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Sequence distribution and stereoregularity in methyl methacrylate–methyl acrylate copolymers at high conversions

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Methyl methacrylate (MMA)–methyl acrylate (MA) copolymerizations have been analysed over a wide range of conversions with the purpose of predicting the changes in copolymer composition and comonomer sequence distribution as a function of conversion. High resolution ^{1}H n.m.r. spectra (200 MHz) of MMA–MA copolymers, prepared at two overall comonomer concentrations by free radical copolymerization in benzene solution at 50°C at low conversion, have been analysed in terms of comonomer composition, sequence distribution and stereoregularity. Reactivity ratios for the terminal model, statistical parameters, P_{ij}, and co-isotacticity parameters, $\sigma_{11}=0.23$ and $\sigma=\sigma_{12}=\sigma_{21}=0.50$, estimated at low conversion were used to describe the changes in copolymer composition and triad fraction intensities with conversion. The experimental sequence distribution intensities were in agreement with the estimated values. From the good agreement found between experimental and calculated values, it can be concluded that the terminal model, through reactivity ratios and Bernoullian statistics, provides a very precise description of copolymerization over the whole range of conversion and composition and overall concentration of monomers.

(Keywords: copolymers; free radical copolymerization; conversion)

INTRODUCTION

It is well known that copolymers of methyl methacrylate (MMA)–methyl acrylate (MA) are commercially useful materials. Copolymers of technical importance are normally obtained at high degrees of monomer conversion. High conversion copolymers have molecular weight distribution, average composition and sequence distribution corresponding to the comonomers and to their configuration in the molecular chain. These three possible sources of heterogeneity exert an appreciable, and in many instances a critical, influence on the physical and mechanical properties of the copolymer. Copolymer samples must be described by these variables. For this reason and for basic research, plant control and product development, it is necessary to obtain information on these values as well as on the control of the copolymerization process. This paper addresses the study of the above-mentioned parameters in the copolymerization of the MMA–MA system.

This system has scarcely been investigated, even in the case of low conversion. It has been studied only from a few points of view: (i) the way in which the monomer feed composition determines the copolymer composition (reactivity ratios)[1–6]; (ii) fractionation by chemical composition[7]; and (iii) sequence distribution of components and stereoregularity[8].

The influence of the conversion on the composition of copolymers has been analysed in detail in only a few cases. Thus O'Driscoll and Huang[9] have used terminal model reactivity ratios to predict the evolution in chemical composition with conversion for the copolymerization of styrene and MMA, and Hill *et al.*[10,11] have analysed the copolymerization of styrene and acrylonitrile with the purpose of predicting the changes in copolymer composition and comonomer sequence distribution with increasing conversion.

In a recent paper[12] we studied the free radical copolymerization at 50°C of MMA and MA at two different overall monomer concentrations (3 and 5 mol l^{-1}) in benzene solution.

The main conclusions drawn were that: (i) reactivity ratios do not, apparently, change by dilution; (ii) copolymer composition at low conversion and cumulative copolymer composition as a function of conversion are independent of total monomer concentration, being described satisfactorily by the integrated Mayo–Lewis equation (terminal model[13,14]); and (iii) the overall copolymerization coefficients are not affected by total monomer concentration.

Taking into account the results obtained previously, we analyse the copolymerization at low conversions to

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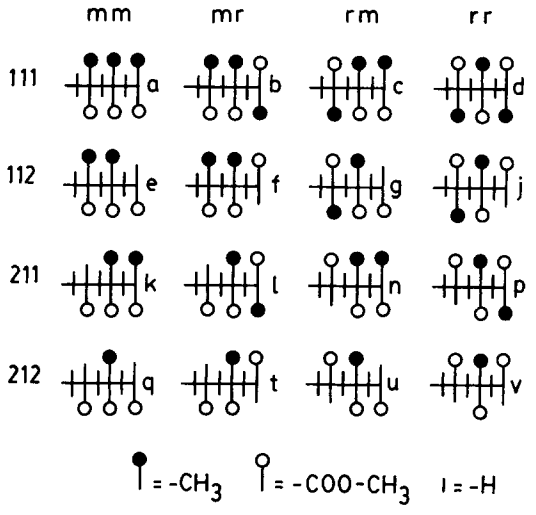

Figure 1 Triads configuration of MMA (**1**) centred triads with MA (**2**) unit in MMA–MA copolymers. **m** and **r** represent meso and racemic units, respectively

verify whether the copolymerization model employed previously to describe our experimental kinetic results can also be used to describe the stereochemical composition of copolymers. Later, we will extend the analysis of sequence distribution to our copolymerization results obtained at higher conversions.

