — $[Reference]_0$: 0.220 mol l^{-1} $[AIBN]_0$: 3.4×10^{-3} mol l^{-1}.

The temperature of the chromatographic columns was programmed as follows: —T_1: 155°C for 60 s —T_2: 210°C for 300 s. Rate of increase: 7°C min^{-1}.

Retention times of the main products under the conditions described above: —2 Methoxy ethanol: 0.55 min —HEMA: 2.57 min — dimethylphthalate: 10.28 min.

Homopolymerization of DHPM. Composition of the initial reaction medium: —$[DHPM]_0$: 1.020 mol l^{-1} — $[Reference]_0$: 0.239 mol l^{-1} —$[AIBN]_0$: 3.24×10^{-3} mol l^{-1}.

Temperature cycle: —T_1: 180°C for 60 s —T_2:230°C for 300 s. Rate of increase: 5°C min^{-1}.

Retention times: —2 methoxy ethanol: 0.51 min — DHPM: 4.05 min —dimethylphthalate: 7.55 min.

Copolymerization DHPM–HEMA. Composition of the initial reaction medium: — $[HEMA]_0$: 0.634 mol l^{-1} — $[DHPM]_0$: 0.631 mol l^{-1} $[Reference]_0$: 0.135 mol l^{-1} — $[AIBN]_0$: 3.15×10^{-3} mol l^{-1}.

Temperature cycle: — T_1: 170°C during 60 s —T_2: 210°C during 300 s. Rate of increase: 5°C min^{-1}.

Retention times: — 2 methoxy ethanol: 0.55 min — HEMA: 2.30 min —DHPM: 6.45 min — dimethylphthalate: 10.60 min.

RESULTS AND DISCUSSION

Preliminary results

Preliminary experiments have been performed to select the adequate experimental parameters to carry out the kinetic investigations.

Solvents. The radical polymerizations of 2-hydroxyethylmethacrylate have been investigated, under standard conditions, in various solvents of the monomer: water, dioxane, THF, ethanol and 2-methoxy ethanol. In all cases, the polymerization occurs. In dioxane and in THF, the obtained polymer is insoluble and it precipitates as soon as it is formed. A similar result is observed in water, even at high dilution: this is a further proof that the compatibility of poly(HEMA) with water is limited. In alcohols, such as ethanol or 2-methoxyethanol, the polymer is soluble and the HEMA polymerization occurs in solution: the medium stays homogeneous.

In all these attempts, attention should be drawn to the fact that if distilled commercial HEMA is used, network formation is observed. With purified monomer (as described in the Synthesis and and Purification section) the polymerization reaction yields linear polymers. This shows the absence of crosslinking agent (ethylene dimethacrylate) in purified HEMA.

Initiation. Two types of radical initiations have been chosen: either a redox system (ammonium persulphate–sodium metabisulphite mixture) or typical radical initiators such as AIBN. In the first case, the $OH^{\cdot}$ radicals obtained are able to initiate the hydroxyalkyl methacrylate polymerization. HEMA has been polymerized in ethanol solution under such experimental conditions, at concentrations extending from 10% to 60% and at the boiling point of the solvent ($Bp = 78$°C). However, owing to the fast reaction rate and to the impossibility of controlling the reaction temperature, it has been concluded that this method cannot be used for our kinetic investigation. Instead, we have chosen another procedure in which HEMA is polymerized at 60°C in 2-methoxyethanol in the presence of AIBN as initiator, yielding soluble polymer which can be easily separated by precipitation in diethyl ether.

Homopolymerizations of 2-hydroxyethylmethacrylate and of 2,3-dihydroxypropylmethacrylate

The concentration of the residual monomer in the reaction medium has been measured as function of time using g.l.c. over a 4 h period for HEMA polymerization, the duration of the reaction being less than 3 h in the case of DHPM. In each case, the duration of the process is short in comparison with the half-time of the initiator and thus the initiator concentration can be considered as constant. *Figure 5* presents the results obtained:

$\ln\frac{[M]_0}{[M]}$ is plotted *versus* time t for HEMA and DHPM.

