

Copolymerization and terpolymerization of methacrylic ester monomers containing hydroxyl groups in their structure

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Copolymerization and terpolymerization of three methacrylic monomers, 3-hydroxyneopentyl methacrylate (NPGMA), 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA), have been studied. Attention has been devoted to quantitative analysis of the experimental results for determining the reactivity ratios, which were obtained by the Kelen–Tüdös and Tidwell–Mortimer methods in the copolymerization reactions. A method developed in our laboratories to determine the reactivity ratios (r_{ij}) in multicomponent systems was used in the terpolymerization of these monomers. The values of r_{ij} obtained were different from those previously calculated by binary copolymerizations. Azeotropic reactions occur in the case of MMA–NPGMA copolymerization and in the terpolymerization extending over practically all the interval of composition. Microstructural effects on the glass transition temperature (T_g) of HEMA–NPGMA copolymers and terpolymers were observed, indicating the influence of sequence distribution of the monomer units on that property. In the other copolymers the values of T_g were not influenced by the sequence distribution and are given directly as a function of the weight fraction of the comonomers. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The chemistry of the radical polymerization of two or more unsaturated monomers has been widely investigated to obtain a better understanding of the polymerization itself and to find the influence of composition and microstructure on the chemical, physical and mechanical properties of the materials. The number of monomers that can undergo radical copolymerization is practically unlimited; however, the copolymerization of monomers containing functional groups such as OH and NH₂ in their structure is rather limited^{1–5} and its study may contribute to improve the knowledge not only of copolymerization, but also of the effect of hydrophilic groups on the properties of the polymers. Copolymers of methyl methacrylate (MMA) with 2-hydroxyethyl methacrylate (HEMA) have been used in different applications^{6–11}, for instance, in microencapsulation of living animal cells. The MMA–HEMA capsules are soft, elastic and tough, having great biocompatibility and mechanical durability. Another advantage of these copolymers is that their compositions are almost identical to the monomer feed ratios.

Other monomers with OH groups in their structure exhibit similar properties to those indicated and even improved mechanical properties. In the work carried out in our laboratories focused on the development of hydrophilic polymers, attention has been paid to the synthesis and kinetics of the polymerization of acrylic

and methacrylic monomers derived from 2,2-dimethylpropane-1,3-diol, *trans*- and *cis*-cyclohexanedimethanol, and other polyalcohols^{12,13}.

This work is extended in this paper to the synthesis of copolymers and terpolymers derived from methyl methacrylate, 2-hydroxyethyl methacrylate and 3-hydroxyneopentyl methacrylate (NPGMA). The main goal of this study is to analyse the copolymerization of the three possible systems that can be obtained with these three monomers in order to determine the reactivity ratios. The terpolymerization of these three monomers will also be analysed and the experimental results compared with those calculated by using the reactivity ratios determined by copolymerization and by other methods. Finally, the glass transition temperatures of the copolymers and terpolymers will be analysed to study the influence of composition and microstructure on this important property.

EXPERIMENTAL

Materials

NPGMA was synthesized from methacryloyl chloride and 2,2-dimethylpropane-1,3-diol (neopentylglycol) as described elsewhere¹⁵. Commercial HEMA (FLUKA, 95%) was purified^{2,13} by solution in water and several extractions with n-hexane to remove most of the dimethacrylate and ethylene glycol. Then the monomer was separated from the reaction mixture by the ‘salting out’ method with an aqueous sodium chloride solution and the process was repeated several times. Finally it was

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dried with anhydrous calcium chloride and distilled under high vacuum. MMA, solvents (dioxane and absolute ethanol) and the initiator (2,2'-azobisisobutyronitrile) were purified by conventional methods. The degree of purity of the two first monomers, as checked by ^{13}C and ^1H nuclear magnetic resonance (n.m.r.) spectroscopy and by high performance liquid chromatography (h.p.l.c.), was $>99.5\%$. The presence of monomers with two double bonds was not detected and was experimentally proved by the fact that the polymers obtained at very high conversions were completely soluble in different organic solvents.

Polymerization reactions

The copolymerization and terpolymerization reactions were carried out in vacuum at 50°C with 2,2'-azobisisobutyronitrile as initiation system. The reactions were followed by conventional dilatometric techniques until conversions below 10% were obtained. The monomer concentrations were 1 mol l^{-1} approximately. Solvent was absolute ethanol for the copolymerizations of HEMA with NPGMA and MMA with NPGMA, and a mixture of dioxane-ethanol (1/1) for the copolymerization of MMA with HEMA and the terpolymerizations.

The reaction mixture was precipitated in an aqueous solution of sodium chloride; the copolymers were washed several times with distilled water, dissolved in dioxane, precipitated into hexane and finally dried under vacuum.

Characterization of the polymers

The copolymers and terpolymers were characterized by ^1H and ^{13}C n.m.r. spectroscopy. The ^{13}C and ^1H spectra were registered in a Varian XL 300 and Varian-Unity 500, respectively, in different deuterated solvents such as dimethylsulfoxide (DMSO), chloroform and acetone; tetramethylsilane was used as internal standard reference.

The glass transition temperatures (T_g s) of the copolymers and terpolymers were determined by differential scanning calorimetry using a Perkin-Elmer DSC calorimeter at a heating rate of 8°C min^{-1} . All the measurements were carried out at the same conditions by first heating the capsules to 25°C above the T_g of the homopolymer with higher T_g , cooling them to room temperature and then starting the measurements.

RESULTS AND DISCUSSION

Composition of the copolymers

The composition of the copolymers was determined by ^1H and ^{13}C n.m.r. spectroscopy. In the case of the copolymers HEMA-NPGMA and MMA-NPGMA, the quantitative composition was obtained from the resonance signals observed in the ^{13}C n.m.r. spectra corresponding to the quaternary carbons of the main chain and from those belonging to the quaternary carbons of the pendent chain of the 3-hydroxyneopentyl methacrylate monomeric unit. As an example, the ^{13}C n.m.r. spectrum of one of the copolymers (MMA-NPGMA) is shown in Figure 1. In this spectrum, quantitative results were obtained by using long pulse delay times and inverse gated decoupling techniques to eliminate the nuclear Overhauser enhancement. Nevertheless, these special techniques were not necessary since the relaxation times of the used carbons were practically equivalent; this was proved for a mixture of the two homopolymers, the composition of which was exactly determined from the areas of resonance signals belonging to these carbons and observed in the conventionally registered spectrum.