EXPERIMENTAL

Copolymerization

Monomers and solvent and their purification procedures were as described elsewhere[12]. The free radical initiator AIBN (Fluka, AG) was recrystallized twice from distilled methanol.

Copolymers were prepared under the same experimental conditions as described in detail elsewhere[12]. The total monomer concentrations were 3 and 5 mol l^{-1} in benzene; the initiator concentration was 1.5×10^{-2} mol l^{-1}. Both conversion and monomer feed were calculated by gravimetry.

Copolymer composition

The chemical and the stereochemical compositions were estimated by nuclear magnetic resonance. ^{1}H n.m.r. spectra were recorded at 40 ± 0.1°C on 8% (w/v) deuterochloroform solution on a Bruker AM-200 n.m.r. spectrometer at 200 MHz. The relative areas of the peaks were measured by the electronic integrator or by triangulation and planimetry. The copolymer compositions given in the text were estimated from the average value of four independent measurements of each sample and by each of the methods.

RESULTS AND DISCUSSION

Microtacticity

If we consider three consecutive monomeric units centred with an MMA unit then there is a series of possible triads, as shown in *Figure 1*, where **1** and **2** refer to MMA and MA, respectively. At first sight of these configurations, it can be expected that the α-methyl groups at the centre of the **b** triad have the same chemical shift as those of the **c** triad, since the adjacent units to the above-mentioned protons are the same for both configurations. The same can be argued for **e** and **k**, **f** and **n**, **g** and **l**, **j** and **p** and finally for **t** and **u** triads. In other words, they can be reduced. Accordingly, the 16 possible triads that may be observed in the spectra have to be reduced to 10 magnetically distinguishable triads.

Figure 2 shows the high field zone of the ^{1}H n.m.r. spectra of MMA–MA copolymers and MMA and MA homopolymers corresponding to the α-methyl protons of MMA at low conversions. As expected, poly(methyl acrylate) (PMA) does not show any chemical shift in this region. However, the n.m.r. spectra of poly(methyl methacrylate) (PMMA) show three signals at 1.19, 1.00 and 0.83 ppm, which have been assigned, according to literature data[8,15], to iso- (**a**), hetero- (**b** and **c**) and syndiotactic (**d**) triads.

Triad fraction assignments

As observed in *Figure 2*, the n.m.r. spectra of the copolymers in the α-methyl region show six peaks which will be designated as β_1 (1.21), β_2 (1.14), β_3 (1.04), β_4 (0.99), β_5 (0.92) and β_6 (0.88 ppm).

The signals β_1 and β_6 decrease in intensity as the molar fraction of MMA in the copolymer (F_{MMA}) decreases, and its position, although a little shifted, almost agrees with **a** and **d** triads in PMMA. For this reason they have been assigned to the **111** iso- and syndiotactic triads, respectively. It is also in agreement with the existing values[8] of $\delta = 1.21$ and 0.91 ppm, respectively. The signal appearing at the lower field, 1.21 ppm, cannot be detected

