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Inter and intramolecular structure predictions in 2-hydroxyethyl methacrylate–*tert*-butyl acrylate copolymers obtained at high conversion

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Abstract

Radical copolymerization at 50°C of 2-hydroxyethyl methacrylate and *tert*-butyl acrylate in a 3 mol l^{-1} N,N'-dimethylformamide (DMF) solution has been analysed over a wide range of conversion and monomer feed compositions with the purpose of predicting the variation of inter and intramolecular structures. To do this, the previously obtained monomer reactivity ratios along with the coisotactic and statistical parameters were used. Overall copolymerization rate coefficients and individual monomer conversions for each monomer on the full range of conversion were also obtained. From the results obtained it follows that the Mayo–Lewis terminal model (MLTM) provides an excellent prediction across the complete conversion range for all comonomer feed compositions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: 2-Hydroxyethyl methacrylate/*tert*-butyl acrylate/DMF copolymerization; High conversion; Copolymer inter and intramolecular structures

1. Introduction

The physical and chemical properties of a copolymer are fundamentally determined not only by the chemical structure of the monomers, but also by the intermolecular structure (average and cumulative chemical composition) as well as the intramolecular structure (sequence distribution). Obviously, the inter and intramolecular structures are a reflection of the kinetic history of the reactions that occurred during its formation. Furthermore, if the monomers have different reactivities, they will be consumed at different rates. Hence, at different conversions the monomer feed composition will be different and therefore copolymers with different compositions and sequence distributions will be produced. Considering the above mentioned facts, copolymers obtained at low conversion have, normally, homogeneous chemical and stereochemical compositions and then, its properties can be directly related with its structure. However, copolymers obtained at intermediate or high conversions are formed by a mixture of many individual macromolecules with compositions, microstructures and properties that differ from one to another. Then, the measured bulk properties are an average and must be related with average compositions and microstructures. Notwithstanding, the majority of reported studies of the mechanism of copolymerization have been based upon polymerization to low conversion. Relatively little effort has been devoted to the study of polymerization to high conversion [1], and little attention has been directed to the question of whether mechanisms which have been found to apply at low conversion continue to apply at intermediate and high conversion.

Most of the high conversion copolymerization studies have focussed on the variation of composition with conversion [2] and have ignored the absolute rate behaviour at high conversion. Hill et al. [3,4] have analysed the changes in copolymer composition and comonomer sequence distribution with increasing conversion for the copolymerization of styrene and acrylonitrile. In the same way, copolymer composition and comonomer sequence distribution over the full conversion range have been reported for methyl methacrylate–methyl acrylate [5] and 2-hydroxyethyl methacrylate–styrene [6] systems. Variation of glass transition temperature of copolymers with increasing conversion has also been described [7–10].

Recently, the kinetic behaviour of copolymerization in bulk and in solution has been modelled by Gao and Penlidis [1]. Model calculation includes conversion of monomer, molecular weights and cumulative copolymer composition. They used the Hamielec's pseudo-kinetic rate constant method [11]. Hamielec's method [11] reduces a copolymerization kinetic scheme to that of a homopolymerization and

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Table 1
2-Hydroxyethyl methacrylate mole fraction in the feed (f_{HEMA}), polymerization time, overall conversion and 2-hydroxyethyl methacrylate mole fraction in the copolymer chain (F_{HEMA}) for copolymer of HEMA–TBA obtained in a 3 mol l^{-1} DMF solution at 50°C