Quantitative compositions of MMA-HEMA copolymers were determined from the proton signals belonging to the side chains of both monomeric units. The experimental results corresponding to the feed and

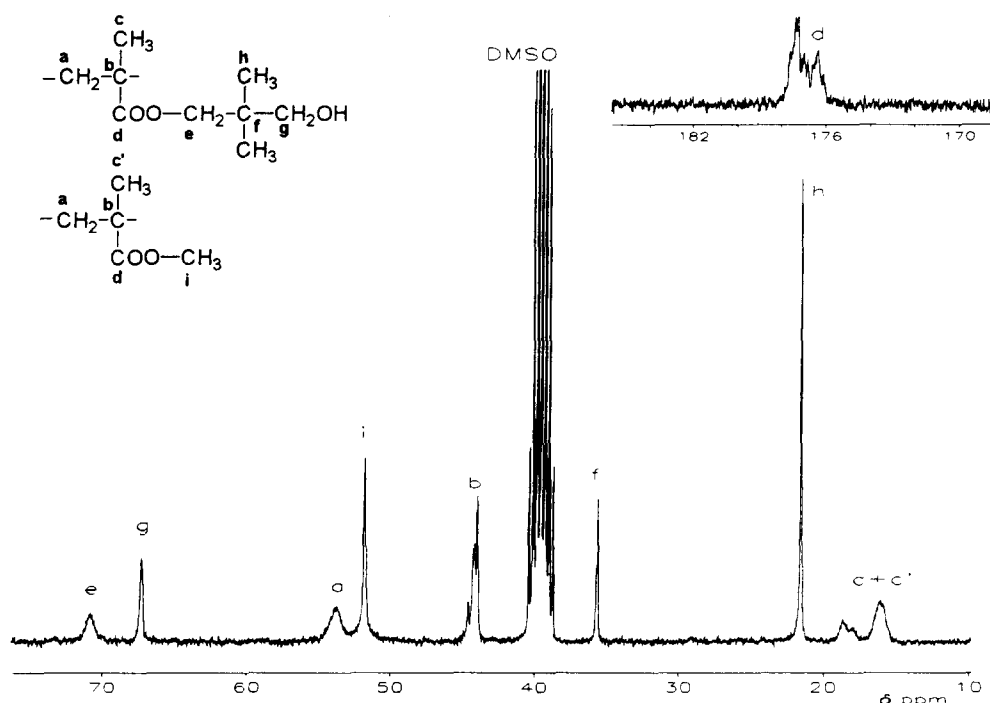


Figure 1 $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum for MMA-NPGMA copolymer with composition 0.61/0.39

Table 1 Calculated and experimental molar fractions of monomer A in the copolymers HEMA (A)–NPGMA (B)

F_A^a	Molar fraction of monomer A in copolymer		
	Exp.	Calc. (TM)	Calc. (KT)
0.129	0.10	0.137	0.118
0.300	0.35	0.327	0.299
0.552	0.63	0.603	0.584
0.680	0.73	0.731	0.722
0.791	0.80	0.834	0.802
0.863	0.90	0.895	0.891
$S^2 \times 10^3$	–	3.74	4.47

^a F_A is the molar fraction of monomer A in the feed

Table 2 Calculated and experimental molar fractions of monomer A in the copolymers MMA (A)–NPGMA (B)

F_A	Molar fraction of monomer A in copolymer		
	Exp.	Calc. (TM)	Calc. (KT)
0.133	0.13	0.132	0.133
0.366	0.36	0.361	0.361
0.555	0.55	0.546	0.546
0.633	0.61	0.623	0.623
0.752	0.76	0.743	0.742
0.899	0.89	0.890	0.893
$S^2 \times 10^3$	–	0.500	0.547

Table 3 Calculated and experimental molar fractions of monomer A in the copolymers MMA (A)–HEMA (B)

F_A	Molar fraction of monomer A in copolymer		
	Exp.	Calc. (TM)	Calc. (KT)
0.104	0.12	0.123	0.125
0.253	0.28	0.269	0.271
0.501	0.45	0.476	0.474
0.621	0.59	0.575	0.571
0.751	0.71	0.691	0.687
0.892	0.82	0.845	0.841
$S^2 \times 10^3$	–	1.83	1.89

copolymer compositions are shown in *Tables 1–3* along with the calculated compositions of the copolymers obtained from the two procedures used to find the reactivity ratios (to be described below). S^2 refers to the squared differences between experimental and calculated compositions of the copolymers.

Reactivity ratios

A good estimate of the reactivity ratios should accomplish different requisites that have been adequately described elsewhere¹⁴. The reactivity ratios can be found using several procedures, almost all of them based on the method outlined by Mayo and Lewis¹⁵ which takes into account the instantaneous rates of consumption of the monomers for a determined monomer feed ratio. According to this method:

$$n = \frac{1 + r_A x}{1 + r_B/x} \quad (1)$$

where n and x are the ratios between the concentrations of monomers in the copolymer and in the reaction mixture, whereas r_A and r_B are the reactivity ratios expressed as the ratio between the homopropagation and cross-propagation rate constants.

Equation (1) can be easily transformed into the well-known Fineman–Ross equation¹⁶ that allows calculation of the reactivity ratios by linearization of the experimental data according to:

$$\frac{n-1}{x} = r_A - r_B \frac{n}{x^2} \quad (2)$$

The straight line thus obtained gives r_A and r_B directly from the intercept and slope, respectively. The values of r_A and r_B are different depending on whether n and x are referred to monomer A or B. Thus, the Fineman–Ross equation admits several other linear forms, but none of them are invariant to the inversion of the data.

The linear least-squares criterion can be applied to the different copolymerization equations to evaluate numerically the reactivity ratios. For instance, from the Fineman–Ross (FR) equation the following may be obtained:

$$r_A \sum_{i=1}^m F_i^2 - r_B \sum_{i=1}^m F_i = \sum_{i=1}^m F_i G_i \quad (3)$$

where

$$F_i = \frac{x_i}{n_i} \quad G_i = \frac{x_i(n_i - 1)}{n_i}$$

If one re-indexes the monomer, then:

$$r_A \sum_{i=1}^m \frac{1}{F_i} - r_B \sum_{i=1}^m \frac{1}{F_i^2} = \sum_{i=1}^m \frac{G_i}{F_i^2} \quad (4)$$

and by combination of the corresponding equations one obtains the reactivity ratios.

