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Monomer reactivity ratios and microstructural analysis of 2-hydroxyethyl methacrylate–*t*-butyl acrylate copolymers

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Abstract

The copolymerization reaction between 2-hydroxyethyl methacrylate and *t*-butyl acrylate in a 3 mol l^{-1} *N, N′*-dimethylformamide solution at 50°C, using 2,2′azobis(isobutyronitrile) as initiator was carried out and values of $r_{HEMA} = 1.792$ and $r_{TBA} = 0.510$ were found for the monomer reactivity ratios. High-resolution ^{1}H NMR spectra of copolymers have been analyzed in terms of sequence distribution and stereoregularity. The α-CH_3 resonance region contains five resonating peaks due to its sensitivity to triad concentrations. From these signals, triad concentrations were determined and its comparison with those calculated from Bernouillian statistics confirms the obtained results.

Keywords: 2-Hydroxyethyl methacrylate/*t*-butyl acrylate/DMF copolymerization; Monomer reactivity ratios; ^{1}H NMR

1. Introduction

In recent years *t*-butyl acrylate (TBA) has attracted considerable interest in order to prepare amphiphilic block copolymers [1–5] since subsequent hydrolysis of the *t*-butyl group leads to block copolymers containing hydrophobic and hydrophilic segments. Furthermore, the poly(*t*-butyl acrylate) (PTBA) block is of great interest not only due to the ease of hydrolysis into a poly(acrylic acid) block, but also the subsequent neutralization of the acid groups with a variety of bases is a direct way to the corresponding ionomer blocks.

Nevertheless, as far as we are aware, only statistical copolymerization of TBA has been carried out with methyl methacrylate, 2,4,5-trichlorophenyl acrylate and *N,N*-dimetyl-2-aminoethyl methacrylate [6]. Copolymerization of TBA with 2-hydroxyethyl methacrylate (HEMA) may be of practical interest considering that linear and crosslinked copolymers based on HEMA are widely utilized in the opthalmic industry [7], as a controlled drug-release matrix [8], as non-thrombogenic materials [9], surgical prostheses [10], etc.

One of the main characteristics of these hydroxylated polymers is the possibility of a noticeable swelling on contact with a hydrating medium, then, the introduction of TBA unit in the copolymer chain can lead eventually to a double hydrophilic statistical copolymer.

As it is widely recognized, the knowledge of the intermolecular (chemical composition and molecular weight distribution) and the intramolecular (sequence distribution and tacticity) structure of copolymers is important because it provides information on the reaction mechanism occurring during polymerization and it plays a key role in the understanding of relationship between the polymerization mechanism, molecular structure and properties [11]. This paper describes the copolymerization of HEMA with TBA in *N,N′*-dimethylformamide (DMF) in the terms expressed above.

2. Experimental

2.1. Materials

The monomers HEMA (Fluka) and TBA (Fluka) were passed through a column of activate basic aluminium 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. THF (Ferosa) was purified by distillation under nitrogen with lithium aluminium hydride. 2,2′-azobisisobutyronitrile (AIBN) from Fluka was

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Table 1
Molar feed composition (f_{HEMA}), conversion, overall copolymerization rate and experimentally determined copolymer composition (F_{HEMA}) for the free radical copolymerization of HEMA and TBA at 50°C in DMF

f_{HEMA}	Conversion	Conv./seg[a] $\times 10^5$	F_{HEMA}
0.90	0.069	3.83	0.941
0.80	0.067	3.72	0.874
0.70	0.066	3.66	0.834
0.60	0.069	3.83	0.709
0.50	0.066	3.33	0.655
0.40	0.070	3.47	0.558
0.30	0.074	4.11	0.439
0.20	0.102	5.66	0.329
0.20	0.095	5.26	0.321

[a] Polymerization time = 30 min.

recrystallized twice from methanol and dried in vacuum (m.p. 104°C). All other reagents were used without further purification.

