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Free radical copolymerization of 2-hydroxyethyl methacrylate with butyl methacrylate: determination of monomer reactivity ratios and glass transition temperatures

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Abstract

Free radical copolymerization of 2-hydroxyethyl methacrylate with butyl methacrylate using 3.0 mol l^{-1} N,N'-dimethyl formamide, DMF, solution and 9.0×10^{-3} mol l^{-1} of 2,2$'$ azobisisobutyronitrile, AIBN, as initiator, was carried out at 50°C. Experiments performed in bulk have evidenced the possible solvent effect in the values of monomer reactivity ratios. Besides, the homopolymers glass transition temperature, T_g, the intra and intermolecular structure along with Johnston's equation have enabled describing the experimental variations of HEMA–BMA copolymers' T_g. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Free radical copolymerization; 2-hydroxyethyl methacrylate; Butyl methacrylate

1. Introduction

Copolymers of hydrophilic and hydrophobic monomers have gained extensive interest in various applications such as hydrogels and biocompatible materials. 2-Hydroxyethyl methacrylate, HEMA, has been widely used as a comonomer in design and synthesis of such materials. That is because HEMA can be easily polymerized, possesses a hydrophilic group, can form hydrogels and found applications in the biomedical fields [1–4]. Further, the balance between the hydrophilic or hydrophobic character of this kind of materials can be controlled by preparing copolymers with a suitable selection of the chemical hydrophobic comonomeric structure. In this sense, a compilation of copolymer systems using HEMA as a comonomer has been published [5]. Examining this compilation and the data from Ref. [6], only a few values of monomer reactivity ratios for HEMA/n-alkyl methacrylate systems have been measured [7–9]. In this sense, although Choudhary and Varma, studied the biocompatibility of HEMA/butyl methacrylate, BMA, copolymers [10] no data on the values of the monomer reactivity ratios have been found in the literature. It is well known that the polymer properties are directly correlated with the chemical composition and comonomer distribution and then, the knowledge of the monomer reactivity ratios is of paramount importance in tailoring copolymers for specific applications. However, although chemical aspects are undoubtedly important, any individual application of copolymers requires the knowledge of its properties. The polymer glass transition temperature, T_g, representing the molecular mobility of the polymer chains, is an important phenomenon that influences the material properties and potential applications of a given polymer.

Besides the amphiphilic properties of HEMA/BMA copolymers and its possible use as a biocompatible material, the study of this system may be interesting as these copolymers can be an important application in other fields. Thus, it is well known [11] that many surface-coating latices are terpolymers that are formed, which have been called as the hardening monomer (i.e. methyl methacrylate, MMA), flexibilizing monomer (i.e. BMA) and other monomers that confer specific effects on the final polymer (i.e. amino meth(acrylates), hydroxy meth(acrylates)). Flexibilizing monomers such as BMA reduce the polymer T_g, which is connected with the minimum film forming temperature, that is the lowest temperature at which a polymer emulsion will form continuous films. Specific monomers such as HEMA are used in relatively small amounts with other comonomers to confer special properties on the resulting polymer. This way, HEMA can be of importance in the preparation of reactive latices with primary hydroxyl groups [12]. These latices are of special interest because of their use in

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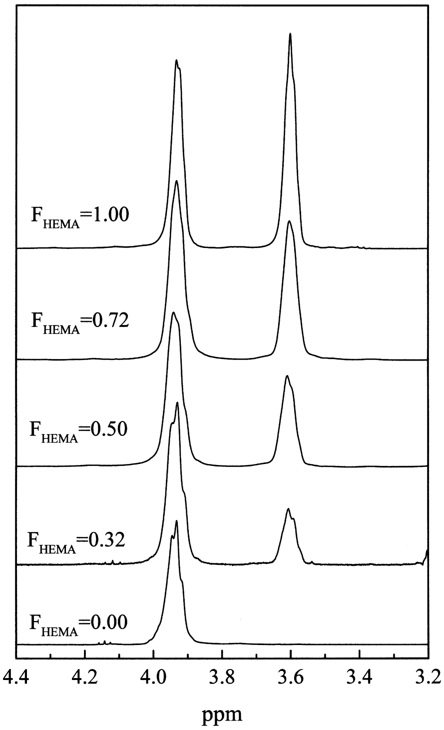