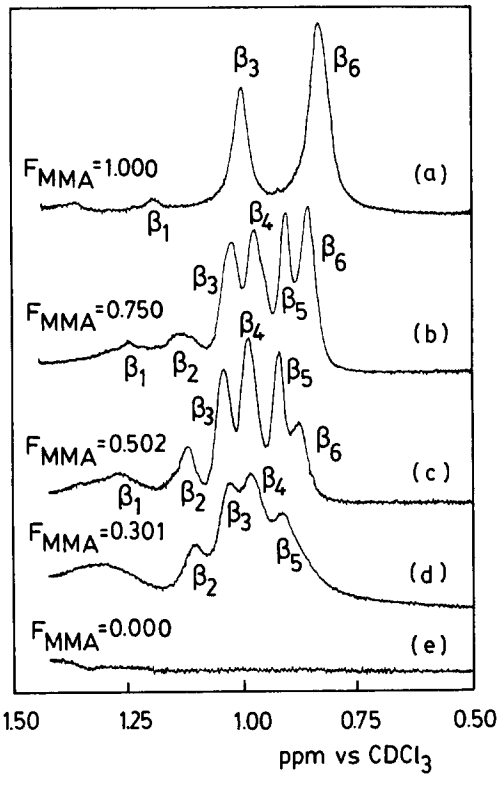

Figure 2 N.m.r. chemical shifts (200 MHz) of α-methyl group for low conversion copolymers, ([MMA]+[MA])=3 mol l^{-1}, obtained at various monomer feed mole fractions of MMA, and MMA and MA homopolymers prepared under the same experimental conditions (see *Table 1*): (a) PMMA homopolymer; (b) copolymer (f_{MMA}=0.548 and F_{MMA}=0.750); (c) copolymer (f_{MMA}=0.300 and F_{MMA}=0.502); (d) copolymer (f_{MMA}=0.175 and F_{MMA}=0.301); (e) PMA homopolymer

at percentages less than 2%, due to the limits of error of the n.m.r. technique.

The intensity of the peak appearing at 1.14 ppm increases when F_{MMA} decreases, so this signal has been assigned to isotactic sequences of **112** (or **211**) and **212** type, since the substitution in **a** of a methyl group by a proton (**e** or **k** triad in *Figure 1*) will lead to a shielding of 0.04 ppm for the signal of the α-methyl protons in the centred unit of **1** according to Mori *et al.*[8]. For the same reason, the **q** sequence will display a chemical shift of 0.04 ppm lower than that of the **e** (or **k**) triad. The limited resolution attained under the experimental conditions used to run the spectra have made it possible for these triads to appear together at 1.14 ppm and they cannot be distinguished. However, Mori *et al.*[8] observed that the **112** (or **211**) isotactic (**e** or **k**) and **212** isotactic (**q**) show different chemical shifts at 1.17 and 1.13 ppm, respectively. With regard to the signal β_3 appearing at 1.04 ppm, it must be mentioned that it decreases initially as the proportion of MMA decreases in the copolymer, to increase quite considerably afterwards. It has been assigned to the **111** heterotactic triad (**b** and **c**) by comparison with the PMMA spectrum, and to the **212** sequence of the same tacticity (**t** and **u**), since it must be expected that the α-methyl protons of the **1** central unit show the same chemical shift when they are surrounded alternatively by two carboxymethyl groups, independently of whether these two groups belong to MA units (**t** and **u**) or MMA units (**b** and **c**). This assignment is in agreement with that described in the literature[8] ($\delta = 1.06$ ppm).

The signal β_4 appearing at 0.99 ppm following Mori *et al.*[8] ($\delta = 1.01$ ppm) has been assigned to **v** with **j** (and **p**) or with **g** (and **l**) triads. In fact, the anisotropic effect of the carbonyl groups would reduce the chemical shifts of the **v** triads with regard to **t** (or **u**) triads. The chemical shift of β_5 at 0.92 ppm following other authors[8] ($\delta = 0.96$ ppm) has been assigned to the **f** (and **n**) with **g** (and **l**) or with **j** (and **p**) sequences.

Low conversion data

Values for the relative intensities for each of these six signals are gathered in *Table 1* for copolymers obtained at low conversions.

The probability of formation of the different MMA centred triads and their configuration as a function of the molar fraction of MMA in the feed (f_{MMA}) have been calculated from the reactivity ratio values, r_1 and r_2, with the co-isotacticity coefficients for homopolymer and copolymer, σ_{11} and $\sigma_{12} = \sigma_{21} = \sigma$, as defined by Bovey and Tiers[16] and Coleman[17]. The value of $\sigma_{11} = 0.23$ was calculated from the α-methyl resonance signal of PMMA (see *Figure 2*). This value for σ_{11} is slightly higher than that estimated by Mori *et al.*[8] for PMMA at 25°C ($\sigma_{11} = 0.20$). However, the difference may lie within experimental error. Moreover the difference may be explained in terms of the temperature. It is known that σ depends on temperature but not on the solvent and the initiator[18].