f_{HEMA}	Time (s)	Overall conversion (%)	F_{HEMA}
0.7	900	3.3	0.834
0.7	3600	12.4	0.838
0.7	7200	23.3	0.793
0.7	10 800	30.9	0.812
0.7	14 400	39.3	0.794
0.7	18 000	46.8	0.787
0.7	25 200	61.2	0.791
0.7	32 400	69.1	0.772
0.5	900	2.6	0.655
0.5	3600	12.5	0.665
0.5	7200	23.9	0.632
0.5	10 800	31.1	0.632
0.5	18 000	48.7	0.620
0.5	25 200	63.7	0.587
0.5	32 400	73.6	0.552
0.5	44 400	83.0	0.546
0.3	900	3.7	0.439
0.3	3600	14.1	0.454
0.3	7200	30.0	0.421
0.3	10 800	40.1	0.420
0.3	18 000	58.4	0.386
0.3	25 200	73.2	0.340
0.3	32 400	83.4	0.320
0.3	44 400	90.0	0.320

it greatly simplifies the rate expression for copolymerization.

In a previous study [12] we have reported the low conversion free-radical copolymerization of 2-hydroxyethyl methacrylate (HEMA) (1) and *tert*-butyl acrylate (TBA) (2) in a 3 mol l^{-1} *N*,*N*′-dimethylformamide (DMF) solution. This system seems to follow the Mayo–Lewis terminal model (MLTM) since the monomer sequence distribution in copolymer chains is described with the values of monomer reactivity ratios $r_1 = 1.792$ and $r_2 = 0.510$, the statistical parameters obtained from them and the coisotacticity parameters $\sigma_{11} = 0.17$ and $\sigma = \sigma_{12} = \sigma_{21} = 0.55$.

In the present paper the effect of conversion on the composition and sequence distribution for copolymerization of HEMA–TBA in DMF will be discussed. The experimentally observed variation with the conversion will be compared with that predicted from reactivity ratios, statistical parameters and coisotacticity parameters estimated at low conversions. From kinetic results the overall copolymerization rate parameter and individual conversion of each monomer as a function of copolymerization time has also been obtained.

2. Experimental

2.1. Copolymerization

Monomers and solvent and their purification procedures have been described elsewhere [12]. The free-radical initiator, 2,2′-azobisisobutyronitrile (AIBN), was recrystallized twice from distilled methanol. Copolymers were prepared under the same experimental conditions as described in detail elsewhere [12]. The total monomer concentration was 3 mol l^{-1} in DMF; the initiator concentration was 9.0×10^{-3} mol l^{-1}. Both conversion and monomer feed composition were calculated gravimetrically.

2.2. Copolymer composition

The chemical composition of copolymer was estimated by nuclear magnetic resonance. ^{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.

3. Results and discussion

3.1. Kinetic analysis

Copolymerization throughout the whole range of conversions of HEMA–TBA, using 0.7; 0.5 and 0.3 HEMA mole fractions in the feed were carried out at 50°C with an overall monomer concentration of 3 mol l^{-1} in DMF solution and 9.0×10^{-3} mol l^{-1} of AIBN as initiator. Experimental results are given in Table 1.

Modelling conversion against time is difficult because of the uncertainty of the rate parameter values which, usually, are both composition and conversion dependent. However, as stated by Hamielec et al. [11] earlier, the copolymerization rate of the monomers, either in the presence or absence of solvent, can be in a general sense, expressed in a similar manner to that for homopolymerization using average composition-dependent values for the rate parameters, where the composition-dependent parameters are denoted by a bar on the top of the symbols.

$$R_{\mathrm{p}} = \bar{K}[\mathrm{I}]^{1/2}([\mathrm{M}_1] + [\mathrm{M}_2])$$

where

$$\bar{K} = \frac{\bar{k}_{\mathrm{p}}}{\bar{k}_{\mathrm{t}}^{1/2}}(2\overline{fk_{\mathrm{d}}})^{1/2}$$

