Determination of Compositional, Configurational Sequences in High Conversion Methyl Methacrylate-Methacrylic Acid Emulsion Copolymers Using a Rapid and Selective Counting Procedure

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ABSTRACT

High conversion methyl methacrylate (MMA)-methacrylic acid (MA) copolymers prepared by two different emulsion polymerization processes were characterized in terms of composition and sequence distribution by ^{1}H- and ^{13}C-NMR, taking into account the conversion effect. A rapid and selective counting procedure for calculating the compositional configurational pentads (512 values) in these copolymers is described. From this counting procedure and using the Klesper's assignment of the 18 peaks observed in the ^{13}C-NMR carbonyl resonance spectrum of the copolymers, a relatively good agreement was found between the

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calculated and experimental fractions of each peak intensity.
Moreover, this study allows differences in compositional homo-
geneity to be characterized as a function of the nature of the
emulsion polymerization process.

INTRODUCTION

Any polymer structural characterization needs the determination
of configurational and compositional sequence distribution, and NMR
spectroscopic methods (mostly ^{13}C) were found to be very powerful
and useful techniques to derive this information [1]. In some cases
the structural analysis of radical initiated copolymers is relatively
simple, but in many other cases, evaluation of polymer sequence
distributions was very complex and puzzling because of a lack in
resolution and consequent overlapping of many (compositional-
configurational) sequence resonances.

Moreover, theoretical predictions of sequence distribution are of
critical importance for comparison with a given model and for testing
the structural assignments. Since radical initiated copolymerizations
give rise to random copolymers, the most frequently used statistical
methods to calculate sequence distribution are Bernoullian and first-
order Markovian. Based on those methods, many efforts have been
developed in this field. Price [2] proposed computer programs for
calculating sequences and stereosequences in polymers and copoly-
mers. Harwood [3] described flexible Fortran programs for calcu-
lating most features of copolymer structure, and applicable to
instantaneous and high conversion copolymers. Ito et al. [4] also
worked out a general procedure to calculate sequence and stereo-
sequence distributions in copolymers.

As a part of a program to investigate alkali-swelling behavior as
a function of the copolymer composition and the emulsion polymeriza-
tion process, methyl methacrylate (MMA)-methacrylic acid (MA)
emulsion copolymers were characterized in terms of composition
and sequence distribution through ^{1}H- and ^{13}C-NMR analyses. The
complexity of the structural analysis of these copolymers was particu-
larly pointed out by Klesper [5, 6] who examined the sequence distri-
bution in low conversion methyl methacrylate-methacrylic acid co-
polymers prepared in dioxane solution. In terms of compositional
effects, only triads showed an influence on chemical shift. The
authors, by a rigorous study of the strong configurational pentad
influence on the chemical shift, were able to propose a complete
assignment of the resonances in terms of configurational pentad-
compositional triad sequences.

In fact, due to the high number of sequences (theoretically 512
for a kinetic chain in the case of pentad sequences of a binary copoly-
mer, taking into account both compositional and configurational

aspects), each of the 18 peaks obtained through copolymer spectra analysis includes different types of compositional triads and, for each of them, part of the corresponding configurational pentads. As reported by Klesper, the experimental relative fraction of each peak intensity was found to be in good agreement with calculated values derived from statistical models.

In this work our main objective was to obtain a rapid and precise theoretical prediction of the compositional-configurational pentad distribution (512 values) and to confirm the experimental values obtained through ^{13}C-NMR analysis based on Klesper's assignment. A convenient microcomputer program, easily handled, has been worked out for selecting the compositional-configurational pentads and directly to obtain in a very short time the relative fraction of each peak intensity. Moreover, since reactivity ratios of this sytem in emulsion conditions (r_{MMA} = 0.6; r_{MA} = 1.55) were found to be notably different from those given by Klesper (r_{MMA} = r_{MA} = 0.98) [6], and because copolymerizations were carried out up to high conversion, the simulation program was also set up in order to account for the conversion effect.

EXPERIMENTAL

Copolymer Synthesis

Methyl methacrylate-methacrylic acid copolymer latexes were prepared by emulsion polymerization using either the conventional batch technique or a semicontinuous method. Polymerization procedures and recipes have been described in detail elsewhere [8].