By considering Bernoullian statistics, we have calculated the co-isotacticity coefficient for the copolymers, σ, from the n.m.r. spectra of the copolymers. From the values given above and by means of a trial-and-error method we have estimated $\sigma = 0.5$. This value agrees with the results obtained by Mori *et al.*[8] for high conversion MMA–MA copolymers obtained at 70–80°C by emulsion copolymerization using benzoyl peroxide initiator.

Therefore theoretical triad values were calculated for the copolymer, assuming $r_1 = 2.36$, $r_2 = 0.42$, $\sigma_{11} = 0.23$ and $\sigma = \sigma_{12} = \sigma_{21} = 0.5$ as a function of f_{MMA}.

The changes in the triad compositions from *Table 1* at low conversion with 12 initial values of f_{MMA} are shown in *Figure 3* together with the variation calculated using the above parameters and the terminal model. The good agreement between experimental and calculated values shown in *Figure 3* reveals two facts: (i) that the assignments for triads in the α-methyl region for copolymers of MMA–MA are correct; and (ii) that the terminal model provides a very good fit to our experimental data.

Although the formation probability for the triad **e** (and **k**) is the same as that for the **f** (and **n**) triad, we emphasize that when $\sigma = 0.5$, the same occurs for **j** (and **p**) and **g** (and **l**). For this reason, and similarly to the findings of other authors[8], it has not been possible to make a definitive assignment for the β_4 (0.99) and β_5 (0.92) ppm signals caused due to the overlapping of **v** triads with **g**

Table 1 Comonomer feed composition (f_{MMA}), copolymer composition (F_{MMA}) and values for the relative intensities of the ^{1}H n.m.r. signals in the α-methyl region for the copolymerization at low conversion, expressed as mole fraction of MMA, for the copolymerization of MMA and MA at 50°C in benzene at two different overall monomer concentrations

Sample	[MMA]+[MA] (mol l^{-1})	Monomer feed (f_{MMA})	Conversion (%)	Copolymer composition (F_{MMA})	β_1	β_2	β_3	β_4	β_5	β_6
1	3.0	0.54_8	4.7	0.75_0	0.03_3	0.04_5	0.19_7	0.20_1	0.22_3	0.30_1
2	3.0	0.49_6	8.2	0.68_9	0.03_3	0.05_1	0.18_6	0.21_3	0.24_6	0.27_1
3	3.0	0.45_2	5.0	0.66_0	0.03_2	0.05_1	0.18_5	0.22_7	0.26_4	0.24_1
4	3.0	0.30_0	3.8	0.50_2	–	0.09_8	0.22_8	0.28_1	0.25_7	0.13_6
5	3.0	0.19_9	8.1	0.35_9	–	0.13_9	0.28_0	0.29_5	0.20_2	0.08_4
6	3.0	0.17_5	7.8	0.30_1	–	0.16_3	0.29_3	0.28_9	0.18_5	0.07_0
7	3.0	0.14_2	7.9	0.32_9	–	0.16_0	0.31_0	0.29_5	0.17_5	0.06_0
8	5.0	0.54_9	2.6	0.73_5	0.03_4	0.05_4	0.20_4	0.19_2	0.21_6	0.30_0
9	5.0	0.49_7	3.0	0.67_5	–	0.05_9	0.20_2	0.21_8	0.24_4	0.27_7
10	5.0	0.30_2	2.9	0.47_9	–	0.12_5	0.23_6	0.26_6	0.22_4	0.14_9
11	5.0	0.19_9	2.8	0.40_4	–	0.14_4	0.27_7	0.29_2	0.20_3	0.08_4
12	5.0	0.17_7	3.0	0.32_9	–	0.15_0	0.28_8	0.28_7	0.21_0	0.06_4