2.2. Copolymerization reactions

HEMA–TBA copolymers were synthesized in glass ampoules sealed with rubber septa, using DMF as solvent and AIBN as initiator. The total monomer and initiator concentrations were kept at 3.0 mol l^{-1} and 9×10^{-3} mol l^{-1}, respectively. Dissolved oxygen was removed from the reaction solution by nitrogen purging for 30 min prior to immersion in a water bath at 50°C. The copolymerization system was homogeneous in all the cases investigated. After a specified length of time each ampoule was

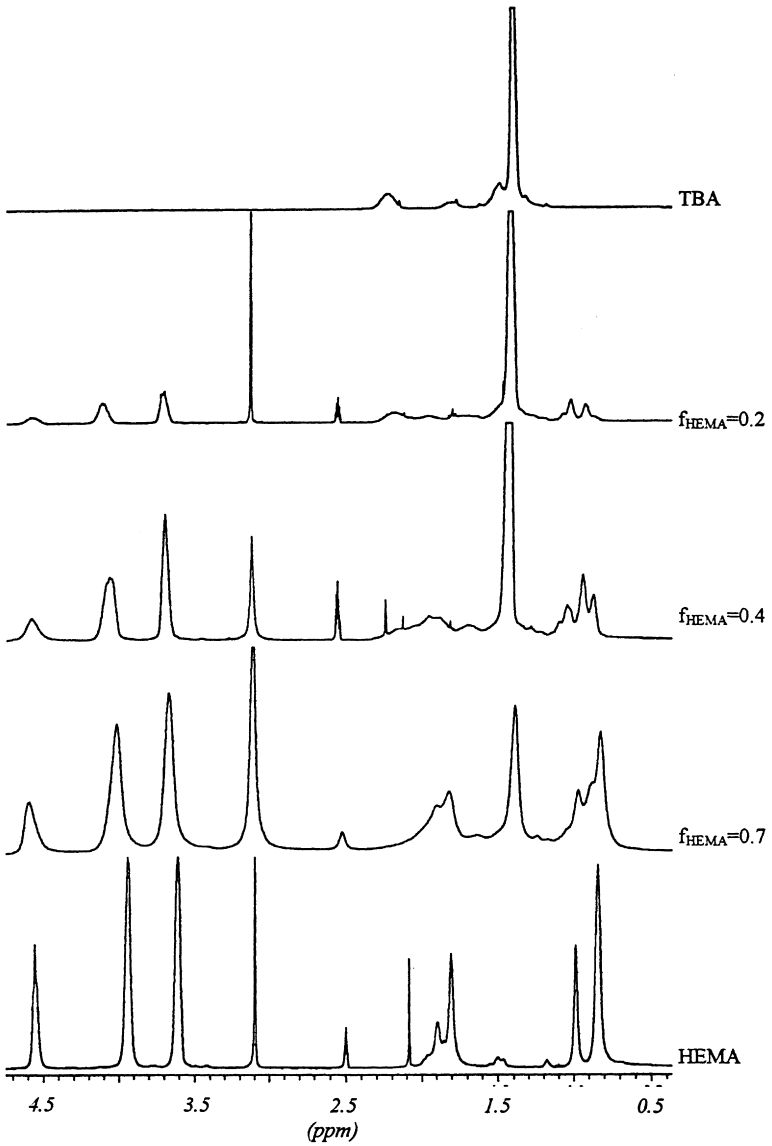

Fig. 1. ^{1}H NMR spectra of homopolymers and copolymers samples of HEMA–TBA prepared by free-radical copolymerization at 50°C. The monomer molar fractions of HEMA in the feed are indicated on the right.