$\bar{K}$ being the overall copolymerization rate parameter, $\bar{k}_{\mathrm{p}}$ and $\bar{k}_{\mathrm{t}}$ the average values of propagation and termination rate constants, respectively, which are also functions of the conversion, because of composition drifts. [I] and [M$_i$] are the initiator and monomers *i* concentrations, respectively, and $2\overline{fk_{\mathrm{d}}}$ the effective rate coefficient for initiation which varies linearly with monomer feed composition according to the following empirical relationship [2]

$$2\overline{fk_{\mathrm{d}}} = f_1(2fk_{\mathrm{d}})_1 + f_2(2fk_{\mathrm{d}})_2$$

where $f_i = (1 - f_j)$ is the mole fraction of monomer fraction *i* in the feed and $(2fk_{\mathrm{d}})_i$ are the effective rate coefficient for

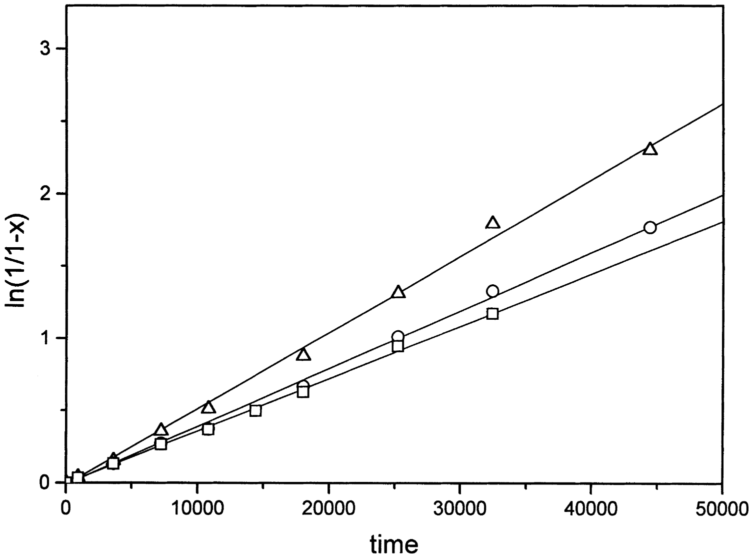

Fig. 1. Semilogarithmic kinetic diagrams for the free radical copolymerization of the HEMA/TBA/DMF system at 50°C. f_{HEMA} 0.7 (△); 0.5 (○); and 0.3 (□).

monomer i, f being the efficiency factor and k_d the decomposition rate coefficient, respectively.

As shown in Fig. 1, where semilogarithmic kinetic plots are presented, the copolymerization rate varies significantly with the molar monomer feed composition being higher when the TBA molar fraction in the feed increases. From the initial slope of the lines in Fig. 1 and the initiator concentration, the rate coefficients $\bar{K}$ were estimated and the values are quoted in Table 2.

The individual conversion for each monomer as a function of the copolymerization time can be obtained from the overall conversion and its corresponding mole fraction in the copolymer chain. Experimental results are presented in Fig. 2. As can be seen from this figure, the amount of the individual monomer consumed is closely related to the mole fraction in the feed. As an indication of the overall kinetic coefficient for individual monomer consumption, we have measured the initial slope of the lines (S_i) represented in Fig. 2. From the estimated values, quoted in Table 2, it is clear that as expected from the quoted reactivity ratios HEMA is more rapidly consumed than TBA.

3.2. Inter and intramolecular structure

Since MLTM describes the copolymerization composition and tactic triads fractions at low conversion, it has been used to predict inter and intramolecular structures with increasing conversion. The effect of conversion on both the cumulative copolymer composition and the stereochemical composition of copolymer chain has been approximated by a step function [5]. Copolymerization theory allows us to derive the amount of each monomer that is polymerized; instantaneous copolymer composition and microstructure for each step are then accumulated over the conversion to yield integrated values.

Table 2
Overall copolymerization rate coefficient ($\bar{K}$) and overall kinetic coefficient for individual monomer conversion (S_i)

f_{HEMA}	$\bar{K}(10^4\ \mathrm{mol^{-1/2}\ l^{1/2}\ s^{-1}})$	$S_{HEMA}(10^5)$	$S_{TBA}(10^5)$
0.7	3.82	4.43	2.24
0.5	4.23	5.24	3.43
0.3	5.28	6.87	5.10

The cumulative copolymer composition as a function of conversion for the different mole fractions in the feed is shown in Fig. 3. The solid lines were drawn according to the described procedure using the MLTM and the monomer reactivity ratios given above, i.e. $r_1 = 1.792$ and $r_2 = 0.510$. It is clear that experimental and predicted data agree very closely.