Copolymer Structure Characterization by ^{13}C-NMR Spectroscopy

Polymer samples, as obtained after latex flocculation and further drying, were analyzed as 15 to 20 wt% solutions in deuterated pyridine d_5 using hexamethyldisiloxane (HMDS) as internal reference. Fourier transform (FT) ^{13}C-NMR spectra were recorded at 120°C using a Bruker WP 80 Spectrometer (20.1 MHz for ^{13}C). The pulse angle was 90°.

Spectral Examination

As shown in Figs. 1 and 2, the carbonyl carbon resonances of the copolymers are very complex, as reported by Klesper [6]. It is worth recalling that the low-field group of signals (179.5-182 ppm)
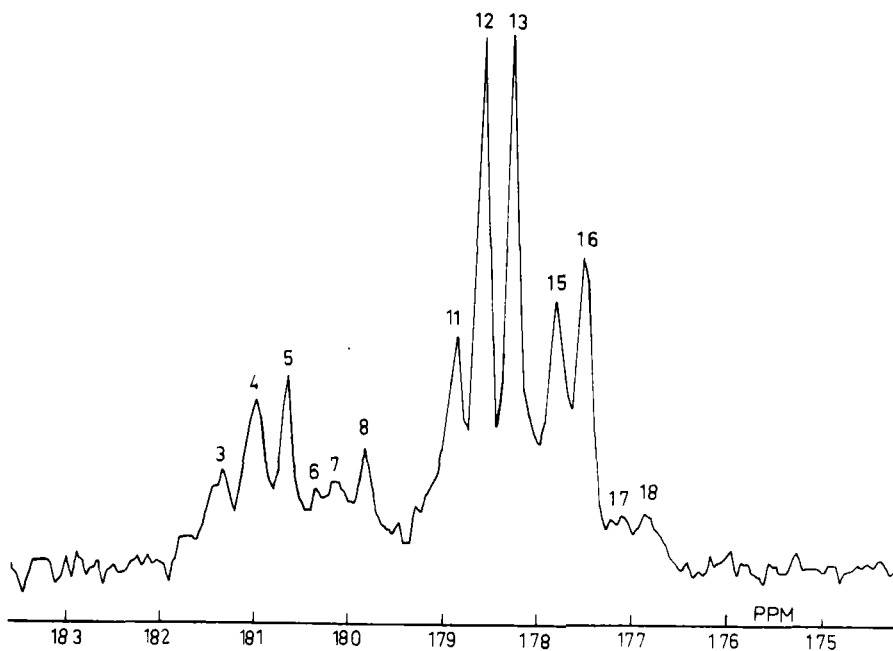
FIG. 1. ^{13}C-NMR spectra of carbon carbonyl resonances of emulsion (MMA-MA) batch copolymer with 0.718 mol% MMA.

corresponds to the carbonyl carbon resonances of methacrylic acid, and the high field one to the carbonyl resonances of methyl methacrylate (176.5-179 ppm). Based on Klesper's assignment, the carbonyl carbon resonances of the copolymer's spectrum were interpreted in terms of 18 signals as indicated in Figs. 1 and 2. The peak area separation was carried out using a Dupont Curve Resolver, and area measurements were made with a planimeter.

SIMULATION PROGRAM

The 18 peaks are composed of structural sequences which are listed in Table 1 taken from Klesper's work [6]. MMA and MA are schematically designated by A and B, respectively. The theoretical prediction needs the calculation of the relative fraction of each compositional configurational pentad, and the following procedure was used.
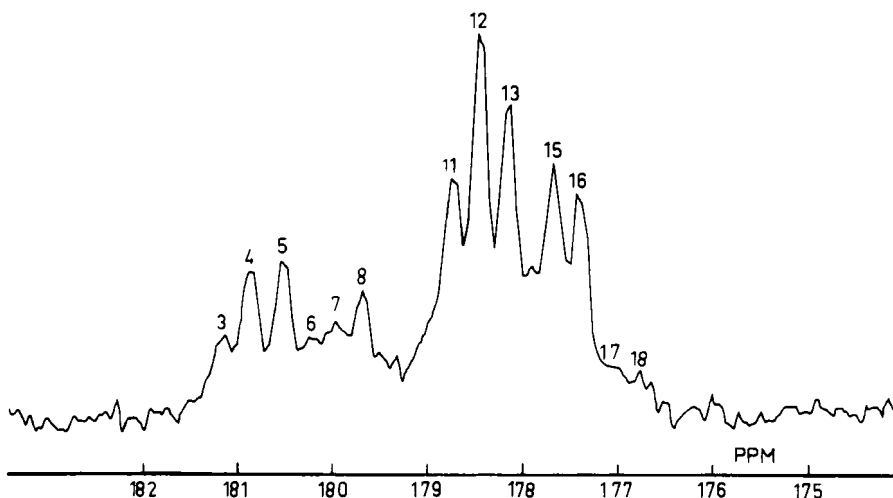
FIG. 2. ^{13}C-NMR spectra of carbon carbonyl resonances of emulsion (MMA-MA) semicontinuous copolymer with 0.718 mol% MMA.

