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Sequence distribution of the methyl methacrylate–ethyl acrylate copolymer by ^{13}C n.m.r. spectroscopy

Giao Nguyen, Daniel Nicole* and Michel Swistek
Université de Nancy I, Laboratoire d'Etude des Systèmes Organiques et Colloïdaux, UA CNRS 406, BP 239, F-54506 Vandoeuvre-lès-Nancy Cedex, France

and Marek Matlengiewicz
Polish Academy of Sciences, Institute of Coal Chemistry, Sowińskiego 5, PL-44100 Gliwice, Poland

and Bernard Wiegert
Centre de recherche ELF-ATOCHEM, BP 1005, 57501 Saint Avold Cedex, France
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A method for characterizing triad and pentad distribution by ^{13}C n.m.r. spectroscopy has been developed and applied for an acrylate–methacrylate copolymer for which the chemical shifts of the homopolymers were sufficiently separated to observe mixed sequences up to pentads. Calculation of the intensity was performed applying Markov–Bernoulli statistics while the chemical shift for each sequence was calculated by a separately developed incremental method. Based on these data, the cabonyl signal was simulated yielding very good agreement at the triad level and satisfactory agreement at the pentad level. © 1997 Elsevier Science Ltd.

(Keywords: PMMA/PEA; ^{13}C n.m.r; microstructure)

INTRODUCTION

In our recent work[1] we have developed a method for characterizing the microstructure of acrylate–methacrylate copolymers by computer aided analysis of the carbonyl signal of its ^{13}C n.m.r. spectrum. For this type of copolymer the chemical shifts of the carbonyl signal of the respective homopolymers are sufficiently separated to offer well resolved signals of mixed sequences up to pentads. The method is related to those described by Cheng[2–4] and is based on the calculation of line intensities for different configurational and compositional sequences (according to Bernoulli or Markov distribution) followed by attribution of the lines and simulation of the carbonyl signal using the Lorentzian line-shape model to obtain the smallest difference between the experimental and calculated spectra[2–4]. The first results obtained for an equimolar industrial sample of the methyl methacrylate–ethyl acrylate copolymer (50/50), PMMA/PEA, prepared by radical copolymerization performed until complete consumption of the comonomers, have shown that unequivocal assignment of the lines, even at the triad level, cannot be done correctly based only on the intensity data. Three other samples of this copolymer with different composition and small conversion ratio have been prepared in order to verify the distribution of the compositional sequences by the calculation based on the copolymerization equation. Then, a method of incremental calculations of the chemical shifts have been developed taking into account previous positive results for an acrylic copolymer[5,6] and for an aromatic copolyterephthalate[7]. It requires *a priori* assignment of the symmetric sequences for the initial simulation. However, there could be discrepancies if the assignment is not exact, as it takes place in the case of sequences of small intensity. These assignments can be modified in order to obtain a better agreement between the experimental and theoretical spectra.

EXPERIMENTAL

The industrial samples of the methyl methacrylate–ethyl acrylate copolymer, PMMA/PEA, were synthesized at the Centre de Recherches Elf-Atochem (Carling, France), by free radical copolymerization. The comonomers taken in respective weight ratio, were poured into butan-2-one to obtain 40 wt% mixture and then were placed in a double-coated reactor under nitrogen. The mixture was heated up to 78°C and azobisisobutyronitrile (AIBN) was added as radical initiator (0.5 wt% with respect to the total solution). The reactions were conducted up to about 10% conversions and then the reaction mixture was poured into a cold container (0°C) and monomethylether of hydroquinone (EMHQ) was added as stabilizer. A small part of this mixture was separated and after evaporation

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* To whom correspondence should be addressed

of the solvent under vacuum the conversion of the reaction was determined. In this way three samples of the copolymer were synthesized for the initial content of methyl methacrylate in the liquid phase equal to $F_M = 0.30$, 0.50 and 0.70 which correspond to the conversions of 9.61, 13.10 and 11.47, respectively.