In the case of HEMA polymerization, a straight line is obtained, the slope of which is given by:

$$P_{HEMA} = k_p\left(\frac{k_d f}{k_t}\right)^{1/2}[I]^{1/2}$$

From these experimental data, a 'total' constant for the rate of polymerization R_{HEMA} can be calculated:

$$R_{HEMA} = P_{HEMA}[I]^{-1/2} = k_p\left(\frac{k_d f}{k_t}\right)^{1/2} = 1.01\,10^{-3}\ mol^{-1/2}\,l^{1/2}\,s^{-1}$$

As in the case of HEMA, preliminary attempts have been performed with purified DHPM. Whatever solvents used, radical polymerization yields soluble polymers. However some differences have to be mentioned:

In aqueous solution, the DHPM polymerization takes place in the homogeneous phase regardless of the

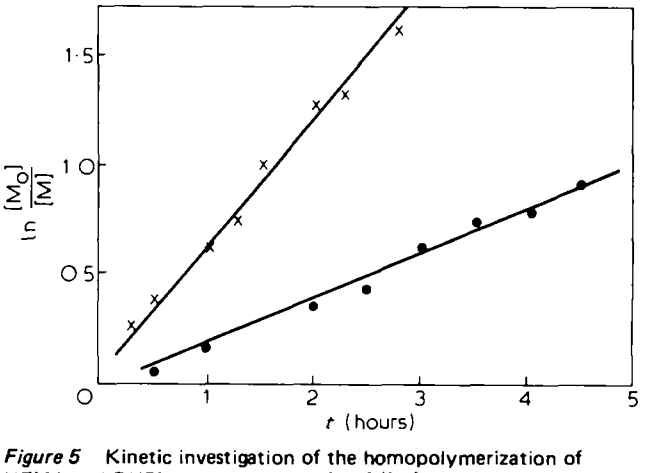


Figure 5 Kinetic investigation of the homopolymerization of HEMA and DHPM: variation of ln [Mo]/[M] as a function of time t: (●), HEMA; (X), DHPM

Table 1 Kinetic investigation of the radical copolymerization of 2-hydroxyethyl methacrylate and of 2,3-dihydroxypropylmethacrylate

t (min)	[HEMA]* (mol l^{-1})	$\ln \frac{[HEMA]_0^*}{[HEMA]}$	X_{HEMA}** (%)	[DHPM]* (mol l^{-1})	$\ln \frac{[DHPM]_0^*}{[DHPM]}$	X_{DHPM}** (%)	X_{tot}** (%)
0	0.634	0	0	0.631	0	0	0
20	0.603	0.058	5	–	–	–	–
40	0.551	0.140	13	0.512	0.209	19	16
60	0.532	0.175	16	0.439	0.365	30	23
120	0.425	0.400	33	0.307	0.721	51	42
140	0.405	0.448	36	0.258	0.894	59	48
180	–	–	–	0.225	1.031	64	–
200	0.329	0.656	48	–	–	–	–
240	0.277	0.828	56	–	–	–	–
300	0.237	0.984	63	–	–	–	–

* $[HEMA]_0$, $[DHPM]_0$, [HEMA] and [DHPM] are the molar concentrations of [HEMA] and of [DHPM] at times $t = 0$ and t, respectively
** X_{HEMA}, X_{DHPM} and X_{tot} are the degrees of conversion at time t for HEMA, DHPM and copolymer DHPM–HEMA, respectively

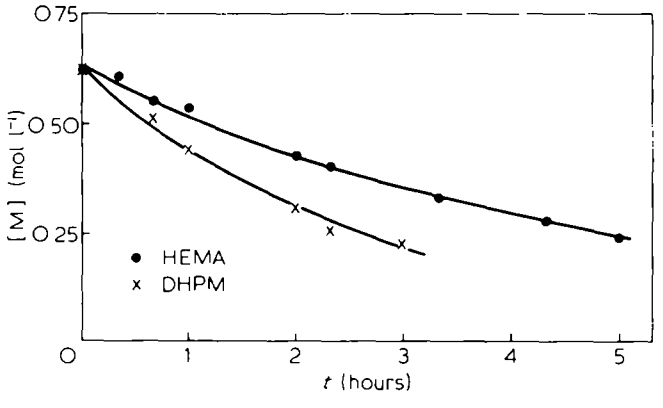


Figure 6 Consumption of the monomers during the radical copolymerization of HEMA and DHPM