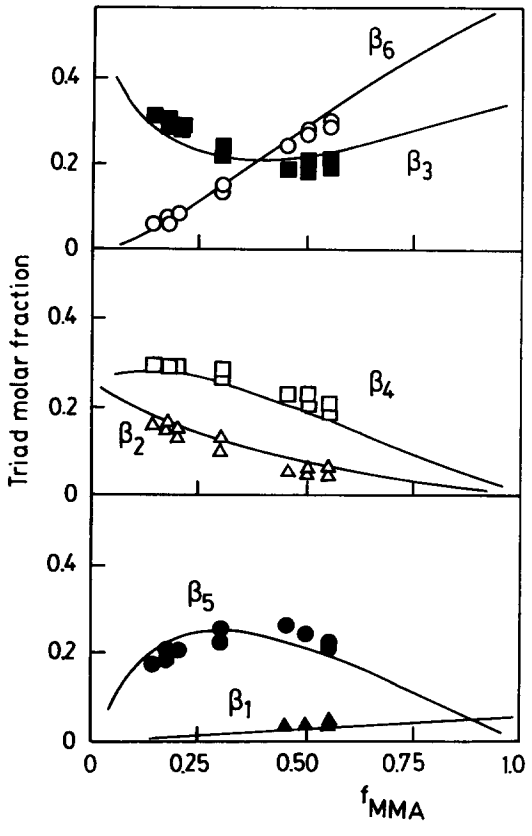

Figure 3 Dependence of relative intensities of the chemical shifts in the α-methyl region as a function of the MMA mole fraction in the feed, f_{MMA}. Solid and open symbols represent experimental data (see *Table 1*). The full lines are based and drawn on calculations made using the values of r_1, r_2, σ_{11} and $\sigma=\sigma_{12}=\sigma_{21}$ given in the text

Table 2 Assignments for triads in the α-methyl region of the ^{1}H n.m.r. spectra for copolymers of MMA and MA. See *Figure 1* for triads centred with an MMA unit configuration

Peak	δ (ppm)	Assignment of triads
β_1	1.21	**a**
β_2	1.14	**e**(and **k**)+**q**
β_3	1.04	**b**(and **c**)+**t**(and **u**)
β_4	0.99	**v**+**g**(and **l**) or **v**+**j**(and **p**)
β_5	0.92	**f**(and **n**)+**j**(and **p**) or **f**(and **n**)+**g**(and **l**)
β_6	0.88	**d**

(and **l**), respectively. All the assignments performed are shown schematically in *Table 2*.

A closer inspection of the experimental data of *Table 1*, plotted in *Figure 3*, shows that experimental values obtained at 3 and 5 mol l^{-1} are approximately equal. We conclude that the sequence distribution and the stereoregularity of the monomers in the polymeric chain are independent of the overall concentration of monomers in the feed, when the polymerization is carried out at low conversions. In other words they do not change upon dilution. This confirms once again that the terminal model provides an extremely good fit for data obtained at different overall monomer concentrations.

For this reason, with the reactivity ratios, the co-isotacticity parameter and the sequence distribution assignments previously described, we have extended our study to examine copolymerization to higher conversions. Since the terminal model describes the copolymer compositions and triad molar fraction at low conversions, it has been employed to describe the changes in copolymer stereochemical composition as a function of increasing conversion.

High conversion data

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 this changes with increasing conversion. For these reasons, during copolymerization reactions at high conversion there may be a distribution of compositions and a change of monomeric sequence distribution along the main chain; it may be necessary to describe these variations precisely to solve problems associated with the industrial production of certain types of copolymers and their final products.

Changes with conversion in the stereochemical copolymer composition and MMA centred triad fractions have been measured for copolymers obtained at various MMA/MA comonomer feed compositions (70/30, 50/50 and 30/70) and two overall monomer concentrations (3 and 5 mol l^{-1}) respectively.

The ^{1}H n.m.r. spectra of MMA/MA copolymers obtained at an initial monomer feed composition of 70/30 show six signals in the α-methyl region. They agree with those observed for copolymers obtained at low degree of conversion. They have been assigned in the same manner as indicated above for the low conversion copolymers.

MMA contents of 50 and 30% in the feed yield copolymers whose spectra show only five well differentiated signals. It has not been possible to detect the signal appearing at 1.21 ppm which we assigned previously to the **111** isotactic (**a**) triad. This can be explained easily if we keep in mind that when the initial concentration of monomer MMA decreases, the weight of this triad is approximately equal to or lower than 2% of the whole. This percentage cannot be estimated very precisely since it lies within the margin of error of the experimental technique.