It is very well established that the probability of formation of any tactic sequence distribution is a function of the monomer feed mole fraction, and it changes with increasing conversion. Then, during the copolymerization reactions at high conversion there may be a distribution of compositions and a change of monomeric sequences distribution along the main chain [13].

As it is well known [14,15], if we consider three consecutive monomeric units with an HEMA centred unit, there are three kinds of triads along the copolymer chain: HHH, HHA/AHH and AHA where H and A represent HEMA and TBA units, respectively. Each one of these triads may be with coisotactic (*mm*), coheterotactic (*mr* or *rm*) and cosindiotactic (*rr*) configuration. NMR is one of the advanced methods of determining intramolecular structure in the copolymers [14,15]. Using NMR technique, we have observed [12] that α-methyl proton region of low-conversion HEMA/TBA copolymers split into five peaks whose intensities are a function of the molar composition of

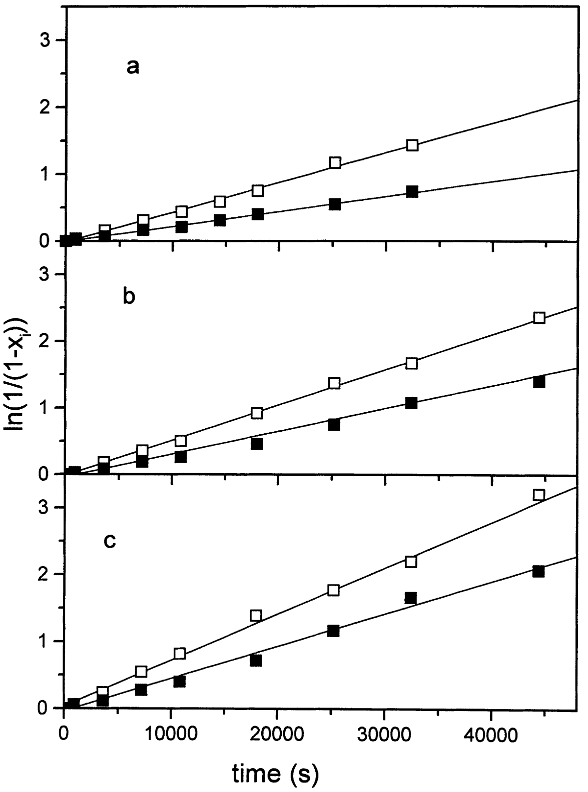

Fig. 2. Semilogarithmic kinetic plot for each monomer consumption. HEMA (□), TBA (■) in the copolymerization of HEMA–TBA in a 3 mol l^{-1} DMF solution at 50°C. f_{HEMA}: (a) 0.7; (b) 0.5; and (c) 0.3.

monomer in the feed. These signals were analysed on the basis of the stereochemical configuration of HEMA centred triads. The assignment of the peaks to different triad sequences were confirmed by comparing both the