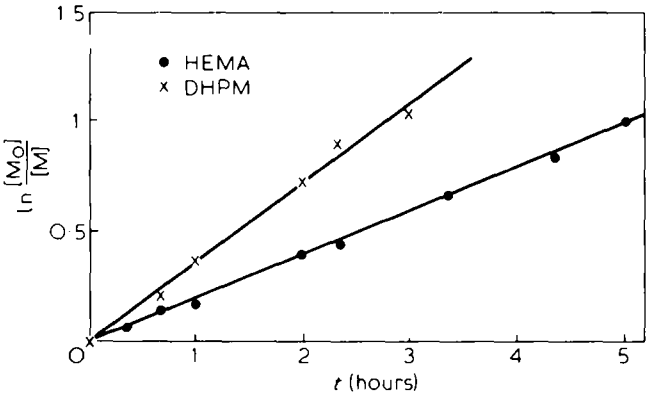


Figure 7 Kinetic investigations of the radical copolymerization of HEMA and DHPM: variation of ln [Mo]/[M] as a function of time t

monomer concentration. This result shows clearly that poly(DHPM) chains are quite compatible with water.

The monomer solubility is low in several organic solvents such as benzene and THF: the reaction medium is heterogeneous in the early stages of the reaction.

2-Methoxy-ethanol and ethanol are good solvents for DHPM and for the corresponding polymer as well.

As is shown in *Figure 5*, the DHPM consumption also follows a first order law. The slope of the straight line P_{DHPM} allows the determination of the 'total' constant for the rate of the polymerization:

$$R_{DHPM} = P_{DHPM}[I]^{1.2} = k_p\left(\frac{k_d f}{k_t}\right)^{1.2}$$
$$= 2.5\,10^{-3}\ \text{mol}^{-1.2}\,l^{1.2}\,s^{-1}$$

From these results, it can be seen that the polymerization of DHPM is faster (by factors of 2.5 and 8, respectively) than those of HEMA and of methylmethacrylate, the experimental conditions being identical.

Radical copolymerization of a mixture of 2-hydroxyethylmethacrylate and of 2,3-dihydroxypropylmethacrylate

An equimolar DHPM/HEMA mixture was submitted, at 60°C, to radical copolymerization initiated by AIBN in 2-methoxyethanol medium. As shown in *Table 1*, the residual concentration of the monomers have been determined by g.l.c. at regular time intervals over a 300 min period. The variation curves of the monomers concentration M with respect to the time t are shown in *Figure 6*. Here again, the DHPM consumption is faster than that observed for HEMA. As a consequence, the percentage amount of HEMA in the monomer mixture increases as the radical copolymerization progresses. Moreover, the variation of $\ln\frac{[M]_0}{[M]}$ as a function of time (*Figure 7*) discloses a particularity of the DHPM-HEMA system: for each of the monomers, these curves are straight lines, the slopes of which are given by:

$$P'_{HEMA} = 5.6\,10^{-5}\,s^{-1}$$
$$P'_{DHPM} = 1.02\,10^{-4}\,s^{-1}$$

From these values, the 'total' constant of the rate of the copolymerization results in:

$$Q'_{HEMA} = P'_{HEMA}[I]^{-1.2} = 0.95\,10^{-3}\,\text{mol}^{-1.2}\,l^{1.2}\,s^{-1}$$
$$Q'_{DHPM} = P'_{DHPM}[I]^{-1.2} = 1.72\,10^{-3}\,\text{mol}^{-1.2}\,l^{1.2}\,s^{-1}$$