The experimental relative intensities (triad molar fraction) are given in *Tables 3*, *4* and *5* as a function of the conversion for each of the three different compositions studied in the present paper.

The effect of conversion on the stereochemical composition of the copolymer chain has been approximated by a step function. 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 interval to yield integrated values.

Comparison between theoretical and experimental values are shown in *Figures 4*, *5* and *6*. The slight deviations observed between experimental and predicted values are expected because of errors in calculating MMA–MA centred triads due to the overlap between different n.m.r. signals. Notwithstanding the experimental difficulties, it is clear from *Figures 4*, *5* and *6* that the experimental and predicted values agree very closely.

The good correlation found for values of the composition as well as of the sequence distribution as a function of conversion means that a unique model is able to describe the copolymerization of the MMA–MA system over the whole range of conversions. In other

Table 3 Comonomer feed composition (f_{MMA}), copolymer composition (F_{MMA}) and values for the relative intensities of the ^1H n.m.r. signals in the α-methyl region for the copolymerization at high conversion, expressed as mole fraction of MMA, for the copolymerization of MMA and MA at 50°C in benzene at two different overall monomer concentrations (MMA/MA = 70/30)

Sample	[MMA]+[MA] (mol l^{-1})	Monomer feed (f_{MMA})	Conversion (%)	Copolymer composition (F_{MMA})	β_1	β_2	β_3	β_4	β_5	β_6
13	3.0	0.70	12.1	0.87_0	0.04_1	0.05_2	0.22_5	0.14_7	0.18_3	0.35_3
14	3.0	0.70	22.1	0.84_0	0.03_5	0.04_8	0.22_0	0.15_2	0.18_3	0.36_2
15	3.0	0.70	31.0	0.84_6	0.03_5	0.04_6	0.22_1	0.14_5	0.18_1	0.37_2
16	3.0	0.70	39.4	0.84_7	0.03_9	0.05_2	0.21_8	0.15_7	0.18_9	0.34_5
17	3.0	0.70	58.1	0.78_0	0.04_3	0.05_7	0.21_2	0.16_4	0.19_9	0.32_6
18	3.0	0.70	65.8	0.79_3	0.04_1	0.05_6	0.21_3	0.16_7	0.19_9	0.32_4
19	5.0	0.70	9.2	0.81_6	0.03_9	0.04_9	0.22_2	0.14_9	0.17_7	0.36_4
20	5.0	0.70	18.5	0.82_5	0.03_6	0.04_5	0.21_4	0.16_2	0.17_8	0.36_5
21	5.0	0.70	30.3	0.82_8	0.03_2	0.04_3	0.21_3	0.16_8	0.18_0	0.36_4
22	5.0	0.70	40.1	0.81_9	0.03_8	0.05_0	0.21_8	0.16_0	0.18_9	0.34_5
23	5.0	0.70	62.4	0.80_0	0.03_6	0.05_2	0.21_5	0.16_5	0.19_7	0.33_5
24	5.0	0.70	70.8	0.78_7	0.03_4	0.04_7	0.20_5	0.17_4	0.19_8	0.34_2
25	5.0	0.70	75.6	0.77_0	0.04_2	0.05_7	0.20_9	0.17_6	0.20_3	0.31_3
26	5.0	0.70	87.2	0.75_0	0.03_8	0.05_2	0.20_5	0.18_5	0.20_4	0.31_7

Table 4 Comonomer feed composition (f_{MMA}), copolymer composition (F_{MMA}) and values for the relative intensities of the ^1H n.m.r. signals in the α-methyl region for the copolymerization at high conversion, expressed as mole fraction of MMA, for the copolymerization of MMA and MA at 50°C in benzene at two different overall monomer concentrations (MMA/MA = 50/50)