Fig. 1. Signals between 3.2 and 4.4 ppm of the ^{1}H-NMR spectra of poly(2-hydroxyethyl methacrylate), pHEMA, poly(butyl methacrylate), pBMA, and several HEMA–BMA copolymer samples.

post-cross-linkeable systems, where they are mixed with another latex bearing complementary reactivity. In the study of multicomponent polymerization, the multicomponent system is broken down (decomposed) into much more straightforward parts, to obtain a fundamental understanding of each of these parts. The study of HEMA/BMA system as a part of terpolymers latices may be of industrial importance.

Considering the above mentioned, this article focuses on the low conversion free-radical copolymerization of HEMA with BMA in *N,N′*-dimethyl formamide, DMF. From the composition data, the monomer reactivity ratios were determined and using differential scanning calorimetry the glass transition temperature of HEMA–BMA copolymers and both the homopolymer counterparts were determined. The variation of the glass transition temperature as a function of copolymer composition was analyzed considering its dependence with the intra and intermolecular structure of the copolymer chain.

2. Experimental

2.1. Materials

HEMA and BMA (both Fluka ≥99%) were passed through a column of activate basic aluminum oxide (Aldrich) and purged with high-purity nitrogen prior to use. DMF (Scharlau) was purified by shaking with phosphorus pentoxide for four days. Then, it was washed with potassium hydroxide pellets and distilled at 47°C at 14 Torr. The middle fraction was used. 2,2′-azobisisobutyronitrile, AIBN, (Fluka) was purified by crystallization from methanol and dried in vacuum (mp 104°C). All other reagents were used as received without further purification.

2.2. Copolymerization reactions

Copolymerization reactions were carried out in solutions of DMF in glass vessels sealed with rubber septa. The total monomer and initiator concentrations were 3.0 and 9.0×10^{-3} mol l^{-1}, respectively. The comonomer mixtures in ratios ranging from HEMA/BMA = 80/20 to 10/90 were prepared. Dissolved oxygen was removed from the reaction solution by nitrogen purging for 30 min prior to immersion in a water bath kept at a temperature of 50 ± 0.1°C. The copolymerization system was homogeneous in all cases investigated. After a specified period of time each reactor vessel was removed from the water bath and 0.5 ml of 10 wt.% solution of hydroquinone in THF was injected through the septum to stop the polymerization. The solutions were poured into a large excess of methanol/water (3:1, v/v) or diethyl ether/heptane mixtures to precipitate the copolymers. All of these were reprecipitated from THF solutions into the diethyl ether/heptane mixtures, filtered and dried under reduced pressure in the presence of phosphorus pentoxide until constant weight was attained.

2.3. Copolymer composition

The ^{1}H-NMR spectra were recorded at 400 MHz on a Varian Inova 400 spectrometer with deuterated dimethyl sulfoxide, DMSO-d_6 (Scharlau), as the solvent and locking agent at 80°C. The proton solvent signal was used as the chemical shift marker. The spectra were obtained after accumulating 100 scans by using a sample concentration of 10 wt.% solutions. The relative signal intensities of the spectra were measured from the integrated peak area, calculated by means of an electronic integrator.

2.4. Glass transition temperatures

The T_gs were measured using a Differential Scanning Calorimeter, Perkin–Elmer DSC/TA7DX, PC series with a water circulating system. The temperature scale was calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples (~10 mg) weighed to ±0.002 mg with a electronic autobalance (Perkin–Elmer AD4) were scanned at 10.0 K min^{-1} under dry nitrogen (20 cm^3 min^{-1}). Each sample was cooled from room temperature to 278 K and maintained at this temperature for 1 min. From this temperature the sample was heated to 413 K, then quenched to 278 K. This procedure was repeated twice.