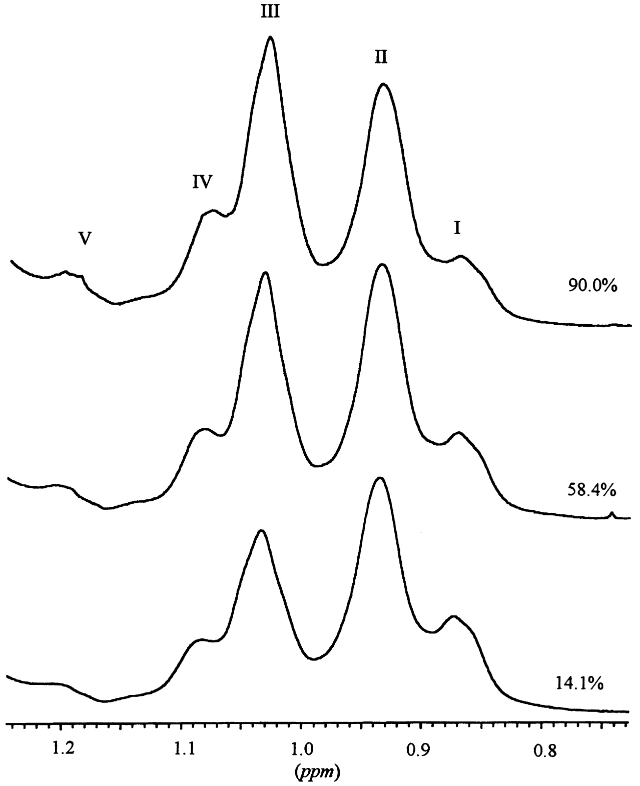

Fig. 4. ^{1}H NMR spectra of the expanded α-methyl proton region for three HEMA/TBA copolymer samples performed by free-radical copolymerization at 50°C in DMF solution. $f_{\mathrm{HEMA}} = 0.3$. The overall conversion for each sample are indicated on the right.

experimentally determined triad fraction and those calculated theoretically using Bernouillian statistics with coisotactic parameter $\sigma_{11} = 0.17$ and $\sigma_{12} = \sigma_{21} = \sigma = 0.55$ as defined by Bovey [16] and Coleman [17], where σ_{ij} is the

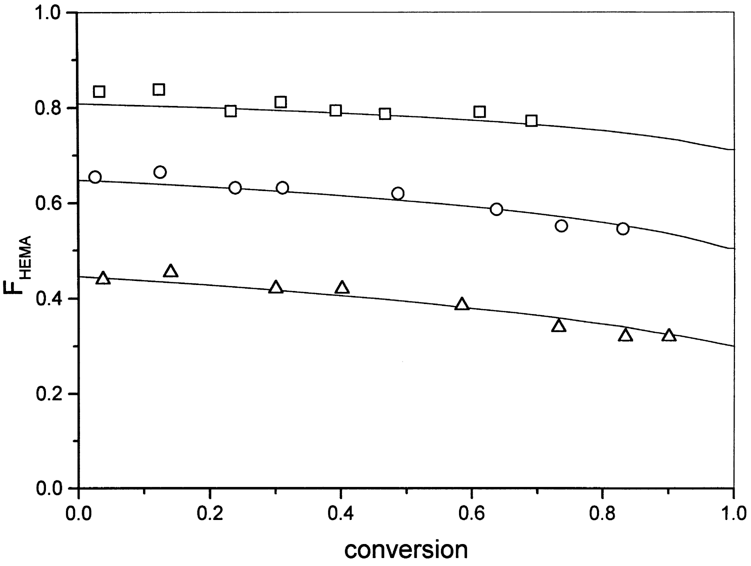

Fig. 3. Dependence of cumulative copolymer composition with conversion for the polymerization of the HEMA/TBA/DMF system at 50°C with $f_{\mathrm{HEMA}} = 0.7$ (○); 0.5 (△); and 0.3 (□). Solid lines were calculated according to the MLTM with $r_1 = 1.792$ and $r_2 = 0.510$.