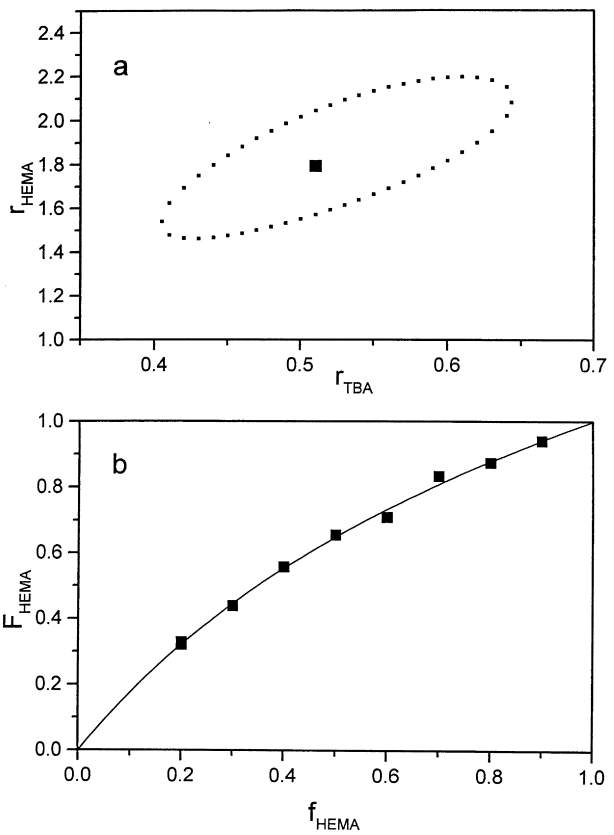

Fig. 2. (a) 95% Joint confidence intervals for reactivity ratios for the HEMA–TBA system. (b) Experimental NMR data (copolymer composition F_{HEMA} versus monomer composition f_{HEMA} and the fit with the terminal model with $r_{HEMA} = 1.792$ and $r_{TBA} = 0.510$).

removed from the water bath and the reaction stopped with 0.5 ml of a 10 wt.% solution of hydroquinone in THF. Methanol–water mixtures were used to isolate the copolymers. All samples were purified by reprecipitation using THF as the solvent and methanol–water mixtures as the precipitant and then dried in vacuum in the presence of phosphorus pentoxide until constant weight was attained.

2.3. Characterization of copolymers

The ^{1}H NMR spectra were recorded at 300 MHz in a Varian Inova 300 spectrometer at 80°C with DMSO-d_6 (10% w/v) as the solvent. The proton solvent signal was used as a chemical shift marker. The relative signal intensities of the spectra were measured from the integrated peak area, calculated by means of an electronic integrator.

3. Results and discussion

Free radical copolymerization of HEMA–TBA, 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. As can be seen in Table 1 the overall rate of copolymerization, expressed as conversion/second, hardly change up to a HEMA molar fraction in the feed of 0.4, but increases when the molar fraction of TBA in the feed is higher than 0.6.

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 spectra of poly(2-hydroxyethyl methacrylate) (PHEMA), PTBA and several HEMA–TBA copolymer samples. The analysis was performed by comparing the integrated intensities of the signals that appear at 1.4 ppm (corresponding to the protons in *t*-butyl ester group in the acrylate units) with the peak at 3.65 ppm (ascribed to the –CH_2–OH protons in the HEMA units).

The molar fraction composition of monomer feed (f_{HEMA}), final conversion and the average molar fraction composition of copolymer (F_{HEMA}) for each low conversion DMF solution copolymerization are quoted in Table 1. The monomer reactivity ratios for HEMA–TBA copolymerization in DMF solution were determined from the average composition of copolymers listed in Table 1. Considering the Mayo–Lewis terminal model [12] (MLTM) the results were obtained using the nonlinear least-squares analysis suggested by Tidwell and Mortimer [13] with the following monomer reactivity ratios values; $r_{HEMA} = 1.792$ and $r_{TBA} = 0.510$. The accuracy of our estimated data is represented in Fig. 2a where the 95% joint confidence interval is plotted.

Fig. 2b shows the experimental composition data and the line calculated with the reactivity ratios obtained after fitting the data. It can be seen that the agreement is satisfactory.

However as Berger and Kunz [14] pointed out, sequence distribution analysis is necessary for discriminating between the alternative kinetic schemes in copolymerization. As shown in Fig. 1, the ^{1}H NMR pattern of copolymer samples exhibits different signals, the intensities of which are a function of molar composition of monomer in the feed. Fig. 3 presents expanded ^{1}H NMR spectra of the α-CH_3 proton resonance signals of PHEMA along with several HEMA–TBA copolymers samples. The α-CH_3 group of PHEMA gives three resonances at 0.85, 0.99 and 1.18 ppm. Following the assignment of the same chemical residue for pure poly(methyl methacrylate) [15] we have assigned these resonances to iso (*mm*), hetero (*mr* + *rm*) and syndiotactic (*rr*) triads in order of increasing field. A similar assignment has also been proposed by Stevenson et al. [16] and by Gallardo and San Román [17].