Table 1
The molar fraction composition of monomer feed, f_{HEMA}, the molar fraction compositions of copolymers, F_{HEMA}, the final conversion and the copolymers glass transition temperature

	f_{HEMA}	F_{HEMA}	Conversion (%)	T_g (K)
DMF	0.8	0.82	7.5	367.6
	0.7	0.72	4.0	359.8
	0.6	0.60	5.6	352.8
	0.5	0.50	4.0	347.6
	0.4	0.41	5.4	342.1
	0.3	0.32	3.5	331.7
	0.2	0.25	5.1	326.0
	0.1	0.11	4.2	319.4
Bulk	0.6	0.72	4.3	361.4
	0.4	0.53	6.2	348.2
	0.2	0.29	8.7	333.8

The actual value for T_g has been estimated as the temperature at midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent, drawn through the point of inflection of the trace and the temperature of intersection of the tangent, drawn through the point of inflection with the final tangent. The values that are estimated according to this criterion might be apparently higher, when they are compared with those obtained following some other procedures. In our case this is also because of the employed rate of heating (10.0 K min^{-1}).

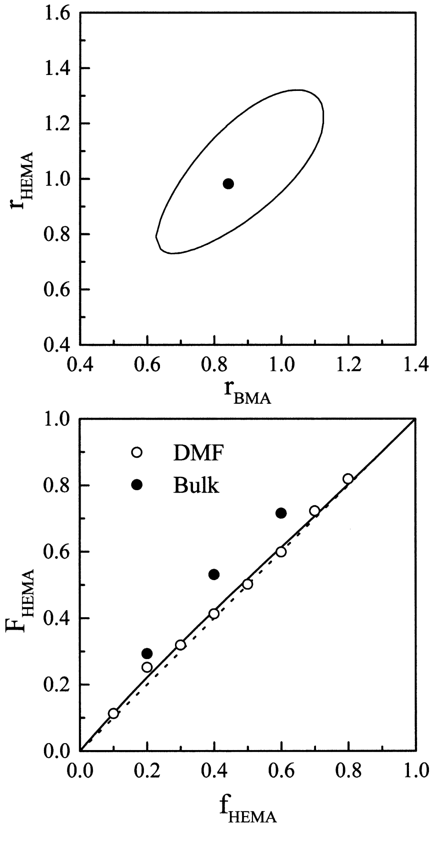

Fig. 2. (a) The 95% joint confidence interval of reactivity ratios. (b) The experimental composition data and the curve calculated with the reactivity ratios.

3. Results and discussion

3.1. Copolymerization

Free radical copolymerization of HEMA–BMA, using 3.0 mol l^{-1} DMF solution and 9.0×10^{-3} mol l^{-1} of AIBN as initiator, was carried out at 50°C. Conversions, lower than 10%, were obtained to satisfy the differential copolymerization equation. The average molar fraction composition of copolymers was quantitatively determined from the corresponding ^{1}H-NMR spectra of copolymer samples prepared with different monomer feeds. Fig. 1 shows the ^{1}H-NMR signals between 3.2 and 4.4 ppm of the spectra of poly(2-hydroxyethyl methacrylate), pHEMA, poly(butyl methacrylate), pBMA, and several HEMA–BMA copolymer samples. The analysis was performed by comparing the integrated intensities of the signals that appear at 3.95 ppm (corresponding to the protons in the $-O-\underline{CH_2}$ ester group in the methacrylate units) with the peak at 3.65 ppm (ascribed to the $-\underline{CH_2}-$OH protons in the HEMA units).

The molar fraction composition of the monomer feed, f_{HEMA}, final conversion and the average molar fraction compositions of copolymers, F_{HEMA}, are annotated in Table 1. The monomer reactivity ratios for HEMA–BMA copolymerization in DMF solution were determined from the average composition of copolymers listed in Table 1. Considering the Mayo–Lewis terminal model [13], MLTM, and using the nonlinear least-squares analysis suggested by Tidwell and Mortimer [14], the obtained monomer reactivity ratios values were $r_{HEMA} = 0.982$ and $r_{BMA} = 0.841$.The accuracy of the estimated data is represented in Fig. 2a where the 95% joint confidence interval is drawn. Fig. 2b shows the experimental composition data and the curve calculated with the reactivity ratios obtained after fitting the data. It can be seen that the agreement is satisfactory.