Principle

In a copolymer chain, any structural sequence (pentad in our case) can be rigorously described by two terms: a compositional sequence term (pentad, in our case, say ABABB, where A and B are two different monomer units) and a configurational term (say iisi, where i and s correspond, respectively, to the isotactic and the syndiotactic placement of two adjacent monomer units).

With the notation (A ≡ 1, B ≡ 0) and (i ≡ 1, s ≡ 0), each pentad is defined by a couple of binary numbers (2). For example, to the following pentad defined by the two terms (ABABB, iisi) are associated the following couple of binary numbers (10100, 1101) which correspond to a couple of decimal numbers (20, 13). Hence, any compositional-configurational pentad is defined by a couple of decimal numbers such as (C, T), where the compositional term C is in the range (0-31) and the configurational term T is in the range (0-15). Conversely, varying C and T in these respective ranges allows one to generate any kind of the 512 expected pentad sequences (512 = 32 × 16). For example, let us consider the couple (20, 13) and calculate the compositional and configurational probability contributions (P_C and P_T) on the basis of the first-order Markovian and Bernoullian statistic models.

TABLE 1. Collection of All Possible Pentad-Triad Sequences According to the Number of Group Sequences According to Compositional Triads (rows) and Number of Group Sequences (columns) [6] [a]

Triad	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
BBB	issi	isss*, issi	ssss, issi		iisi*, sisi*, iiss*, siss*		iiii, iiis*, siis											
ABB*		issi	isss, sssi	ssss		iisi, sisi, isii, isis, ssii, ssis	iiss, siss		iiii, iiis, siii, siis									
ABA			issi	isss*	ssss		iisi*, sisi*	iiss*, siss*			iiii, iiis*, siis							
AAB*										issi	isss, sssi	ssss		iisi, sisi, isii, isis	iiss, siss, ssii, ssis		iiii, iiis, siii, siis	
BAB									issi	isss*	ssss		iisi*, sisi*	iiss*, siss*		iiii, iiis*, siis		
AAA											issi	isss*	ssss		iisi*, sisi*	iiss*, siss*		iiii, iiis*, siis

[a] MMA (methyl methacrylate) and MA (methacrylic acid) are designed by A and B, respectively. The pentad triad sequences are written with the compositional triad on top of the configurational pentad, thus $\overset{AAA}{iiii}$ represents $_iA_iA_iA_i$. A plus sign indicates that the corresponding sequence may be reversed without changing the chemical shift, e.g., $\overset{AAA}{iiis^+}$ means that $_iA_iA_iA_s$ has the same shift as $_sA_iA_iA_i$, and $\overset{AAB^+}{iiis^+}$ represents $_iA_iA_iB_s$ and $_sB_iA_iA_i$. The vertical lines represent the separation of the resonance areas of neighboring groups of strongly overlapping pentad-triad sequences (without regard to the chemical shift scale).

$C = 20 \equiv 10100 \equiv ABABB \qquad P_C = (A)\, p_{ab} \cdot p_{ba} \cdot p_{ab} \cdot p_{ab} p_{bb} \cdot$

$T = 13 \equiv 1101 \equiv iisi \qquad P_T = \sigma_{ab} \cdot \sigma_{ba} \cdot (1 - \sigma_{ab}) \cdot \sigma_{bb}$

where, for example, p_{ab} is the conditional probability that a "b" unit follows an "a" unit, and, for example, σ_{ab} is the conditional probability that a compositional diad "ab" has the "ii" configuration.