The 100 MHz ^{13}C n.m.r. spectra of the PMMA/PEA copolymer were recorded on a Bruker AM 400 spectrometer for 5 wt% solutions in $CDCl_3$ at 40°C. To avoid the nuclear Overhauser effect a gated decoupling sequence was applied and a reasonable signal to noise ratio was obtained after 1200 scans. In order to obtain quantitative spectra the time delay between the pulses has to be at least five times greater than the longest relaxation time[8]. Because, $T_{1(C=O)} \approx 3$–6 s, the delay was set to 30 s. The quantitative nature of the spectra was verified by comparison of the intensities for the C=O signal to the sum of those for α-CH_3 (in the methyl methacrylate units) and OCH_2 (in the ethyl acrylate units) which yielded very good agreement. The composition of the copolymer was calculated from the ratio between the intensity of the O–CH_3 signal of ethyl acrylate and intensity of the carbonyl signals: $f_M = 0.50$, 0.65 and 0.81 for the copolymers corresponding to $F_M = 0.30$, 0.50 and 0.70, respectively. Knowing the conversion ratios, the composition of the copolymers was verified by titration of the residual monomer and by gas chromatography (with internal reference and correction factors) by precipitating the copolymers in the mixture methanol–water (60/40). The difference between the values of f_M obtained by these two methods did not exceed 5%.

CALCULATION OF THE LINE INTENSITIES

The intensities of configurational triads were calculated according to Bernoulli distribution. The values of the isotacticity parameters $\sigma_{MM} = 0.218$ for the methyl methacrylate units (M) and $\sigma_{EE} = 0.345$ for the ethyl acrylate units (E) were calculated from the spectra of respective homopolymers, while the coisotacticity parameters, postulated to be indistinguishable, $\sigma_{ME} = \sigma_{EM} = \sigma^{*}$[9,10], were assumed to be equal to 0.41, according to San Román[11]. Initially, the intensities of compositional triads were calculated from reactivity ratios, assuming that for low conversions (~ 10%) the concentration of each monomer in the liquid phase was equal to its initial concentration[12]

$$P(M/E) = \frac{1}{1 + r_M(F_M/F_E)} \tag{1}$$

$$P(E/M) = \frac{1}{1 + r_E(F_E/F_M)} \tag{2}$$

where $P(M/E)$ and $P(E/M)$ are the conditional probabilities. Since, by definition

$$P(\overline{EM}) = \frac{P(E/M)P(E)}{0.5} \tag{3}$$

and

$$P(\overline{ME}) = \frac{P(M/E)P(M)}{0.5} \tag{4}$$

where $P(\overline{EM}) = P(\overline{ME}) = P(ME) + P(EM)$, it can be written that

$$\frac{P(E)}{P(M)} = \frac{1 + r_E(F_E/F_M)}{1 + r_M(F_M/F_E)} \tag{5}$$

This formula is similar to the copolymerization equation with $P(M) = d[M]$, i.e., monomer consumption in the liquid phase. Upon application of this equation to the copolymer with $F_M = 0.30$, where $P(M) \approx P(E) = 0.50$, the ratio r_M/r_E is found to be 5.44, while it is equal to 16.38 (or 8.46) if we take the reactivity ratios given in the literature: $r_M = 2.13$, $r_E = 0.13$[11] (or $r_M = 2.03$, $r_E = 0.24$[13]) even though these radical copolymers were obtained in different experimental conditions. This difference indicates that even for conversion of 10% it is not justified to apply the composition of the copolymer formed instead of differential values for the monomers consumed. However, since the equality $P(\overline{EM}) = P(\overline{ME})$ should always be obeyed it means that equation (5) leads to *apparent*-reactivity ratios corresponding to the given conversion. So, for $P(M) \approx P(E) = 0.50$, $r'_M = 5.44r'_E$. A second relation can be derived for copolymer of $F_M = 0.50$ where the conversion is slightly different than previously: $r'_M = 2r'_E + 1$, hence $r'_M = 1.57$ and $r'_E = 0.29$. These values make it possible to recalculate the conditional probabilities and then the sequence probability for $P(\overline{ME})$ [equations (1)–(4)]. The values obtained in this way are practically identical (*Table 1*) with those determined by n.m.r. utilizing the β-CH_2 signals[1] yielding the information on distribution of even compositional sequences according to the method described previously for this copolymer. It was therefore possible to verify the validity of this method for the third sample of $F_M = 0.70$. Taking the previous values of r'_M and r'_E we