The α-CH_3 proton resonance signals of copolymer samples split into five peaks whose intensities are a function of the molar composition of monomer in the feed. These signals could be analyzed on the basis of the stereochemical configuration of HEMA centered triads shown in Fig. 4, in which 1 and 2 indicate HEMA and TBA, respectively. From a detailed analysis of these signals it is clear that peak I (0.85 ppm), peak III (0.99 ppm) and peak V (1.18 ppm)

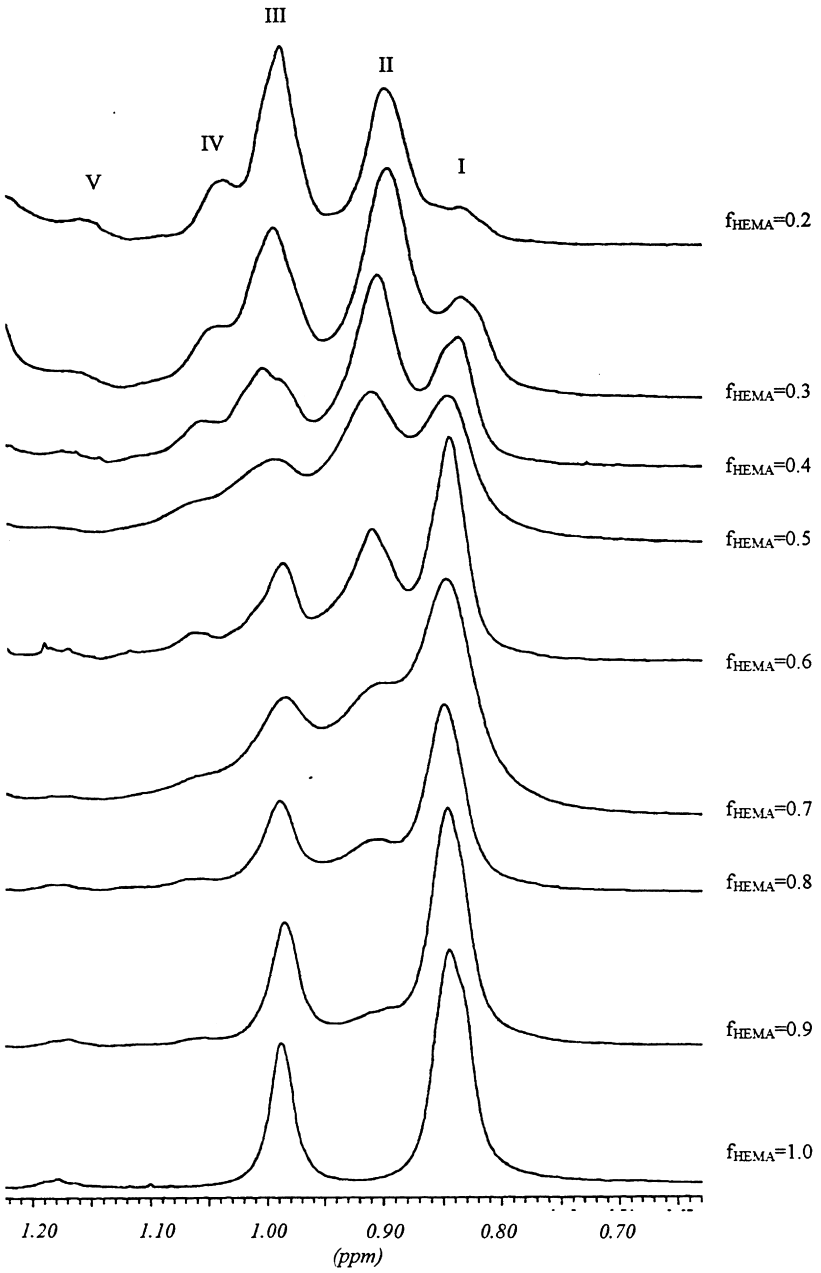

Fig. 3. Expanded ^{1}H NMR patterns of the α-methyl resonance signals of HEMA–TBA copolymers. The monomer molar fractions of HEMA in the feed are indicated on the right.

correspond to the chemical shifts of the *rr*, *rm* (*or mr*) and *mm* triads of PHEMA, respectively. As a consequence, these peaks have been assigned to the same kind of 111 triads in the copolymer chain *d* (peak I) *b* and *c* (peak III) and *a* (peak V) in Fig. 4. The assignment of two new signals II and IV, which do not appear in the spectra of the homopolymers (see Fig. 3) presents more difficulty and indicates that one can expect not only an effect of stereochemical configuration but also a slight influence of the composition of HEMA centered sequences on the chemical shift of the corresponding resonance signals.