Radical reactivity ratios determination

From the latter results presented in *Figure 6*, it follows that the concentration of each monomer can be written as:

$$[M] = [M]_0 e^{-kt}$$

Table 2 Determination of the radical reactivity ratios for HEMA and DHPM

t (min)	[HEMA]* (mol l^{-1})	[DHPM]* (mol l^{-1})	$\frac{d[HEMA]}{dt}$ (mol l^{-1})	$\frac{d[DHPM]}{dt}$ (mol l^{-1})	x	y	$\frac{x}{y}(y-1)$	$\frac{x^2}{y}$
0	0.634	0.631	−0.125	−0.227	1.005	0.551	−0.819	1.833
20	0.597	0.561	−0.117	−0.201	1.064	0.582	−0.764	1.945
40	0.559	0.497	−0.110	−0.178	1.125		−0.695	2.048
60	0.524	0.442	−0.103	−0.158	1.186	0.652	−0.633	2.157
80	0.490	0.392	−0.096	−0.140	1.250	0.686	−0.572	2.278
100	0.459	0.348	−0.090	−0.125	1.319	0.720	−0.513	2.416
120	0.430	0.308	−0.084	−0.111	1.396	0.757	−0.448	2.574
140	0.403	0.274	−0.079	−0.098	1.471	0.806	−0.354	2.685
160	0.378	0.243	−0.074	−0.087	1.556	0.851	−0.272	2.845
180	0.354	0.215	−0.069	−0.077	1.647	0.900	−0.183	3.014

* [HEMA] and [DHPM] are the molar concentrations of HEMA and of DHPM in the radical copolymerization at the time t, respectively
x = [HEMA]/[DHPM] and y = d[HEMA]/d[DHPM]

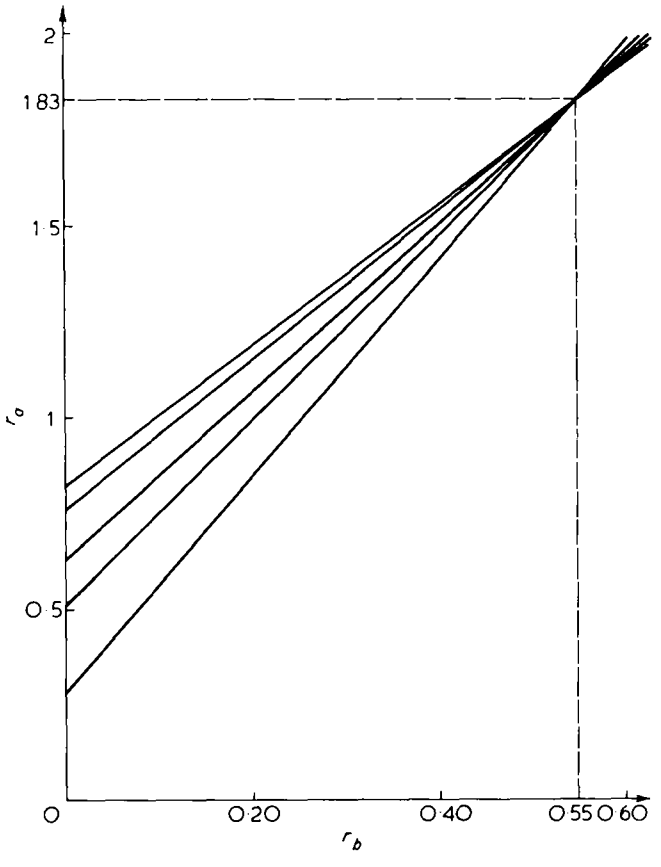


Figure 8 Determination of the radical reactivity ratios by Fineman-Ross linearization method