Finally, the molar fraction of the pentad sequence corresponding to the couple (20, 13) is equal to

$$P_C \cdot P_T = (A)(p_{ab})^2 \cdot p_{ba} \cdot p_{bb} \sigma_{ab} \cdot \sigma_{ba} \cdot (1 - \sigma_{ab}) \cdot \sigma_{bb} \cdot$$

This is the basic framework of the simulation program which was built up to count and calculate the different pentad sequences, all these "time-consuming" operations being easily computed.

Two further improvements were introduced in the computer program in the form of subroutines:

A "decoding" subroutine allowing the sequences associated with each of the 18 signals of the copolymer spectrum to be read. Then it was possible to directly calculate the relative contribution of each peak intensity.

A "conversion" subroutine which allows us to account for the drift of the comonomer composition in the feed (because of difference in reactivity ratios) as polymerization proceeds.

A schematic organigram of the computer program is presented as Scheme 1.

List of structural sequences associated to a given NMR ray according to Klesper's assignment

↓

Binary and decimal associated numbers

↓

Monomer composition at time t

↓

Calculation of relative fraction of peak area

Plots of instantaneous and average fractions versus conversion

Monomer composition variation at (t + Δt) based on Lewis-Mayo equation
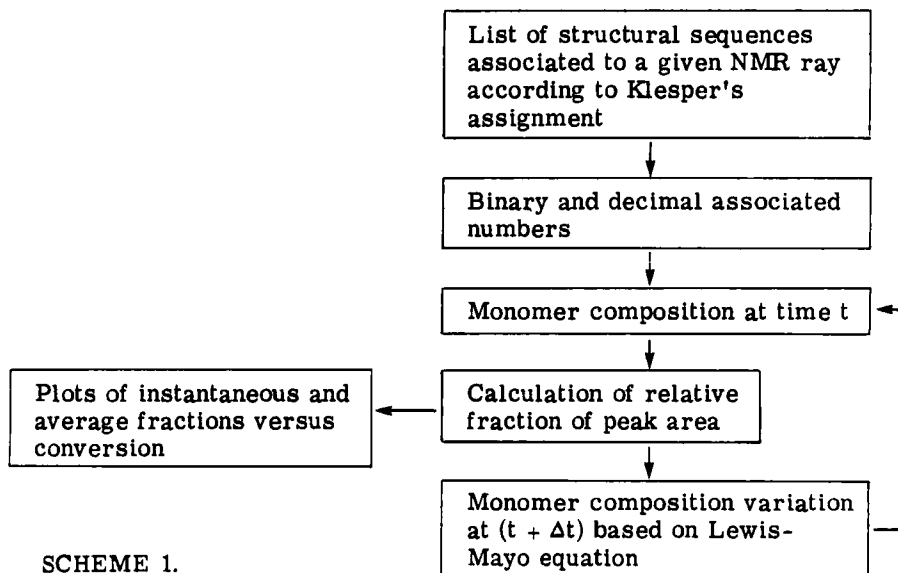
SCHEME 1.

This simulation program, run on a Hewlett-Packard (HP 9825 A) microcomputer, allows rapid delivery of a plot of the relative fraction of peak area versus conversion.

Calculation of Conditional Probabilities

These calculations were done for methyl methacrylate (MMA)-methacrylic acid (MA) copolymers.

Conditional probabilities related to the compositional term of the pentad sequences were calculated using reactivity ratios determined in another study [7]: $r_{MMA} = 0.6$, $r_{MA} = 1.55$.

It is interesting to note that these values, different from those generally obtained in solution conditions [11], were found to be very close to the values corresponding to bulk conditions ($r_{MMA} = 0.6$, $r_{MA} = 1.60$) [12].

Regarding the configurational probabilities, the values estimated by Klesper [9, 10] were used:

$$\sigma_{(MMA - MMA)} = \sigma_{(MA - MA)} = 0.20$$

$$\sigma_{(MMA - MA)} + \sigma_{(MA - MMA)} = 0.392$$

$$\sigma_{(MMA - MA)} \times \sigma_{(MA - MMA)} = 0.37$$

RESULTS AND DISCUSSION

From the carbon carbonyl resonances of the different copolymer spectra (see the example described in Figs. 1 and 2), it was first possible to derive the relative fractional intensity of each of the 18 peaks. Using the simulation program, the corresponding calculated values were obtained as a function of comonomer mixture composition and conversion. For comparison, all the results are summarized in Table 2 for three various compositions. It is worth noting that relatively good agreement between experimental and calculated values (corresponding to the conversion where polymerizations are stopped, i.e., 95%) was obtained, regardless of the comonomer mixture composition.