The triads were assigned as shown in Table 2, considering the following: the intensity of signal I decrease with decreasing molar fraction of HEMA in the copolymer samples analyzed. Consequently, we assigned this peak only to HEMA-centered triads with stereochemical configuration of *rr*. When a 2-hydroxyethyloxycarbonyl group is replaced by a *t*-butyloxycarbonyl group, the signal of the α-methyl central group is deshielded and consequently the triads *h* and *l* appear of higher frequency, i. e. signals II (0.92 ppm). On the same basis the triad *p*, in which two 2-hydroxyethyloxycarbonyl groups are replaced by two *t*-butyloxycarbonyl groups, appears in peak III (0.99 ppm). The effect is additive, and it can be observed that the

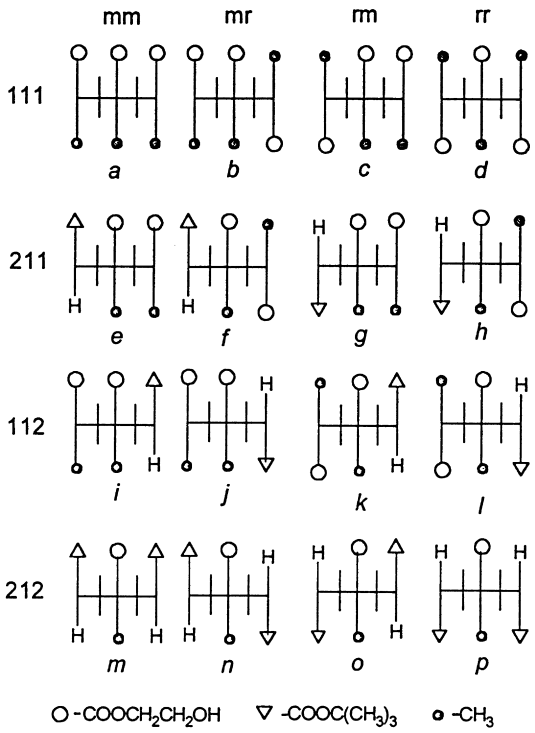

Fig. 4. Schematic representation of HEMA centered triads in HEMA–TBA copolymers.

substitution of one 2-hydroxyethylcarbonyl group shifts the signals by 0.07 ppm, whereas substitution of two 2-hydroxyethylcarbonyl groups shifts the signals by 0.14 ppm. This effect is also noted in the triads *g* and *j* which appear in the signals IV (1.07 ppm).

Table 2
Assignment of the α-CH_3 resonances to sequences of HEMA-centered triads

Spectral signal n°	Chemical shift	Copolymer sequence		
		Composition	Configuration	Triad
I	0.85	111	*rr*	*d*
II	0.92	211	*rr*	*h*
		112	*rr*	*l*
		211	*mr*	*f*
		112	*rm*	*k*
III	0.99	111	*mr*	*b*
		111	*rm*	*c*
		212	*mr*	*n*
		212	*rm*	*o*
		212	*rr*	*p*
IV	1.07	211	*rm*	*g*
		112	*mr*	*j*
		212	*mm*	*m*
V	1.10-1.22	111	*mm*	*a*
		211	*mm*	*e*
		112	*mm*	*i*

When an α-methyl group of the 111 *mr* or *rm* triads is substituted by a hydrogen atom the signal of the α-methyl central group is shifted to lower frequency and as a consequence the triads *f* and *k* appear in the signals II (0.92 ppm). This kind of effect also occurs in the triad *m* which appears in the signals IV (1.07 ppm). The triads *n* and *o* present two opposite effects, i.e. a dishielded and a shielded as consequence of the substitution of a 2-hydroxyethyloxycarbonyl group by a *t*-butyloxycarbonyl group and a shielded as a consequence of the substitution of an α-methyl group by a hydrogen. Thus, both effects are compensated and the triads *n* and *o* appear in the signal III (0.99 ppm).