Sample	[MMA]+[MA] (mol l^{-1})	Monomer feed (f_{MMA})	Conversion (%)	Copolymer composition (F_{MMA})	β_1	β_2	β_3	β_4	β_5	β_6
27	3.0	0.50	13.1	0.69_0	–	0.06_4	0.20_1	0.21_7	0.25_4	0.26_4
28	3.0	0.50	24.8	0.66_0	–	0.06_3	0.20_3	0.22_3	0.25_8	0.25_3
29	3.0	0.50	36.1	0.67_1	–	0.06_2	0.19_9	0.22_9	0.25_9	0.25_1
30	3.0	0.50	45.3	0.66_0	–	0.08_0	0.20_7	0.23_5	0.25_5	0.22_3
31	3.0	0.50	67.0	0.57_0	–	0.08_6	0.22_5	0.24_5	0.25_2	0.19_2
32	3.0	0.50	68.4	0.61_5	–	0.09_3	0.21_3	0.24_6	0.23_5	0.21_3
33	3.0	0.50	78.5	0.56_2	–	0.08_7	0.21_4	0.24_8	0.25_4	0.19_7
34	5.0	0.50	9.5	0.69_0	–	0.07_0	0.20_3	0.21_9	0.24_6	0.26_2
35	5.0	0.50	17.1	0.67_5	–	0.05_8	0.18_8	0.22_5	0.24_7	0.28_2
36	5.0	0.50	25.1	0.69_5	–	0.07_0	0.20_1	0.22_5	0.25_0	0.25_4
37	5.0	0.50	32.9	0.61_5	–	0.06_0	0.20_9	0.23_2	0.24_5	0.25_4
38	5.0	0.50	73.5	0.61_5	–	0.08_5	0.22_3	0.25_2	0.24_2	0.19_8
39	5.0	0.50	90.0	0.60_0	–	0.08_4	0.21_1	0.25_6	0.23_8	0.21_1
40	5.0	0.50	93.6	0.55_6	–	0.09_8	0.22_4	0.25_3	0.23_9	0.18_6

Table 5 Comonomer feed composition (f_{MMA}), copolymer composition (F_{MMA}) and values for the relative intensities of the ^1H n.m.r. signals in the α-methyl region for the copolymerization at high conversion, expressed as mole fraction of MMA, for the copolymerization of MMA and MA at 50°C in benzene at two different overall monomer concentrations (MMA/MA = 30/70)

Sample	[MMA]+[MA] (mol l^{-1})	Monomer feed (f_{MMA})	Conversion (%)	Copolymer composition (F_{MMA})	β_1	β_2	β_3	β_4	β_5	β_6
41	3.0	0.30	12.7	0.49_5	–	0.12_0	0.24_2	0.27_1	0.24_4	0.12_3
42	3.0	0.30	26.4	0.51_0	–	0.12_7	0.23_7	0.27_1	0.22_7	0.13_8
43	3.0	0.30	38.1	0.46_5	–	0.13_2	0.25_0	0.27_3	0.22_6	0.11_9
44	3.0	0.30	89.4	0.32_9	–	0.15_7	0.29_1	0.27_6	0.19_5	0.08_1
45	5.0	0.30	16.1	0.45_6	–	0.11_5	0.24_1	0.27_6	0.24_0	0.12_8
46	5.0	0.30	17.6	0.47_5	–	0.12_4	0.24_8	0.27_3	0.23_4	0.12_1
47	5.0	0.30	32.0	0.43_5	–	0.12_4	0.24_7	0.27_4	0.23_1	0.12_4
48	5.0	0.30	47.6	0.45_0	–	0.13_5	0.25_7	0.27_6	0.22_6	0.10_6
49	5.0	0.30	98.7	0.31_0	–	0.15_4	0.29_2	0.27_9	0.19_0	0.08_5