The methods developed by Mayo and Lewis¹⁵ and improved by Joshi and Joshi¹⁷ are based on the rearrangement of equation (1). Although the last procedure is a non-graphical method, which is not subject to re-indexing errors allowing one to find the confidence limits, it has the same disadvantages as any linear least-squares procedure. Yezrielev–Brokhina–Roskin¹⁸ developed another invariant linear equation based on the combination of the FR equation and its reversed form:

$$r_A \sum_{i=1}^m F_i - r_B n = \sum_{i=1}^m G_i \quad (5)$$

$$r_A n - r_B \sum_{i=1}^m 1/F_i = \sum_{i=1}^m G_i/F_i \quad (6)$$

On the other hand, Kelen and Tüdös¹⁹ have also suggested another procedure for the determination of reactivity ratios that corrects most of the errors involved in the procedures indicated above. These authors suggest the use of the equation:

$$\frac{G_i}{\alpha + F_i} = \left(r_A + \frac{r_B}{\alpha} \right) \frac{F_i}{\alpha + F_i} - \frac{r_B}{\alpha} \quad (7)$$

where α is an arbitrary constant greater than zero. This relationship is invariant to inversion of the data and, by choosing a proper value for α , the experimental results

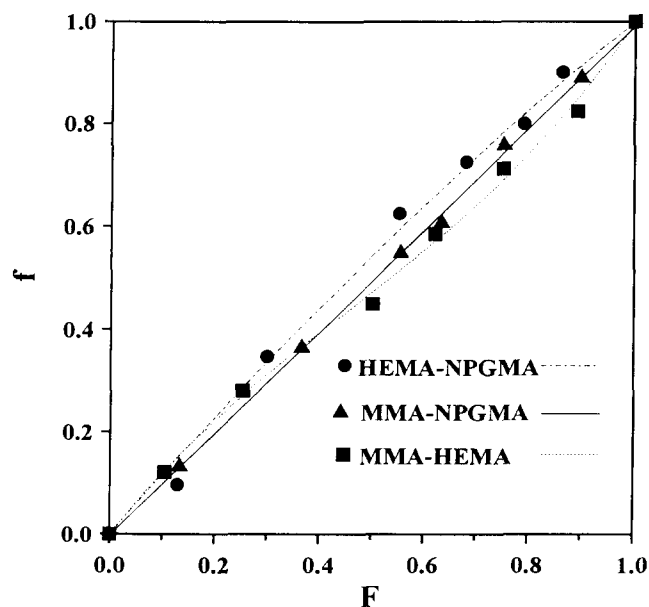


Figure 2 Composition diagrams for the copolymerizations HEMA-NPGMA, MMA-NPGMA and MMA-HEMA. F and f are, respectively, the molar fraction of the first monomer in the feed and in the copolymers

Table 4 Calculated reactivity ratios for the different copolymerizations

Method	HEMA-NPGMA		MMA-NPGMA		MMA-HEMA	
	r_A	r_B	r_A	r_B	r_A	r_B
TM	1.40	0.98	0.94	1	0.60	0.77
KT	1.43	1.19	0.93	0.99	0.58	0.75

are uniformly distributed in the interval (0, 1). By least-squares analysis one obtains the values of the reactivity ratios.

The non-linear least-squares procedure first developed by Behnken²⁰ and Tidwell and Mortimer²¹, and discussed more recently by O'Driscoll and co-workers²², is considered one of the most accurate procedures to determine the reactivity ratios in copolymerization reactions. This method has been properly described and provides the best set of reactivity ratios for which the sum of the quadratic differences (S^2) between the computed and experimental values of the copolymer compositions is a minimum.

In the present work, the two most appropriate procedures, the Kelen-Tüdös (KT) and Tidwell-Mortimer (TM), were used for determination of the reactivity ratios.

The results obtained for the three copolymerizations are shown in Table 4. The reactivity ratios determined by these two procedures do not differ significantly, and can be used to design composition diagrams very similar to the experimental ones given in Figure 2. The values of S^2 for the three copolymerizations reactions are indicated in Tables 1-3 and it can be seen that the TM and KT methods give similar results.

In these copolymerization reactions, the products of the reactivity ratios are not very far from unity. A little tendency to the formation of HEMA blocks is found in its copolymers with NPGMA, whereas the MMA-HEMA copolymers present a slight tendency to alternation because here $r_A r_B$ is lower than 1 with an azeotrope

at $F = 0.37$. The other copolymerization (MMA-NPGMA) is practically azeotropic over the whole interval of composition with both reactivity ratios equal to 1, within experimental error.

Confidence limits

A more adequate idea of the consistence of the calculated reactivity ratios with the experimental data is given by the joint confidence limits^{23,24}. The correct values are believed to lie within the confidence area, thus giving an idea of the goodness of the model used.

The non-linear least-squares procedure provides a method for establishing the joint confidence limits within which the correct values of the reactivity ratios can be asserted to lie with a probability $1 - \alpha$, where α is a number in the interval $0 < \alpha < 1$. The approximate 100 ($1 - \alpha$) percent joint confidence limits are the set of r'_A and r'_B which satisfy the equation:

$$S_C = S^2 + 2s^2 F_\alpha(2, h) \quad (8)$$

where S_C is the value of the differences between the observed and computed molar fraction of each monomer in the copolymer for a set of reactivity ratios, S^2 is the minimum value of S_C , s^2 is an estimate of the experimental error having h degrees of freedom, and $F_\alpha(2, h)$ is the critical value of F taken from the tables of the F distribution.

A good approximation for s^2 is:

$$s^2 = \frac{S^2}{n - 2} \quad (9)$$

that allows

$$F_\alpha(2, h) = F_\alpha(2, n - 2) \quad (10)$$

n being the number of experiments.

Although the solution of equation (8) is described as very tedious so that approximate calculus is often used, we have determined the correct solutions of this equation by using suitable computer programs.