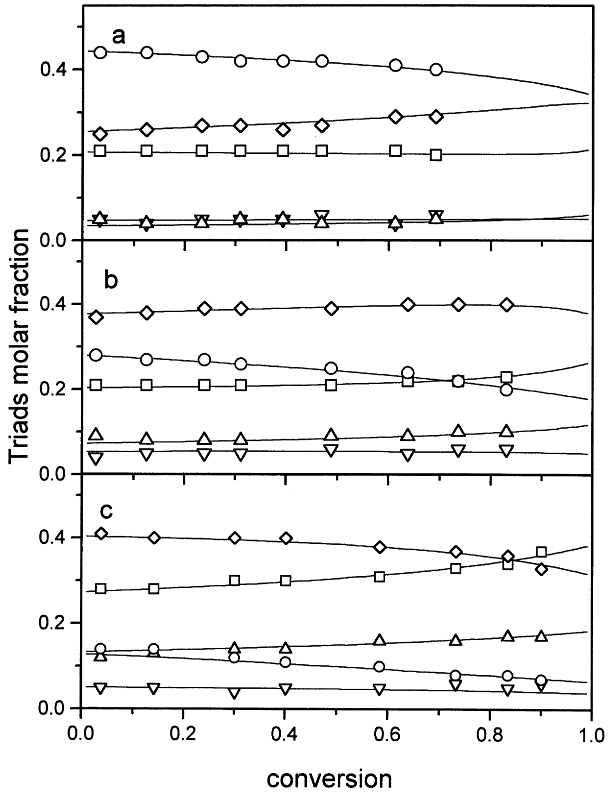

Fig. 5. Comparison between the observed and calculated HEMA-centred triad molar fractions obtained with increasing conversion, for the high conversion copolymerizations of HEMA and TBA carried out in DMF at 50°C. (a) $f_{\mathrm{HEMA}} = 0.7$; (b) $f_{\mathrm{HEMA}} = 0.5$; and (c) $f_{\mathrm{HEMA}} = 0.3$. Experimental triad molar fraction: I (○); II (◇); III (□); IV (△); and V (▽). The predicted values (full lines) were calculated using the MLTM with $r_1 = 1.792$ and $r_2 = 0.510$ along with the $\sigma_{11} = 0.17$ and $\sigma_{12} = \sigma_{21} = \sigma = 0.55$ obtained for copolymers produced at low conversions.

probability of generating a meso diad between an *i* ending growing radical and incoming *j* monomer.

^{1}H NMR spectra of the expanded α-methyl proton region for three different HEMA/TBA copolymers performed in DMF with initial feed HEMA molar fraction of 0.3 and different degrees of conversion are shown in Fig. 4. In agreement with previously published data we observe five distinctive peaks. The peaks named I–V, have been assigned to different configurational arrangement in the same manner as for the low conversion copolymers since its chemical shift agrees with those observed for copolymers obtained at low degree of conversion [12].

Then, peak I, centred at 0.85 ppm, is assigned to HHH triads in *rr* configuration. Peak II, centred at 0.92 ppm, is assigned to AHH/HHA in *rr* and *mr*/*rm* configuration. Peak III, centred at 0.99 ppm, is assigned to HHH with *mr*/*rm* configuration and to AHA with coheterotactic and cosindiotactic configuration. Peak IV, centred at 1.07 ppm, is assigned to AHA in *mm* configuration along with AHH/HHA in *rm*/*mr* configuration. Finally peak V, from 1.10 to 1.22 ppm is assigned to HHH and AHH/HHA with *mm* configuration.

Changes with the conversion in the stereochemical copolymer composition and HEMA centred fraction triads have been measured for copolymers obtained with comonomer feed composition $f_{\mathrm{HEMA}} = 0.7$, 0.5 and 0.3. The experimental relative intensities (tactic triads molar fraction) are represented in Fig. 5 as a function of the conversion for each of the three different compositions studied in the present paper.

Comparison between theoretical and experimental values, Fig. 5, shows that although there are slight deviations, the experimental and predicted values agree very closely. As previously stated we have found that values of copolymer composition as a function of the conversion can be satisfactorily described by MLTM. Furthermore, considering the good correlation for values of the sequence distribution as a function of conversion, we can conclude that both inter and intramolecular structure of HEMA/TBA copolymers performed in DMF solution can be described by the MLTM in the whole range of conversion.

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