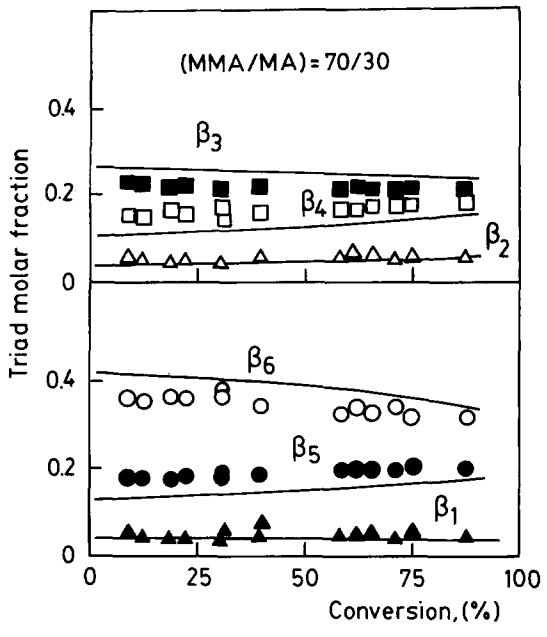

Figure 4 Dependence of relative intensities of the chemical shifts in the α-methyl region as a function of conversion (%). Solid and open symbols represent experimental data (see *Table 3*) (MMA/MA = 70/30). The full lines are based and drawn on calculations made using the values of r_1, r_2, σ_{11} and $\sigma = \sigma_{12} = \sigma_{21}$ given in the text

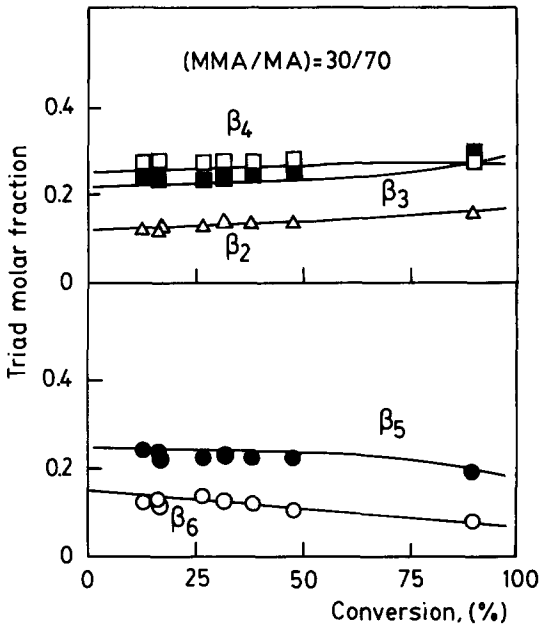

Figure 6 Dependence of relative intensities of the chemical shifts in the α-methyl region as a function of conversion (%). Solid and open symbols represent experimental data (see *Table 5*) (MMA/MA = 30/70). The full lines are based and drawn on calculations made using the values of r_1, r_2, σ_{11} and $\sigma = \sigma_{12} = \sigma_{21}$ given in the text

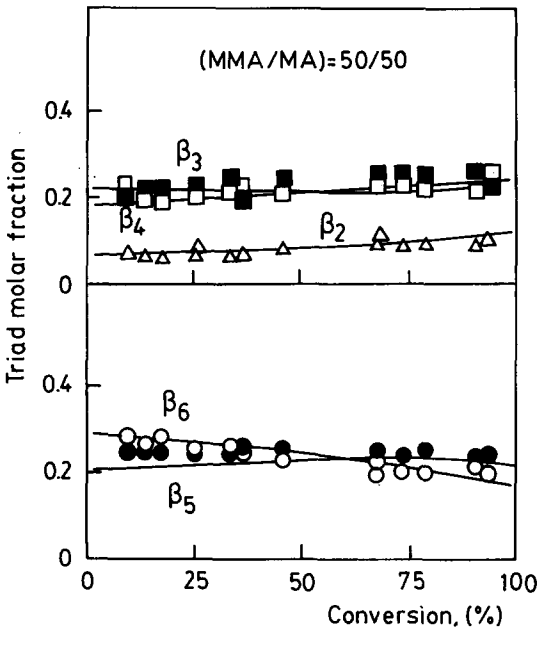

Figure 5 Dependence of relative intensities of the chemical shifts in the α-methyl region as a function of conversion (%). Solid and open symbols represent experimental data (see *Table 4*) (MMA/MA = 50/50). The full lines are based and drawn on calculations made using the values of r_1, r_2, σ_{11} and $\sigma = \sigma_{12} = \sigma_{21}$ given in the text

words, the copolymerization theory of Mayo and Lewis and the associated composition equation holds within the whole range of copolymer conversions.

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