From differences reported for each composition, it appears that the average discrepancy is approximately 10% which is within the experimental errors of the planimetric measurements. Some exceptions have to be pointed out: abnormal differences in some cases are probably due to bad resolution of the corresponding signals in the

TABLE 2. Comparison of Experimental and Calculated Relative Spectral Areas of Groups of Configurational Pentad-Compositional Triad Sequences in the Carbonyl ^{13}C-NMR Resonance of Methyl Methacrylate (MMA)-Methacrylic Acid (MA) Emulsion Copolymers

Peak no.	Mole fraction MMA in copolymers								
	0.718			0.773			0.884		
	Expt	Calc	Δ%	Expt	Calc	Δ%	Expt	Calc	Δ%
1 } 2 }	0.014	0.014	0	-	0.004	-	-	-	-
3	0.040	0.034	15	0.023	0.024	4.3	0.020	0.008	60
4	0.068	0.070	2.9	0.055	0.052	5.4	0.032	0.028	12.5
5	0.064	0.072	12.5	0.060	0.061	1.7	0.041	0.038	7.3
6	0.022	0.020	9.1	0.020	0.017	15.0	-	0.004	-
7	0.032	0.028	12.5	0.021	0.023	9.5	0.019	0.011	42
8	0.048	0.044	8.3	0.040	0.040	0.0	0.027	0.027	00
9	0.017	0.005	70.0	0.007	0.004	43	-	-	-
10	0.025	0.020	20.0	0.034	0.016	53	0.038	0.007	-
11	0.076	0.083	9.2	0.059	0.075	27.1	0.078	0.051	34.6
12	0.158	0.187	18.3	0.162	0.190	17.3	0.180	0.211	18.3
13	0.160	0.162	1.2	0.224	0.195	12.9	0.262	0.285	8.8
14	0.041	0.040	2.4	0.038	0.034	10.5	0.034	0.016	50
15	0.085	0.076	10.0	0.100	0.078	22.0	0.100	0.077	23
16	0.097	0.101	4.1	0.117	0.121	8.5	0.151	0.177	17.2
17	0.033	0.013	60.0	0.014	0.012	14.3	0.000	0.008	-
18	0.020	0.015	25.0	0.024	0.022	8.3	0.018	0.027	50

copolymer spectra (see, for example, Peaks 6, 7, 9, 17 in Fig. 1). Errors larger than the average are also observed for Peaks 12 and 13, which are difficult to measure accurately.

However, such results confirmed that the structural interpretation proposed by Klesper is also valid for these emulsion copolymers which are of the random type.

From the computer program it is particularly interesting to check which among the 18 signals of the spectra are predominantly representative of a given sequence. We investigated signals containing

TABLE 3. Contribution of Long Monomer Sequence Structures in Calculated Spectral Areas of Peaks 3, 5, 12, 13, and 16 for Different Comonomer Composition in Initial Monomer Feed (MMA mol%)[a]

Peak no.	0.718			0.773			0.884		
	Expt	Calc	(BBB) (1) or (AAA) (2) contribution	Expt	Calc	(BBB) (1) or (AAA) (2) contribution	Expt	Calc	(BBB) (1) or (AAA) (2) contribution
3	0.040	0.034	0.112 (1)	0.023	0.024	0.006 (1)	0.020	0.008	0.0008 (1)
5	0.064	0.072	0.0087 (1)	0.060	0.061	0.0046 (1)	0.041	0.038	0.0007 (1)
12	0.158	0.187	0.0736 (2)	0.162	0.190	0.091 (2)	0.180	0.211	0.138 (2)
13	0.160	0.162	0.157 (2)	0.224	0.195	0.194 (2)	0.262	0.285	0.285 (2)
16	0.097	0.101	0.097 (2)	0.117	0.121	0.120 (2)	0.151	0.177	0.177 (2)

[a]B = methacrylic acid; A = methyl methacrylate.