However, the quoted monomer reactivity ratio may be apparent since HEMA being an amphiphilic monomer exhibits different polymerization behavior in different solvents. As a result, inconsistencies exist between the different reported reactivity ratios for the same monomer pairs, depending upon the reaction media and other conditions [15]. This way, the 2-hydroxyethyl methacrylate–methyl methacrylate system, HEMA–MMA, copolymerized in DMF [15] has reactivity ratio values of $r_{HEMA} = 0.67$ and $r_{MMA} = 1.08$, whereas in bulk [16] has values of $r_{HEMA} = 1.054$ and $r_{MMA} = 0.296$. In order to ascertain that the reaction medium has some influence on the copolymer chain composition, experiments of HEMA–BMA copolymerization in bulk have been performed. The obtained results are given in Table 1; and as can be observed in Fig. 2b there are

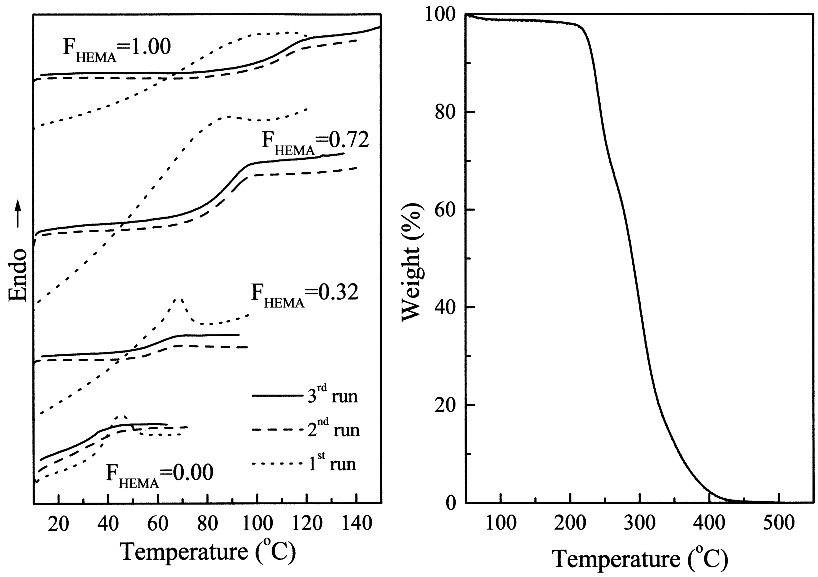

Fig. 3. (a) The DSC curves of both homopolymers and two copolymers. (b) Thermogravimetric analysis of pHEMA.

significant differences in the copolymer composition. Copolymers obtained in bulk have a higher HEMA molar fraction in the copolymer chain than those performed in DMF, which means that HEMA comonomer presents higher reactivity in the bulk copolymerization. The differences in copolymer chain composition as a function of the reaction medium may be a consequence of the distinct polarity of the solvents. This way, Ito et al. [7] have indicated that in the case of 2-hydroxyethyl methacrylate-lauryl methacrylate system, HEMA–LMA, the monomer reactivity ratios are dependent on the polarity of the solvent used in the copolymer preparation. Thus, when copolymerization is carried out in benzene (a solvent with low dipole moment) a value as high as 11.2 is obtained for the apparent monomer reactivity of HEMA. However, when the solvent used has a relatively high dipole moment, i.e. DMF, the apparent monomer reactivity of HEMA has a value of 0.8. The apparent monomer reactivity ratio of LMA is not dependent on the solvent and has a value of 0.7 when the copolymerization is carried out in benzene and a value of 0.8 when the copolymerization is performed in DMF. This behavior was attributed to the different tendency of HEMA to form aggregates. Thus, a high aggregation state of HEMA will exist in benzene as a result of hydrogen bonding, whereas no association will occur in DMF. However, although monomers, such as HEMA, are particularly susceptible to strong solvent effects via specific interaction such as hydrogen bonding, the kinetic consequences of this specific interaction will vary from system to system. In some cases, the radical and/or monomer reactivity will be altered and in other cases, a bootstrap effect will be evident [17]. Harwood [18] in his so-called "boot-strap model", proposed that the solvent does not modify the inherent reactivity of the propagating radical, but a partition coefficient characterizes the distribution of monomers in the system. Therefore, the comonomer ratio available for a growing polymer radical may differ from the global comonomer ratio.