The approximate calculus is based on the change of variable:

$$t'_A = \ln r'_A \quad (11)$$

$$t'_B = \ln r'_B \quad (12)$$

where r'_A and r'_B are the better estimations of the reactivity ratios calculated using the procedures described. The joint confidence will be formed by the set of r_A and r_B values that satisfy the equation:

$$\begin{aligned} & (t_A - t'_A)^2 a_{11} + 2(t_A - t'_A)(t_B - t'_B) a_{12} + (t_B - t'_B)^2 a_{22} \\ & = 2s^2 F_\alpha(2, n - 2) \end{aligned} \quad (13)$$

where

$$\begin{aligned} a_{11} &= (r'_A)^2 \sum_i \left(\frac{\partial G_i}{\partial r_A} \right)^2 \\ a_{12} &= (r'_A r'_B) \sum_i \left(\frac{\partial G_i}{\partial r_A} \right) \left(\frac{\partial G_i}{\partial r_B} \right) \\ a_{22} &= (r'_B)^2 \sum_i \left(\frac{\partial G_i}{\partial r_B} \right)^2 \end{aligned} \quad (14)$$

The values of the reactivity ratios obtained by solving equation (8) exactly have been used to draw the joint

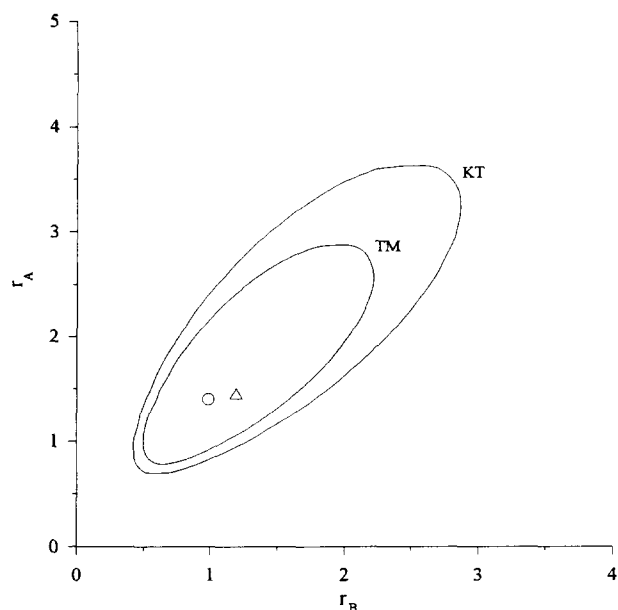


Figure 3 95% confidence limits for the data of reactivity ratios determined by the Kelen-Tüdös and Tidwell-Mortimer methods in the copolymerization HEMA-NPGMA: Δ , KT; O, TM

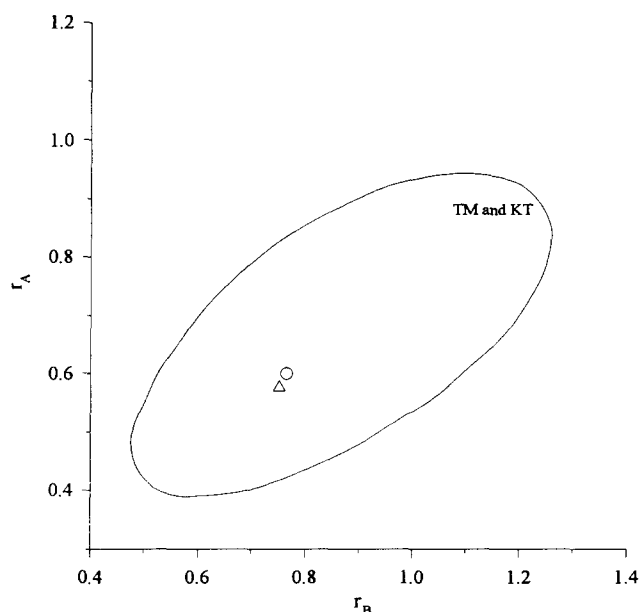


Figure 5 95% confidence limits for the data of reactivity ratios determined by the Kelen-Tüdös and Tidwell-Mortimer methods in the copolymerization MMA-HEMA

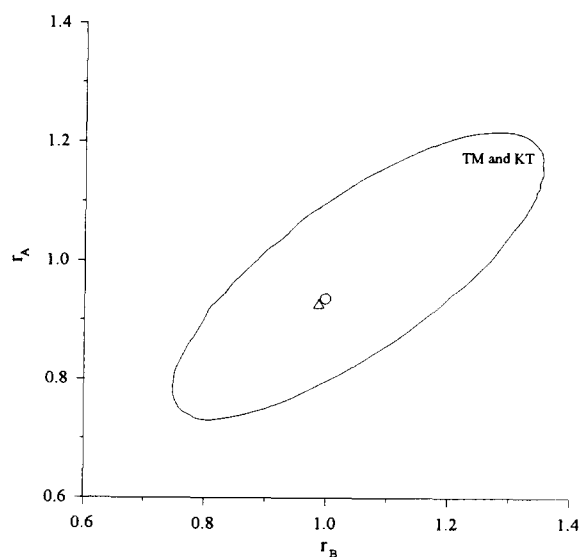


Figure 4 95% confidence limits for the data of reactivity ratios determined by the Kelen-Tüdös and Tidwell-Mortimer methods in the copolymerization MMA-NPGMA

confidence envelopes at 95% level, which are approximately elliptical for all copolymerizations as shown in Figures 3–5. The joint confidence envelopes are practically equal for the two methods except in the copolymerization HEMA-NPGMA (Figure 3). When the same figures are drawn using the values obtained with equations (11)–(14), the joint confidence limits are slightly different so that it is very advisable to avoid these equations, especially in those cases in which the number of experiments is not very high.

Composition of the terpolymers

The composition of the terpolymers formed by the terpolymerization of MMA (monomer A), NPGMA (monomer B) and HEMA (monomer C) was determined

by ^{13}C and ^1H n.m.r. spectroscopy. In most cases, the quantitative composition was obtained from the ^1H n.m.r. spectrum by using the resonance signals corresponding to the hydroxyl groups that appear as singlets (in deuterated DMSO solution) at 4.5 ppm (monomer B) and 4.7 ppm (monomer C) together with the other signals belonging to the protons of the pendent chains of the three monomers. When the spectra are recorded in other solvents, overlapping of the hydroxyl groups occurs and then some resonance signals of the ^{13}C n.m.r. spectrum, particularly those corresponding to the quaternary carbons of the main chain or the three monomers and of the pendent chain for monomer B, were also used to determine the composition of the terpolymers. The ^1H n.m.r. spectrum registered in deuterated DMSO of one of the terpolymers is shown in Figure 6.