The poorly resolved and relatively broad band at about 1.10–1.22 ppm may be easily assigned to a 111 triad with stereochemical configuration *mm*. However, the broad interval of this signal is a consequence of not only the absorption at 1.18 ppm of the *a* triad but also the absorption on this interval of *e* and *i* triads, since an α-methyl group in the 111 *mm* triad has been substituted by a hydrogen. Taking into account the lower content in isotactic triads in a free radical polymerization the amount of this kind of triad is not enough to give separate signals. Thus, the broad interval of signal V has been assigned to *a*, *e* and *i* triads.

In order to correlate the molar concentration of HEMA centered sequences with the statistical sequence distribution and stereochemical configuration of copolymer chains, we have analyzed statistically this copolymer system according to the monomer reactivity ratios, the conditional probabilities calculated from the quoted reactivity ratios and monomer molar fraction in the feed. This analysis has been carried out by making the following assumptions:

1. With respect to the chemical composition of copolymer sequence, it is assumed that the copolymerization reaction is described by MLTM.
2. From a statistical point of view we assume that the configurational sequence distribution may be described according to Bernouillian statistics, with the isotacticity parameters σ_{11}, $\sigma_{12} = \sigma_{21} = \sigma$ as defined by Bovey [18] and Coleman [19], where σ_{ij} is the probability of generating a meso diad between an *i* ending growing radical and incoming *j* monomer.

A value of $\sigma_{11} = 0.17$ has been considered for the statistical distribution of units in pure 111 triads. This value has been determined from the analysis of the α-CH_3 resonance of PHEMA considering the Bernouillian distribution of tactic sequences. The coisotacticity parameter σ_{12} is not accesible directly, but it has been determined by comparison of the integrated intensities of the peak III and V of α-CH_3 resonances (assigned as indicated in Table 2) for several copolymer samples. The application of well-known statistical relationships gives a value of $\sigma_{12} = \sigma_{21} = \sigma = 0.55$.

From this set of stereochemical parameters, the average molar fraction in the monomer feed and the conditional probabilities calculated from the quoted reactivity ratios,

Table 3
Experimental and calculated relative intensities of the resonance lines of the α-methyl group of the HEMA. Values were calculated with $r_{HEMA} = 1.792$, $r_{TBA} = 0.51$, $\sigma_{11} = 0.17$ and $\sigma = 0.55$

	Relative intensities									
	V (1.11–1.22 ppm)		IV (1.07 ppm)		III (0.99 ppm)		II (0.92 ppm)		I (0.85 ppm)	
f_{HEMA}	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
0.9	0.04	0.03	0.01	0.02	0.25	0.26	0.09	0.09	0.61	0.60
0.8	0.04	0.04	0.02	0.03	0.23	0.24	0.18	0.16	0.53	0.53
0.7	0.05	0.05	0.04	0.05	0.21	0.21	0.26	0.25	0.45	0.44
0.6	0.05	0.05	0.05	0.06	0.20	0.20	0.33	0.32	0.37	0.37
0.5	0.05	0.04	0.08	0.09	0.21	0.21	0.38	0.37	0.28	0.29
0.4	0.06	0.05	0.10	0.10	0.23	0.23	0.41	0.40	0.20	0.22
0.3	0.05	0.05	0.13	0.12	0.28	0.28	0.41	0.41	0.13	0.14
0.2	0.04	0.06	0.17	0.16	0.36	0.36	0.36	0.35	0.07	0.07

we obtained the theoretical intensities of the α-CH_3 resonance lines, for each copolymer sample. The results obtained are given in Table 3. The excellent agreement between calculated and experimental values provides support for the assignment of the NMR signals and the validity of the stereochemical parameter considered above.

4. Conclusions

Monomer reactivity ratios of the HEMA–TBA–DMF system have been evaluated. The determination of the stereochemical configuration have confirmed not only the validity of the apparent monomer reactivity ratios found in DMF for the HEMA–TBA system, but also that MLTM satisfactorily describes the copolymer composition and its stereochemical configuration.

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