TABLE 4. Effect of Conversion on the Calculated Peak Area Fractions in the Carbonyl ^{13}C-NMR Resonance Spectrum of a 0.773/0.227 Methyl Methacrylate-Methacrylic Acid Emulsion Copolymer

	Relative spectral areas			
	Calculated			
Peak no.	Initial	Final (instantaneous)	Final (average)	Experimental, final
1 $\}$ 2	-	-	0.005	-
3	0.042	0.0015	0.024	0.023
4	0.082	0.0084	0.052	0.055
5	0.079	0.013	0.061	0.060
6	0.028	0.0005	0.017	0.020
7	0.034	0.003	0.023	0.021
8	0.046	0.010	0.040	0.040
9	-	-	0.004	0.007
10	0.024	0.0018	0.016	0.034
11	0.094	0.035	0.076	0.059
12	0.174	0.211	0.193	0.162
13	0.118	0.332	0.195	0.224
14	0.049	0.005	0.034	0.038
15	0.077	0.080	0.078	0.100
16	0.084	0.240	0.127	0.117
17	0.015	0.003	0.0120	0.014
18	0.014	0.043	0.022	0.024

contributions from BBB or AAA triads to derive information about the lengths of monomer sequences in the copolymers. Peaks 3, 5 (for BBB triads) and 12, 13, 16 (for AAA triads) were chosen. Table 3 shows the relative contribution of these triads compared to experimental and calculated spectral areas (BBB or AAA).

From this table it is clear that Peaks 13 and 16 correspond to a major contribution of AAA sequences (almost 100%) in the whole range of compositions we investigated. Hence, these two peaks are very useful to characterize the long methyl methacrylate sequences in the copolymers. On the contrary, Peaks 3 and 5 are not representative
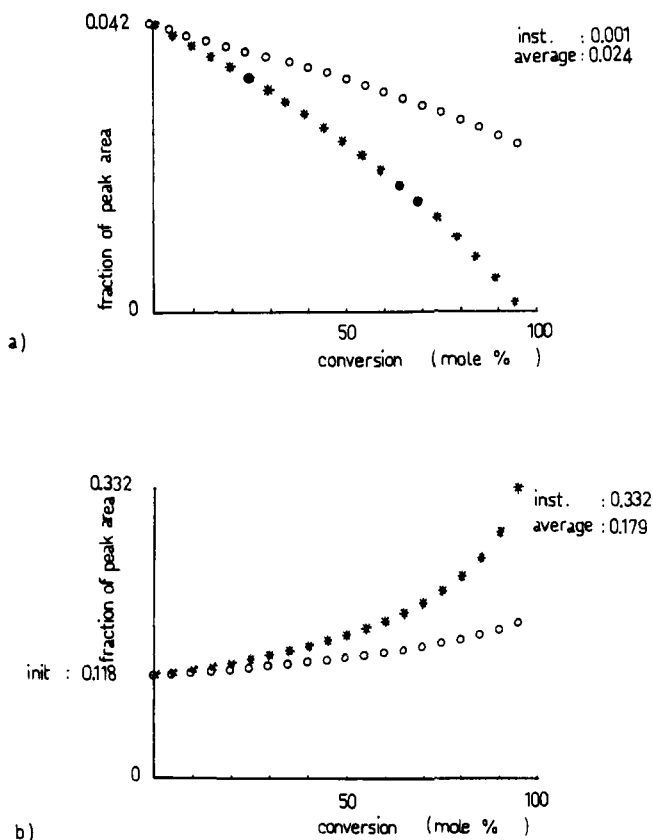
FIG. 3. Relative fraction of peak area from the ^{13}C-NMR spectrum versus conversion in MMA-MA emulsion copolymers (0.773 mol% MMA). a) Peak 3; b) Peak 13. (o) Fraction corresponding to the average contribution of the group of structures. (*) Fraction corresponding to the instantaneous contribution of the group of structures.

of the methacrylic acid long sequences (for the given comonomer composition rich in MMA), the MA unit being mostly incorporated in isolated and dyad sequences.

Because MMA-MA emulsion copolymers were obtained at high conversion, another interesting feature may be investigated from this study: the conversion effect due to the expected drift in the comonomer mixture composition. The simulation program provides the instantaneous and average relative fractions at any conversion and for all compositions. An example is given in Table 4, which summarizes initial relative fractions (at 0% conversion) as well as final

instantaneous and final average values. For many peaks, even though some compensation may occur due to the simultaneous contribution of different structural sequences into one peak, large discrepancies are calculated between initial and final average values (for example, Peaks 3, 4, 5, 6, 7, 13, 14, 16). Final instantaneous fractions are also of special interest. They really pointed out the importance of the drift at 95% conversion. Figure 3 gives a good illustration of that phenomenon. It represents the relative fraction variations of the peak intensity for Peaks 3 and 13. As conversion increases, this fraction continuously decreases for the former and increases for the latter.