In Table 5 the compositions of the terpolymers, as well as the corresponding molar fractions of the three monomers in the feed, are shown. S is the squared differences between calculated and experimental compositions of terpolymers. Figure 7 shows the ternary diagram for this terpolymerization, where it can be seen that the mole fraction of each structural unit is very similar to that of the monomers in the initial reaction mixture.

Multicomponent system polymerization

For the copolymerization of n monomers¹⁴ the disappearance rates are given by:

$$\begin{aligned}
 -\frac{d[\text{M}_1]}{dt} &= k_{11}[\text{M}_1][\text{M}_1] + k_{21}[\text{M}_2][\text{M}_1] + \dots + k_{n1}[\text{M}_n][\text{M}_1] \\
 &\quad \vdots \\
 -\frac{d[\text{M}_n]}{dt} &= k_{1n}[\text{M}_1][\text{M}_n] + k_{2n}[\text{M}_2][\text{M}_n] + \dots + k_{nn}[\text{M}_n][\text{M}_n]
 \end{aligned}
 \tag{15}$$

If the steady-state approximation is considered, which

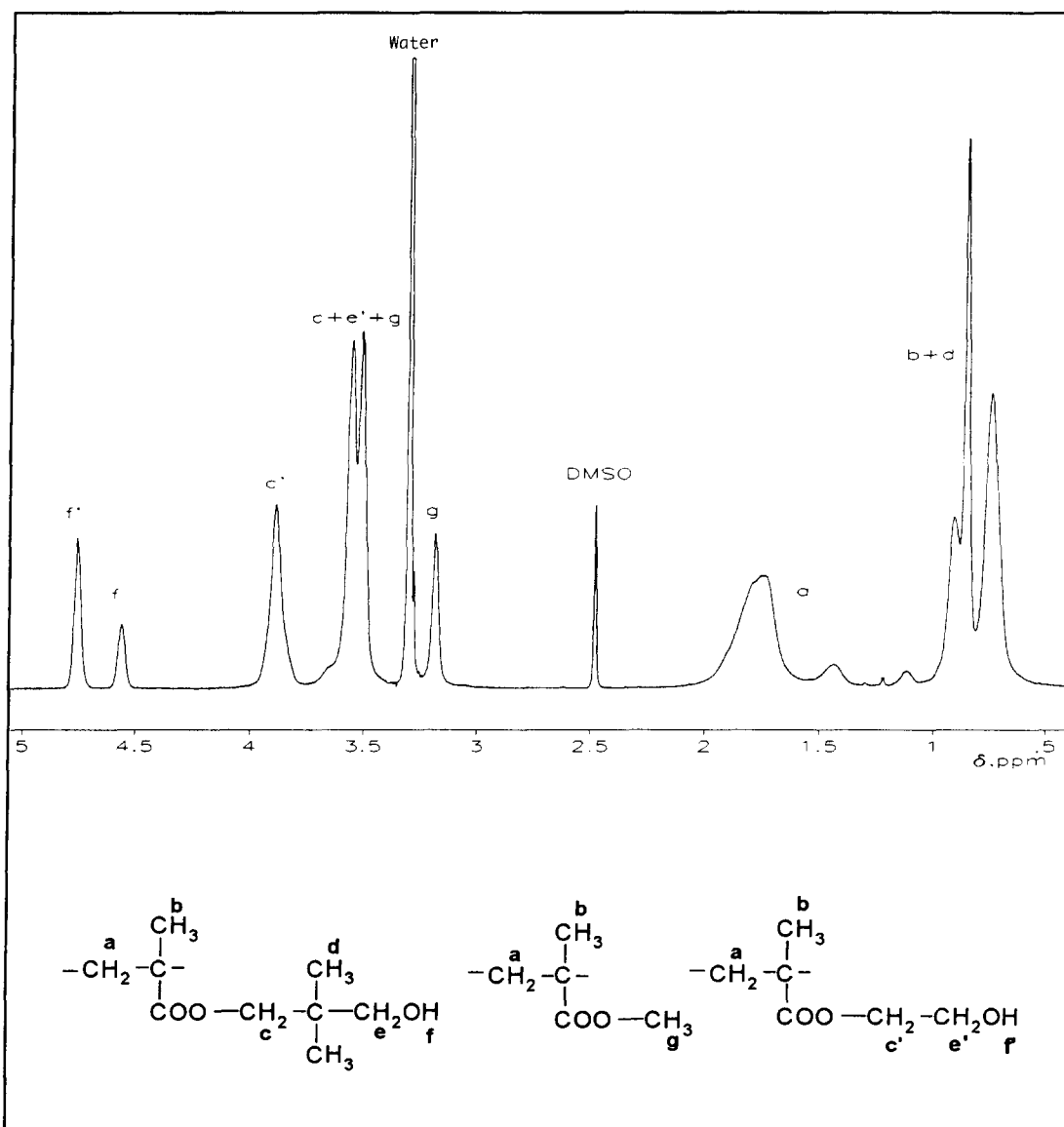


Figure 6 ¹H n.m.r. spectrum (500 MHz) for MMA-NPGMA-HEMA terpolymer with composition 0.405/0.19/0.405

Table 5 Results of the terpolymerization MMA (A)-NPGMA (B)-HEMA (C)

Molar fractions in the feed			Molar fractions in the terpolymers								
			Experimental			Calculated (method I)			Calculated (method II)		
F_A	F_B	F_C	f_A	f_B	f_C	f_A	f_B	f_C	f_A	f_B	f_C
0.322	0.340	0.338	0.28	0.32	0.40	0.337	0.286	0.377	0.284	0.334	0.382
0.207	0.202	0.591	0.20	0.18	0.62	0.231	0.155	0.614	0.181	0.183	0.636
0.200	0.397	0.403	0.16	0.40	0.44	0.222	0.338	0.440	0.169	0.381	0.450
0.200	0.595	0.205	0.14	0.61	0.25	0.214	0.555	0.231	0.160	0.602	0.238
0.410	0.205	0.385	0.40	0.19	0.41	0.412	0.163	0.425	0.377	0.198	0.425
0.620	0.189	0.191	0.58	0.19	0.23	0.596	0.165	0.239	0.595	0.192	0.213
0.099	0.100	0.801	0.05	0.09	0.86	0.119	0.073	0.808	0.085	0.085	0.830
0.792	0.101	0.107	0.78	0.11	0.11	0.757	0.094	0.149	0.783	0.102	0.115
0.411	0.391	0.198	0.37	0.40	0.23	0.415	0.351	0.234	0.366	0.404	0.230
0.106	0.788	0.106	0.10	0.79	0.11	0.112	0.772	0.116	0.077	0.800	0.123
$S \times 10^2$			-			4.09			0.735		