Harwood's [18]"bootstrap model" is based on the observation that the copolymer having the same composition have the same sequence distribution regardless of the solvent employed in their preparation. When two copolymers have the same composition and the same monomer sequence distribution, the conditional probabilities that governed the growth of their chain must have been the same when they are formed. Therefore, the conditional probabilities governing the sequence distribution are unaffected by the polymerization medium and consequently by the monomer reactivity ratios. In this way the copolymerization of HEMA with lauryl methacrylate and the copolymerization of HEMA with styrene are solvent dependent and the observed behavior has been attributed not only to the effect of solvents on the different degrees of intermolecular aggregation of HEMA but also to the preferential solvation of monomers around the active polymer radical [7,19]. Considering that the bootstrap model is the most appealing as a general model [17] and taken into account that the reaction medium is a function of each component polarity and its corresponding molar fraction, HEMA/BMA/bulk system has a lower polarity than the HEMA/BMA/DMF system as the dipolar moment of HEMA and DMF are 3.2 and 3.8 Debye, respectively. Then, the aggregation state of the HEMA comonomer may be different, given rise to an apparent change in the monomer reactivity ratios [20] and the solvent does not modify the inherent reactivity of the propagating radical.

3.2. Thermal properties

The T_g for pHEMA and pBMA are 378.8 and 308.8 K, respectively. It is important to specify that the samples have

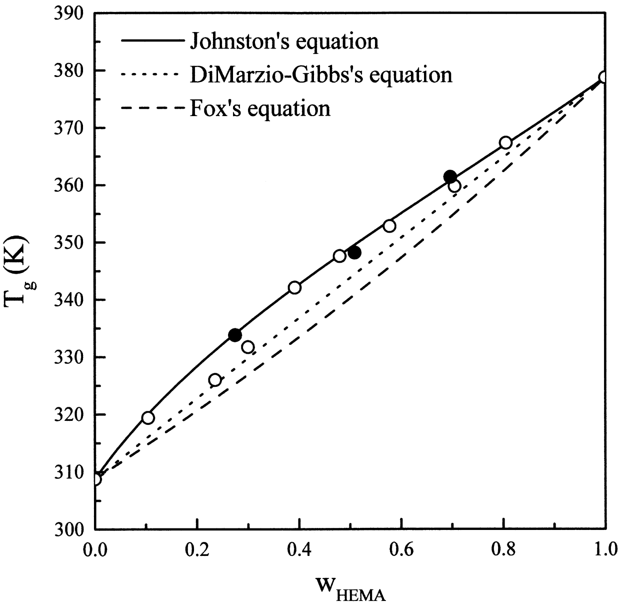

Fig. 4. Glass transition temperatures of HEMA–BMA copolymers as a function of HEMA weight molar fraction, w_{HEMA}, in the copolymer chain: ○, copolymers performed in DMF; ●, copolymers performed in bulk.

been supported by three cycles of heating and cooling. As it can be seen in Fig. 3a, in the case of pBMA the three DSC curves are coincident, while for pHEMA the first is different from the other two. The shift to higher temperatures is also noted for all the copolymers studied and its magnitude is dependent on the HEMA molar fraction in the copolymer chain. The T_g is lower in the first cycle, due to the fact that the HEMA can absorb water. This water reduces the glass transition temperature in the case of pHEMA in around 20 K, but once the water is eliminated the T_g reaches a constant value. The amount of water absorbed by the pHEMA is estimated in 1.5% by the thermogravimetric analysis measurements, as can be observed in Fig. 3b. The T_g depression is consistent with the plasticization theory [21,22]. Besides, the obtained values are consistent with some of the values reported in the literature [23,24]. In the case of pHEMA, Russell et al. [23] have shown that specimens with syndiotactic predominance had a T_g of 378 ± 5 K, which was insensitive to small changes in tacticity. On the other hand, isotactic pHEMA had a T_g of 308 K, some 70 K lower than its syndiotactic counterpart. However, other authors have reported values [25,26] of 358 K probably because of the annealing of the sample has not been suitable.