Since the peak areas, as already explained, correspond to the contribution of many different structural sequences, it is not possible to interpret the results in terms of monomer sequence length. However, from the sequence assignment listed in Table 1, peak area 13 is a good representation of the MA triad sequences, and in a first approximation, peak area 3 is representative of the MA dyad sequence length. It is clear that, as polymerization proceeds, long MA sequence formation drops to a value close to 0, whereas long MMA sequence generation increases (see Fig. 3 and Table 4).

This is a good indication that MMA-MA emulsion batch copolymers are composed of copolymer mixtures with various copolymer compositions. Unfortunately, no experimental data were collected to confirm the effect of conversion on the structural sequence distribution in these copolymers. However, in order to obviate this heterogeneous distribution, latex copolymers were also prepared using a semicontinuous process in which the rate of monomer feed addition is much lower than the maximum rate of polymerization. Since under this condition better uniform copolymer composition is expected, structural characterization was also investigated by ^{13}C-NMR on these copolymers. Experimental results are reported in Table 5 for a 71.8 mol% MMA and compared to those related to batch copolymers. No drastic differences are displayed for the various relative spectral areas, except for Peaks 11, 12, 13, 14, which is an indication of change in the MMA sequence distribution (see also Fig. 2).

Because actual comonomer compositions at the reaction locus are not well known for the semicontinuous process, it was difficult to simulate the pentad sequence distribution for comparison with the experimental results. Moreover, mainly due to MA hydrophilicity, it seems reasonable to assume an initial batch period at the beginning of the process where polymerization occurs in the aqueous phase as well as in formed polymer particles. That causes a small drift in the copolymer composition which increases with the MA content [8] and results in a complex mixture of copolymer compositions. This mixture is probably more homogeneous than in that obtained in the batch copolymerizations. However, it must be mentioned that differences in compositional homogeneity are definitively demonstrated through the alkali swelling behavior of the copolymer latexes [7]. Indeed, the distribution of carboxyl groups in semicontinuous copolymer

TABLE 5. Comparison of Experimental and Calculated Relative
Spectral Areas of Groups of Configurational Pentad-Compositional
Triad Sequences in the Carbonyl ^{13}C-NMR Resonance of Emulsion
Methyl Methacrylate (MMA)-Methacrylic Acid (MA) Copolymer
(MMA molar fraction: 0.718)

Relative spectral areas of group of sequences	Batch		Semicontinuous experimental
	Experimental	Calculated	
1	0.014	0.006	-
2		0.008	-
3	0.040	0.034	0.042
4	0.068	0.070	0.065
5	0.064	0.072	0.074
6	0.022	0.020	0.037
7	0.032	0.028	0.035
8	0.048	0.044	0.058
9	0.017	0.005	-
10	0.025	0.019	-
11	0.076	0.083	0.111
12	0.158	0.187	0.140
13	0.160	0.160	0.140
14	0.041	0.040	0.055
15	0.085	0.076	0.099
16	0.097	0.101	0.098
17	0.033	0.013	0.029
18	0.020	0.015	0.017

latexes was found to be more uniform than in batch copolymer latexes.
That corroborates the differences in compositional sequence distri-
bution as qualitatively suggested by ^{13}C-NMR investigation.

CONCLUSION

It was first demonstrated that the microstructure of high conver-
sion methyl methacrylate-methacrylic acid emulsion copolymers

could be rapidly simulated by using the rapid procedure described in this work. It can be used to count and calculate any kind of structure in a random copolymer. Relatively good agreement was found with the theoretical prediction based on ^{13}C-NMR spectra analysis of the copolymers.

However, in this particular case, the configurational pentad effects add to the compositional triad effects and cause overlapping. This is why the calculated fraction of a given compositional triad can only be compared to the experimental relative areas in the signals where the contribution of this type of triad is predominant.

This investigation also appears quite useful in reflecting differences in compositional homogeneity as a function of copolymer composition, conversion, and effect of emulsion polymerization process.

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