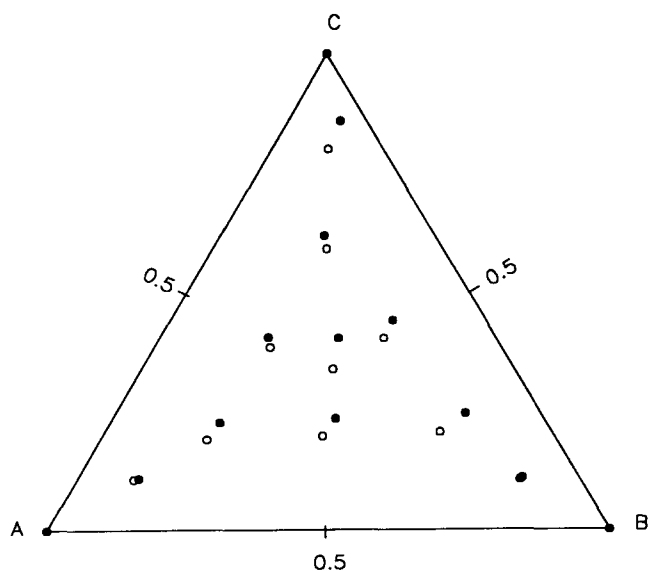


Figure 7 Ternary composition diagram for the terpolymerization MMA (A)–NPGMA (B)–HEMA (C): ○, molar fractions in the feed; ●, molar fractions in the terpolymers

Table 6 Calculated reactivity ratios for terpolymerization

Method	r_{AB}	r_{BA}	r_{AC}	r_{CA}	r_{BC}	r_{CB}
I	0.94	1	0.60	0.77	0.98	1.40
II	1.03	1.55	1	1.19	0.88	1.25

supposes that the number of growing chains that disappear in unit time is equal to the number that form, the so-called Walling–Briggs equation²⁵ is obtained. This equation allows the calculation of the composition of a copolymer formed by n monomers if the monomer concentrations and the $n(n-1)$ reactivity ratios are known.

The Walling–Briggs equation is very useful to calculate the composition of multicomponent systems by using the reactivity ratios obtained in binary copolymerization reactions, which can be different from those directly evaluated from the experimental data of terpolymers, tetrapolymers, etc. Rudin *et al.*²⁴ and more recently Duever *et al.*²⁶ have calculated the reactivity ratios in these systems more accurately.

A computer calculation program has been developed in our laboratory to obtain reactivity ratios in multicomponent systems. The method, based on the procedure suggested by Duever *et al.*²⁶, incorporates an optimization method like that described by Tidwell and Mortimer²¹ for calculation of the reactivity ratios in binary copolymerizations by non-linear least-squares analysis. This procedure allows the calculation of the best set of reactivity ratios that yields a minimum value for the sum of squares of the differences between the observed and computed molar fractions of comonomers in the polymer for all the monomers intervening in the polymerization.

The method will be briefly described. The molar fractions of each monomer in the polymer (G_{li}^j), corresponding to the i th experimental run and from the j th estimate, are obtained from the equations as a function of the initial fraction of each monomer (f_{li}) in

the experiment i , using the corresponding reactivity ratios. The experimental fraction of each monomer in the polymer (F_{li}) can be approximately related to G_{li}^j by:

$$F_{li} = G_{li}^j + \sum_{k=1}^{n(n-1)} \frac{\partial G_{li}^j}{\partial r_k} (r_k^0 - r_k^j) \quad (16)$$

where n is the number of monomers that intervene in the polymerization, $l = 1, 2, 3 \dots n$, $k = 1, 2, 3, \dots n(n-1)$, $i = 1, 2, 3 \dots m$ with m the number of experimental runs and r_k are the corresponding reactivity ratios.

The differences between the experimental and computed molar fraction of each monomer in the polymer will be given by:

$$d_i = \sum_{l=1}^m \sum_{k=1}^{n^2-n} \beta_k \frac{\partial G_{li}^j}{\partial r_k} \quad (17)$$

where

$$\beta_k = r_k^0 - r_k^j \quad (18)$$

The least-squares estimate of β_k provides a new estimate of r_k^{j+1} so that, when it is substituted in equation (16), the value of d_i^2 decreases. To obtain the best results it is necessary to repeat the calculation for all the monomers until the minimum value of

$$S = \sum_{i=1}^n d_i^2$$

is reached: this suggests the calculation of $n^2(n-1)$ derivatives, the $n^2(n-1)[1+n(n-1)]/2$ products among the derivatives, also the $n^2(n-1)$ products $d_{li} \delta G_{li} / \delta r_k$ and for all the experimental runs. The difficulties for the calculation in multicomponent systems with $n > 3$ are clear.

The reactivity ratios corresponding to this terpolymerization, calculated with this last method (method II) from the experimental compositions of the terpolymers, are shown in Table 6. Values of r_{ij} obtained from the binary copolymerizations and indicated above are also given in the first row of the same table (method I). Although the differences seem not to be very high, the first reactivity ratios give a value of S (Table 5) around 5.5 times lower than that calculated with the second values of r_{ij} .

Azeotropic terpolymerizations

Generally, the instantaneous composition of a copolymer does not coincide with that of the feed and only in special cases, called azeotropes, is this fact observed. The results previously obtained for the copolymers show that an azeotrope exists in the copolymerization MMA–HEMA, whereas in the copolymerization MMA–NPGMA the reaction is azeotropic over the whole interval of composition. In copolymerization and in terpolymerization it is very important to determine the composition of these azeotropes, especially regarding the possible applications of the products.

In terpolymerization reactions, some authors consider that the necessary condition for the existence of a ternary azeotrope is that there exists at least one binary azeotrope, although others believe that it is not essential²⁷.