The physical properties of a copolymer are fundamentally determined by its sequence as well as its chemical structure and composition. Differences in the monomer reactivity ratio mean that, the copolymer synthesized with the same monomer feed composition have different copolymer compositions. However, if, as we previously assumed, the values of the monomer reactivity ratios are apparent, the two copolymers with the same molar fraction in the copolymer chain will have the same sequence distribution [18] and consequently the same T_g value regardless of the solvent employed for their preparation. Therefore, in the remaining article we will analyze the T_g behavior for the copolymer obtained using DMF as a solvent and further we will introduce the bulk copolymer T_g values in order to test if bootstrap model holds.

In Fig. 4 is represented the copolymers' glass transition temperatures as a function of the weight molar fraction of HEMA in the copolymers, w_{HEMA} and the experimental results are given in Table 1. The simplest relationship that describes the effect of the composition of the involved monomer units of a linear copolymer on T_g is the DiMarzio–Gibbs [27], which can be expressed as

$$T_g = m_{HEMA}T_{gHEMA} + m_{BMA}T_{gBMA} \tag{1}$$

where T_g is the glass transition of a copolymer composed of two monomer units HEMA and BMA with the mole fractions m_{HEMA} and m_{BMA}, and T_{gHEMA} and T_{gBMA} are the glass transition for HEMA and BMA homopolymers, respectively. For this system we have considered $m_{HEMA} \approx w_{HEMA}$, without introducing significant errors. As it can be seen the DiMarzio–Gibbs relationship drawn, as a dotted line, does not seem to reproduce the experimental results. However, due to that this is a thermodynamic theory based on the change of the material configurational entropy as a function of temperature, we have attempted to explain the glass transition behavior on the basis of free volume theory. Other simple relationship is the Fox equation [28], which assumes that T_g depends only on the relative amounts of each monomer and T_g of the respective pure homopolymers according to the following expression:

$$\frac{1}{T_g} = \frac{w_{HEMA}}{T_{gHEMA}} + \frac{w_{BMA}}{T_{gBMA}} \tag{2}$$

The comparison of the relationship with the experimental results is also depicted in Fig. 4 as a dashed line where it can be seen that it has not found a good agreement.

There are other equations such as the Gordon–Taylor–Wood equation [29,30], which includes additional adjustable parameters or the Johnston [31], Barton [32], and Couchman [33] equations, which predict T_g in terms of the monomer unit sequences (dyad sequences) in the copolymer. Having in mind the "free volume" concept and the microstructure of the copolymer we have tried to adjust the results to the Johnston's equation.

Johnston [31] assumes that M_1M_1, M_1M_2 or M_2M_1 and M_2M_2 dyads have their own glass transition temperature, with the overall T_g of a copolymer described by the following expression:

$$\frac{1}{T_g} = \frac{w_1P_{11}}{T_{g11}} + \frac{w_2P_{22}}{T_{g22}} + \frac{w_1P_{12} + w_2P_{21}}{T_{g12}} \tag{3}$$

where w_1 and w_2 are the weight fraction of two monomer units M_1 and M_2 respectively. T_{g11}, T_{g22} and T_{g12} denote the