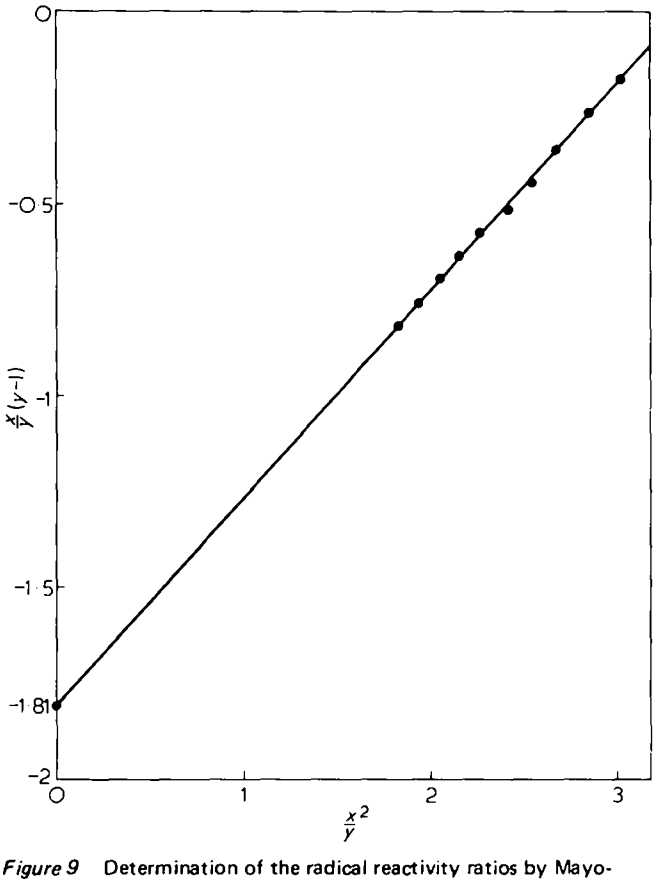


Figure 9 Determination of the radical reactivity ratios by Mayo-Lewis linearization method

The k constant has been determined by curves adjustment using a Hewlett-Packard calculator, and thus the k values are given by:

$$[HEMA] = [HEMA]_0 e^{-0.196t}$$ (correlation coefficient: 0.999)

$$[DHPM] = [DHPM]_0 e^{-0.359t}$$ (correlation coefficient: 0.993)

From these expressions, the values of [HEMA], [DHPM], $d[HEMA]_{/dt}$ and $d[DHPM]_{/dt}$ have been calculated and are shown in *Table 2*.

Using these data, the radical reactivity ratios have been calculated, using the linearization methods of Mayo-Lewis[21] and of Fineman-Ross[22]. *Figures 8* and *9* exhibit the graphic determinations of r_a and r_b, which gives: $r_{a(DHPM)} = 1.83$, $r_{a(DHPM)} = 1.81$, $r_{b(HEMA)} = 0.55$ (Mayo-Lewis), $r_{b(HEMA)} = 0.55$ (Fineman-Ross).

It turns out that the product of the radical reactivity ratios $r_a.r_b$ is close to unity showing that the radical copolymerization of DHPM and HEMA is an 'ideal' copolymerization system.

Amplitude of the fluctuations in composition

Owing to the different rates of conversion of two comonomers, one can expect fluctuations in composition to occur in the copolymers formed. From a given conversion this amplitude results from the integration of the Skeist's equation[18]. *Figure 10* shows the results