Different graphical and numerical methods of determination of ternary azeotropes have been described by

many investigators^{28,29}, based particularly on the equations of Alfrey and Goldfinger³⁰ and on the simplified equation of Ham^{31,32}. The necessary condition for the existence of a ternary azeotrope is given by the values of P , Q and R [equation (19)], which should be of the same sign and different from zero^{29,33,34}:

$$P = \left(1 - \frac{1}{r_{AC}}\right) \left(\frac{1}{r_{CB}} - 1\right) - \left(\frac{1}{r_{AB}} - \frac{1}{r_{AC}}\right) \left(\frac{1}{r_{AC}} - 1\right)$$

$$Q = \left(\frac{1}{r_{BA}} - \frac{1}{r_{BC}}\right) \left(\frac{1}{r_{AB}} - \frac{1}{r_{AC}}\right) - \left(1 - \frac{1}{r_{BC}}\right) \left(1 - \frac{1}{r_{AC}}\right)$$

$$R = \left(\frac{1}{r_{CA}} - 1\right) \left(1 - \frac{1}{r_{BC}}\right) - \left(\frac{1}{r_{CB}} - 1\right) \left(\frac{1}{r_{BA}} - \frac{1}{r_{BC}}\right)$$
(19)

If this condition is accomplished, the mole fractions of the monomers in the azeotropic mixture of terpolymerization can be written as:

$$f_A : f_B : f_C = R \left(\frac{Q}{r_{AC}r_{CB}} + \frac{P}{r_{AB}r_{BC}} + \frac{R}{r_{AB}r_{AC}} \right)$$

$$: P \left(\frac{P}{r_{BA}r_{BC}} + \frac{Q}{r_{BC}r_{CA}} + \frac{R}{r_{BA}r_{AC}} \right)$$

$$: Q \left(\frac{Q}{r_{CA}r_{CB}} + \frac{P}{r_{BA}r_{CB}} + \frac{R}{r_{AB}r_{CA}} \right)$$
(20)

By using the reactivity ratios given in the last row of Table 6, values with the same sign for P and Q but not for R were obtained. At first sight this result would suggest that a ternary azeotrope does not exist. Nevertheless, it is convenient to point out that the values of P , Q and R are near zero, a result that can be accomplished in two cases: (1) when the reactivity ratios are equal and different from unity, and in this case a ternary azeotrope always exists with equal compositions for the three monomers; and (2) when all the reactivity ratios are equal to unity when, obviously, the terpolymerization is ideal. In spite of this, the possible existence of a ternary azeotrope in this terpolymerization was investigated by writing a computer simulation program, that permitted the calculation of primary, binary and ternary azeotropes in terpolymerization reactions. The calculations showed that a ternary azeotrope effectively does not exist; however, pseudoazeotropic regions are observed with differences between the molar fractions of the three monomers in the feed and in the terpolymers in many cases < 0.01 . In this sense it can be said that this terpolymerization is practically azeotropic in almost the entire range of composition.

Glass transition temperatures of the copolymers and terpolymers

Different authors have indicated the factors that govern the T_g of copolymers and several semi-empirical equations have been suggested. One of these relations is the Fox equation³⁵ that for n comonomers takes the form:

$$\frac{1}{T_g} = \sum_{i=1}^n \frac{w_i}{T_{gi}} \quad (21)$$

where w_i are the weight fractions of the different monomers in the polymer, and T_g and T_{gi} refer to the

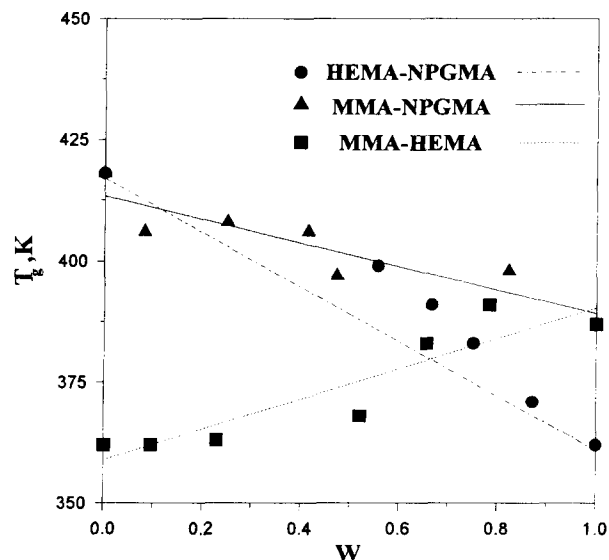


Figure 8 Experimental glass transition temperatures data plotted versus the weight fraction of the first monomer (W) for the three different copolymers. The straight lines correspond to the Fox equation

glass transition temperatures of the polymer and the homopolymers, respectively.

This equation, based on the assumption that certain properties of the polymer formed by reaction of n monomers are additive combinations of the properties of the homopolymers, does not consider the sequence distribution. Johnston suggested an equation for copolymers that relates T_g and microstructure by considering the probabilities of different dyads; in the case of n monomers the Johnston equation³⁶ is given by:

$$\frac{1}{T_g} = \sum_{i=1}^n \frac{w_i P_{ii}}{T_{gi}} + \sum_{\substack{i,j=1 \\ i \neq j}}^n \frac{w_i P_{ij}}{T_{gij}} \quad (22)$$

where T_{gij} is the glass transition temperature for the ideal alternating copolymers, and P_{ii} and P_{ij} are the different conditional probabilities that a growing chain adds a particular monomer; the latter can be determined easily from experimental kinetic data and from the values of reactivity ratios.

Other treatments have been suggested by some authors, such as the Barton equation³⁷ based on the Gibbs-DiMarzio theory³⁸. However, because of intramolecular interactions, which in turn depend on the sequence distribution, many copolymers do not follow these equations. On the other hand, Tonelli³⁹ has shown that the influence of this distribution on observed T_g in many copolymers can be related to the intramolecular equilibrium flexibility, expressed as a function of the conformational entropy.