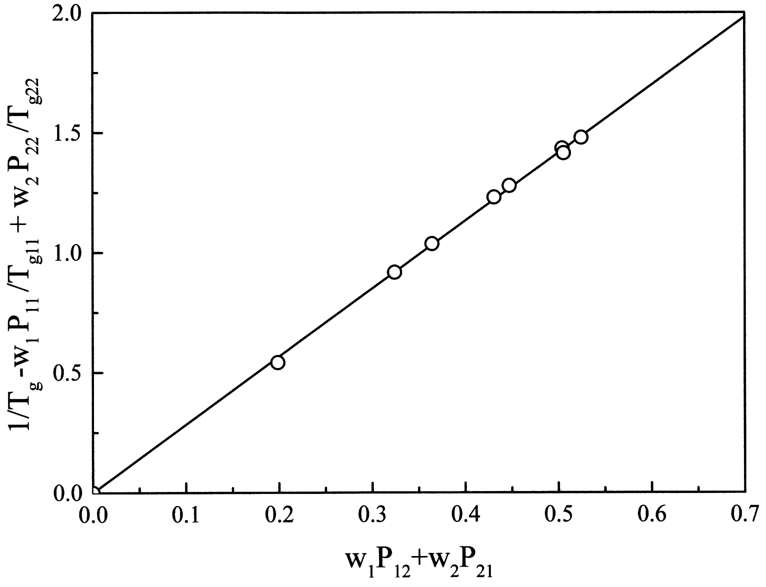

Fig. 5. Plot of the glass transition temperatures of HEMA–BMA copolymers performed in DMF according to the linearized expression of Johnston [31].

T_g contribution of the M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 dyads in the copolymer, and can be substituted by the T_g of M_1 homopolymer, M_2 homopolymer and the supposed T_g for the alternating the M_1M_2 copolymer, respectively. P_{11}, P_{22} and P_{12} or P_{21} indicate the probabilities of M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 dyads in the copolymer chain, respectively, and can be calculated by using the monomer feed compositions and monomer reactivity ratios [34].

T_{g12} for HEMA–BMA copolymers is unknown, but they have been estimated from our own experimental data of the involved homopolymers and those of HEMA–BMA copolymers and using a linearized form of Johnston's equation [31]. Experimental data yields, as can be seen in Fig. 5, to a straight line from which the value of 348.5 K is obtained. As it has been mentioned the deviation from the DiMarzio–Gibbs and Fox relationships could be explained as an influence of the copolymer microstructure on the T_g. From the monomer feed composition, monomer reactivity ratio values and using the Bernoullian statistic, it is easy to calculate the formation probabilities of M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 dyads as a function of the monomer molar fraction in the feed. Knowing this data, it is trivial to determine the dyads molar fraction as a function of the weight fraction of the monomer unit. In Fig. 6 are represented the calculated dyads molar fractions for this system. As can be observed, at w_{HEMA} less than 0.30 the HEMA–HEMA, (11), dyad concentration is lower than 10%, which means that the contribution of T_{g11} to the overall copolymer T_g is not

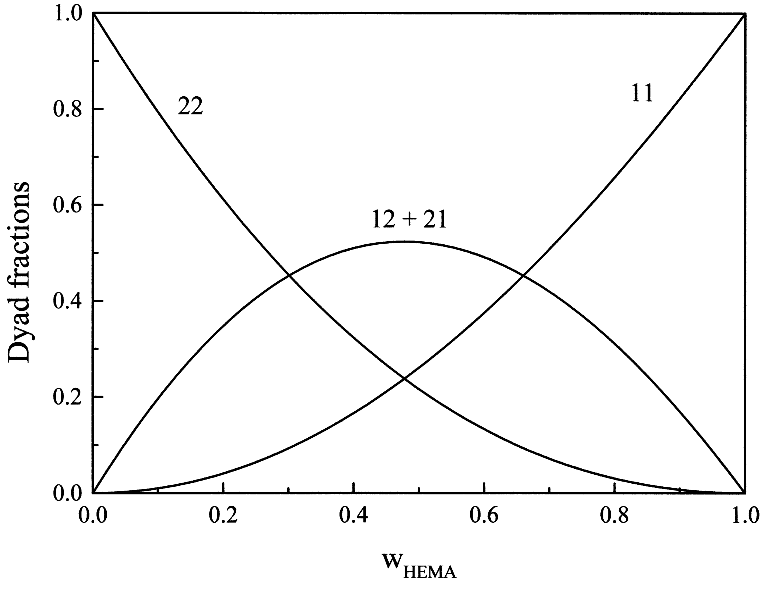

Fig. 6. Dyad molar fractions versus HEMA weight molar fraction in the copolymer chain for HEMA–BMA copolymers performed in DMF.