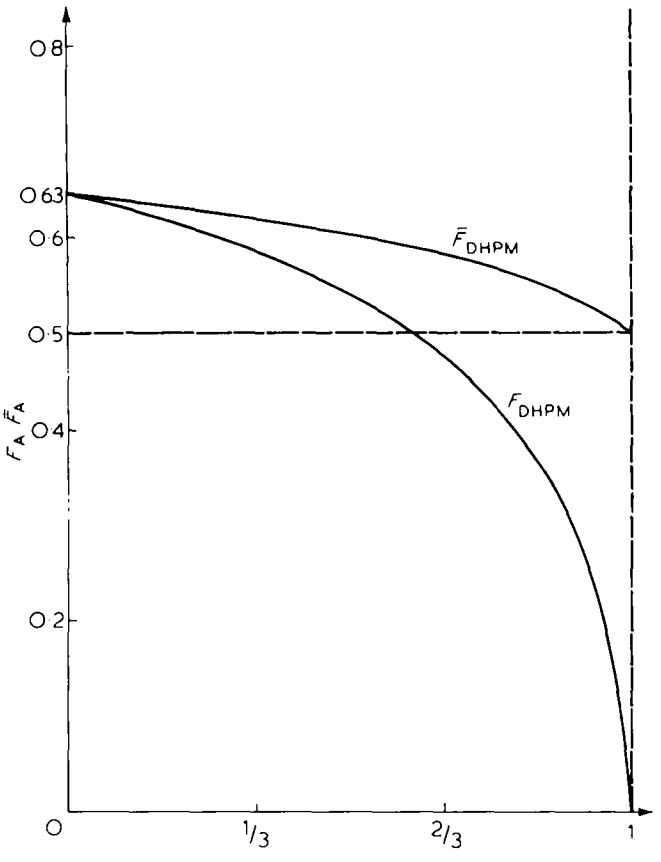


Figure 10 Variation of F_{DHPM} and $\bar{F}_{DHPM}$ as a function of the degree of conversion

obtained starting from an equimolar mixture of the monomers $(f_a)_0 = 0.5$ and using the radical reactivity ratios determined above ($r_{DHPM} = 1.83$ and $r_{HEMA} = 0.55$). The variation of 'integrated' composition of the copolymers is also plotted on the same Figure, *versus* the degree of conversion. It is observed that the amplitude of the fluctuations in composition around this 'integrated' value is of order of $\pm 5\%$ for $X = 0.5$ but reaches beyond $\pm 15\%$ for a degree of conversion of 0.8.

Special property of DHPM–HEMA system

It has been established that the composition of each of the monomers during the radical copolymerization process obeys first order laws. As a consequence $\ln\frac{[A]_0}{[A]}$ and $\ln\frac{[B]_0}{[B]}$ are a linear function of time t (*Figure 7*). Let us discuss this unexpected result.

Assuming the validity of the stationary state condition, the total radical concentration is given by a constant value:

$$[M^{\cdot}] = [A^{\cdot}] + [B^{\cdot}]$$

The same is not true for the individual concentrations $[A^{\cdot}]$ and $[B^{\cdot}]$: they depend on the proportions of [A] and [B] in the reaction medium, and they vary appreciably with time t.

$$\text{One can write: } \frac{[A^{\cdot}]}{[B^{\cdot}]} = \frac{k_{ba}}{k_{ab}}\frac{[A]}{[B]}$$

The rate of A and B consumptions can be written as:

$$\frac{d[A]}{[A]} = \left[(k_{aa} - k_{ba})[A] + k_{ba}[M]\right]dt$$

$$\frac{d[B]}{[B]} = \left[(k_{bb} - k_{ab})[B^{\cdot}] + k_{ab}[M^{\cdot}]\right]dt$$

From the preceding results, integration of these equations involves expressions such as:

$$\ln\frac{[A]_0}{[A]} = Zt \quad \text{and} \quad \ln\frac{[B]_0}{[B]} = Yt$$

and thus, the conditions to be satisfied are:

$$k_{aa} = k_{ba} \qquad k_{bb} = k_{ab}$$

relations which are compatible with the ideal system

$$k_{aa}k_{bb} = k_{ab}k_{ba}$$

Thus equation (17) results in:

$$\frac{d[A]}{[A]} = r_a\frac{d[B]}{[B]}$$

confirming that in an ideal system, if the consumption of one of the monomers obeys a first order law, it is also true for the second monomer.

CONCLUSION

In the present paper, the synthesis and the quantitative purification of 2-hydroxyethylmethacrylate (HEMA) and of 2,3-dihydroxypropylmethacrylate (DHPM), containing no detectable trace of crosslinking agent as ethylene dimethacrylate, have been performed.

These two pure monomers undergo radical copolymerization. The radical reactivity ratios determination shows that such a system is ideal. 2,3-dihydroxypropylmethacrylate is more reactive than 2-hydroxyethylmethacrylate in homopolymerization and it also enters into the copolymer more rapidly, resulting in fluctuations in composition in the copolymer formed. With respect to the degree of conversion, these fluctuations can be evaluated with satisfactory accuracy. Finally, the distribution of the monomer units is determined by only one parameter and it can be considered as obeying Bernouillan statistics.

In a future paper[25], the synthesis and the thermodynamic properties of hydrogels of 2-hydroxyethylmethacrylate, of 2,3-dihydroxypropylmethacrylate and of their mixtures will be described.

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