Owing to the importance of T_g we have analysed the influence of microstructure and chemical composition on the glass transition temperatures of the synthesized copolymers and terpolymers. Experimental T_g data plotted versus the weight fraction of the first monomer, with straight lines corresponding to the Fox equation for the three copolymerizations, are shown in Figure 8. It can be seen that in two copolymerizations, MMA-HEMA and MMA-NPGMA, the values of T_g vary between those of the two homopolymers and the experimental

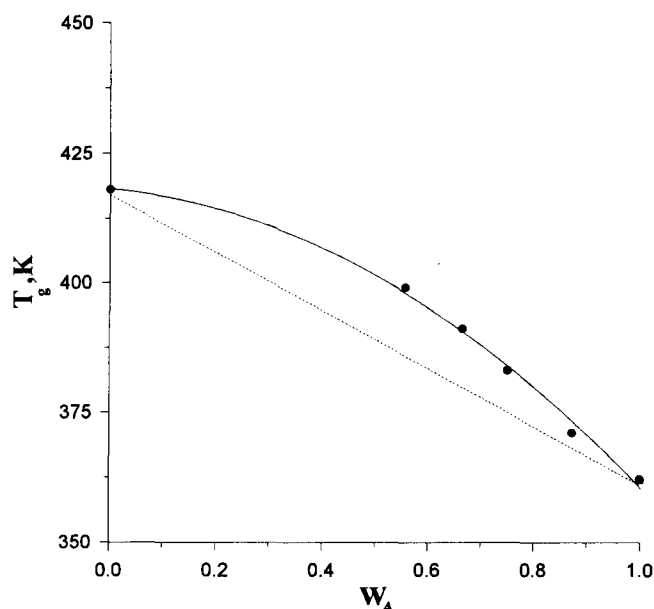


Figure 9 Experimental glass transition data plotted versus weight fraction of the first monomer in the copolymers HEMA-NPGMA. Dashed line, Fox equation; solid line, Johnston equation

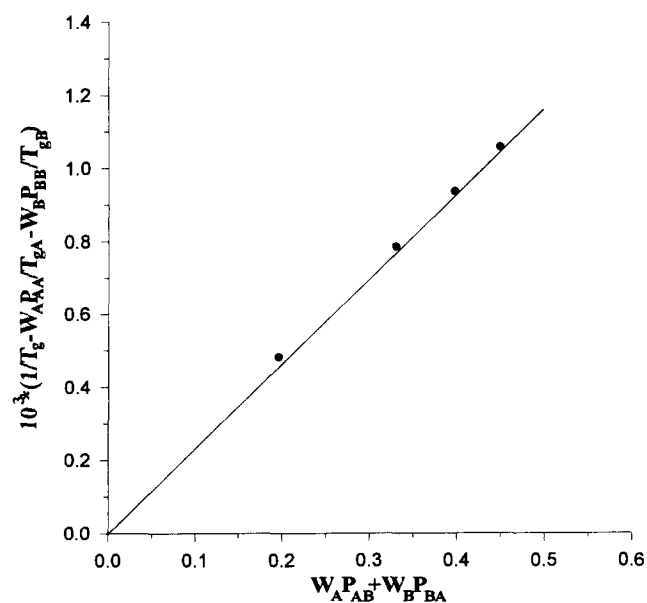


Figure 10 Linearization of the Johnston equation for the determination of T_{gAB} in the copolymers HEMA-NPGMA

data fit a straight line that is coincident with the values calculated by the Fox equation. The effect of the sequence distribution is not observed and the Fox equation offers a good estimate of the T_g of these two copolymers. In the other copolymerization HEMA-NPGMA, it can be observed that the values are higher than those obtained by the Fox equation; this fact can be attributed to a great effect of the sequence distribution in the copolymer. For instance, the copolymer with a weight fraction of 0.66 of HEMA presents a value 12°C higher than that expected. The experimental observation of T_g shows that the Fox equation is not the most adequate for plotting the dependence of T_g on the composition. The Johnston equation seems to be the most appropriate to reflect the

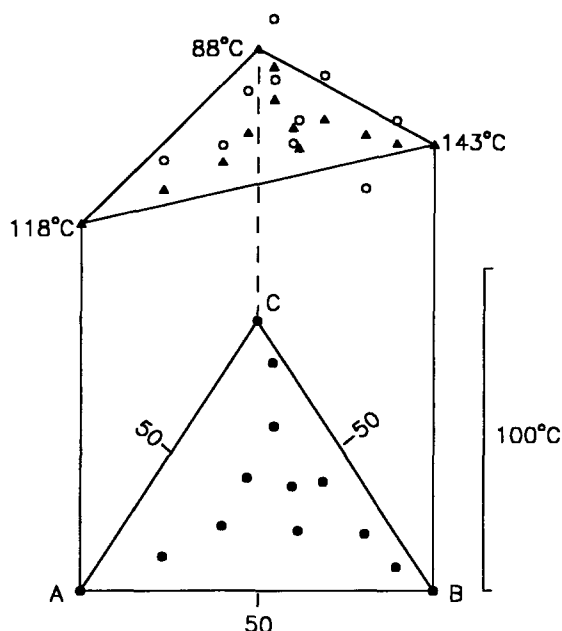


Figure 11 Glass transition temperatures for the terpolymers MMA-NPGMA-HEMA. O, Experimental data; ▲, Fox equation (see text)

influence of both composition and sequence distribution as can be seen in *Figure 9*, which shows the experimental T_g versus the weight fraction of 2-hydroxyethyl methacrylate in the copolymer (W_A) as well as the curves corresponding to the Fox and Johnston equations. The linearization of the Johnston equation³⁶ should yield a straight line with zero intercept and slope = $1/T_{gAB}$. The experimental data plotted in the form indicated in *Figure 10* permit to obtain from the slope a value for $T_{gAB} = 159^\circ\text{C}$, higher than that obtained by interpolating the experimental data with the same composition (132°C) and that calculated by the Fox equation (119°C). This fact shows that the contribution to the rotation and the free volume in these copolymers is influenced not only by their chemical composition but also by their microstructure.

The experimental T_g s of the terpolymers are represented in *Figure 11*. The weight fractions of the terpolymers are shown in the bottom of the figure as a triangle diagram while the points corresponding to T_g (O), top of the figure, have been obtained by drawing perpendicular lines to the base of the triangle with lengths equivalent to their value of T_g .

The upper triangle, formed by the union of the three points corresponding to the T_g of the three homopolymers, limits an area in which it can be considered that the terpolymers follow the Fox equation. The values calculated with this equation have been drawn too (▲) and it can be observed that almost all the experimental values are inside the surface of the triangle. We have shown above the influence of both chemical composition and microstructure on T_g in the copolymers HEMA-NPGMA; taking into account this fact, although the experimental values of T_g are in the Fox probability surface, some differences exist in some terpolymers that would originate from microstructural effects, and therefore the Johnston equation would improve the agreement. The values of T_g thus determined showed better agreement with the experimental ones, indicating

again the effect of the alternating units of the two hydroxylated monomers.

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