predominant. From w_{HEMA} between 0.3 and 0.7 the sum of HEMA–HEMA, (11), and BMA–BMA, (22) is similar to the sum of HEMA–BMA, (12), and BMA–HEMA, (21). Then, the contribution of each T_g to the global T_g is intermediate. For w_{HEMA} higher than 0.70 the BMA–BMA dyad is lower than 10% and within the experimental accuracy its contribution to the overall copolymer T_g vanishes.

The solid curve in Fig. 4 has been drawn according to Johnston's equation [31] considering both, the apparent reactivity ratios obtained when the copolymerization is carried out in DMF and the T_{g12} value. The agreement between the experimental values obtained for the copolymers performed in DMF and the theoretical ones indicate that Johnston's equation [31] and the terminal model through the reactivity ratios may be used to describe the dependence between the experimental T_g of HEMA–BMA copolymers performed in DMF and their sequence distribution. In order to test if the bootstrap model holds, the experimental values of T_g of the copolymer performed in bulk have also been represented versus w_{HEMA} in Fig. 4. The weight molar fraction of HEMA in the copolymers performed in bulk has been determined from the experimental copolymer composition. As it is clearly observed in Fig. 4 the bulk copolymers' experimental data are in good agreement with the theoretically estimated curve using the kinetic parameter obtained from copolymerizations performed in DMF. This means that the M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 dyads for copolymers with the same molar fraction composition are the same irrespective of the solvent used in their preparation. Consequently, the obtained values of monomer reactivity ratios are the apparent values and the reactivity of the growing radical is independent on the reaction medium.

Hirooka et al. [35,36] have concluded that the deviation of the T_g of an alternating copolymer from the T_g of a statistical 1:1 copolymer depends on the type of the T_g-composition relationship of the statistical copolymer involved. T_g of an alternating copolymer is higher, lower or similar than the T_g estimated from the T_g-sequence distribution when the T_g-composition curve for statistical copolymer is convex, concave or linear, respectively.

In order to explain such deviations, Tonelli [37] has used the conformational entropy as a characterizing parameter for the polymer intramolecular chain flexibility. He pointed out that the positive, negative or no deviations from the bulk additive, namely, T_{g12} estimated from the T_g-sequence distribution behavior, are produced when the conformational entropy for a given copolymer chain is lower, higher or similar, respectively, to the weighted sum entropies calculated for the constituent homopolymer chains.

On the other hand, the T_g of the polymer is related to the chain flexibility and this parameter is, to a large extent, a reflection of the rotational barrier about the bond linking the two monomer units. Depending on the rotational barrier of the heterolink bond being similar, higher or lower than the averaged rotational barrier of the homolink bonds, the copolymer's T_g-composition behavior will be linear or show positive or negative deviations from linearity [38]. Hirooka and Kato [36] have proposed that the difference between the average $\overline{T_g} = (T_{g11} + T_{g22})/2$ and the supposed transition temperature of the alternating copolymer T_{g12} may be regarded as a measure of the heterolink stiffness.

The average $\overline{T_g}$ corresponding to the equimolecular random HEMA–BMA copolymers is 343.8 K. The value of T_{g12} obtained using Johnston's equation [31] is slightly higher, 348.5 K, than that of the average $\overline{T_g}$ corresponding to the equimolecular random copolymer, which indicates that the studied system has a heterolink stiffness slightly higher than the average of the homopolymer links. Nevertheless, it is not clear to distinguish visually the positive deviations from the linearity expected in the copolymer T_g-composition behavior drawn in Fig. 4, although the value is acting on the increase of the heterolink stiffness. Nevertheless, the cause of this effect is not obvious as the chain flexibility not only depends on the rotational barrier but also on the chain packing, side chain stiffness, dipole interactions, etc.

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