Table 1 Average composition and conditional probabilities for the free radical copolymerization of ethyl acrylate with methyl methacrylate

Copolymers	f_M		$P(MM)$	$P(\overline{ME})$	$P(EE)$
$F_M = 0.700$	RMN:	0.810	0.629	0.345	0.026
	Calculated:	0.806	0.634	0.345	0.021
$F_M = 0.500$	RMN:	0.650	0.400	0.500	0.100
	Calculated:	0.670	0.410	0.510	0.070
$F_M = 0.300$	RMN:	0.505	0.220	0.560	0.220
	Calculated:	0.500	0.200	0.600	0.200

Table 2 Triad probabilities of the ethyl acrylate–methyl methacrylate copolymer

PMAM/PAE	70/30	50/50	30/70
$P(EmEmE)$	0.014	0.335	1.252
$P(\overline{EmErE})$	0.053	1.286	4.811
$P(ErErE)$	0.051	1.236	4.624
$P(\overline{MmEmE})$	0.388	2.005	3.456
$P(\overline{MmErE})$	0.745	3.853	6.641
$P(MmEmM)$	2.71	3.002	2.385
$P(EmMmE)$	0.636	1.616	2.337
$P(\overline{MrEmE})$	0.558	2.885	4.972
$P(\overline{MrErE})$	1.072	5.544	9.557
$P(\overline{EmMrE})$	1.829	4.652	6.728
$P(\overline{MmMmE})$	2.458	2.756	2.256
$P(ErMrE)$	1.316	3.347	4.841
$P(\overline{MmErM})$	7.798	8.639	6.864
$P(\overline{MmMrE})$	3.537	3.967	3.247
$P(MmMmM)$	2.377	1.175	0.544
$P(MrErM)$	5.611	6.216	4.938
$P(\overline{MrMmE})$	8.792	9.859	8.071
$P(\overline{MrMrE})$	12.651	14.187	11.614
$P(\overline{MmMrM})$	17.001	8.406	3.895
$P(MrMrM)$	30.403	15.034	6.967

arrive at the ratio $P(\mathrm{E})/P(\mathrm{M}) = 0.241$ with respect to 0.248 found by n.m.r. Based on these values the probabilities of 20 triads (*Table 2*) and 272 pentads were calculated for the three copolymer samples.

RESULTS AND DISCUSSION

Simulation according to the literature assignment

In our previous paper[1] we have tried to obtain the best fit of the PMMA/PEA carbonyl signal simulated only on the basis of intensity calculation (1st order Markov–Bernoulli model for distribution of compositional and configurational sequences, respectively) and assignment of triads according to literature data[7,11]. Nevertheless, this simulation was not satisfactory, mainly for the outermost symmetric sequences MrMrM and EEE, which was due to the synthesis method applied (100% conversion). The simulation performed here in the same way for the three samples but using the modified method of calculation for $P(\mathrm{M/E})$ and $P(\mathrm{E/M})$ shows that intensities of the homotriads mentioned above are in good agreement with experimental ones (*Figure 1*). However, it is not the case for the signal at 175.25 ppm which was assigned to triads $\overline{\mathrm{MmMrE}}$ and $\overline{\mathrm{MmMmE}}$. This difference indicates that there is a possibility of different assignment, hence the attribution of chemical shifts to respective sequences, cannot be based only on their intensity.

Incremental calculation of line positions

If we assume that the attribution of the major lines is correct (*Figure 1c*) it can be observed that for M-centred triads of the same configuration, exchange of the outermost monomers leads to a constant shift of its position. For example for the MrMrM triad, replacement of the outer M by E shifts the signal to higher field, with $\Delta\delta = \delta_{\mathrm{MrMrE}} - \delta_{\mathrm{MrMrM}} = -1.09$ ppm. Replacement of the second outer M by E leads to a further shift of the

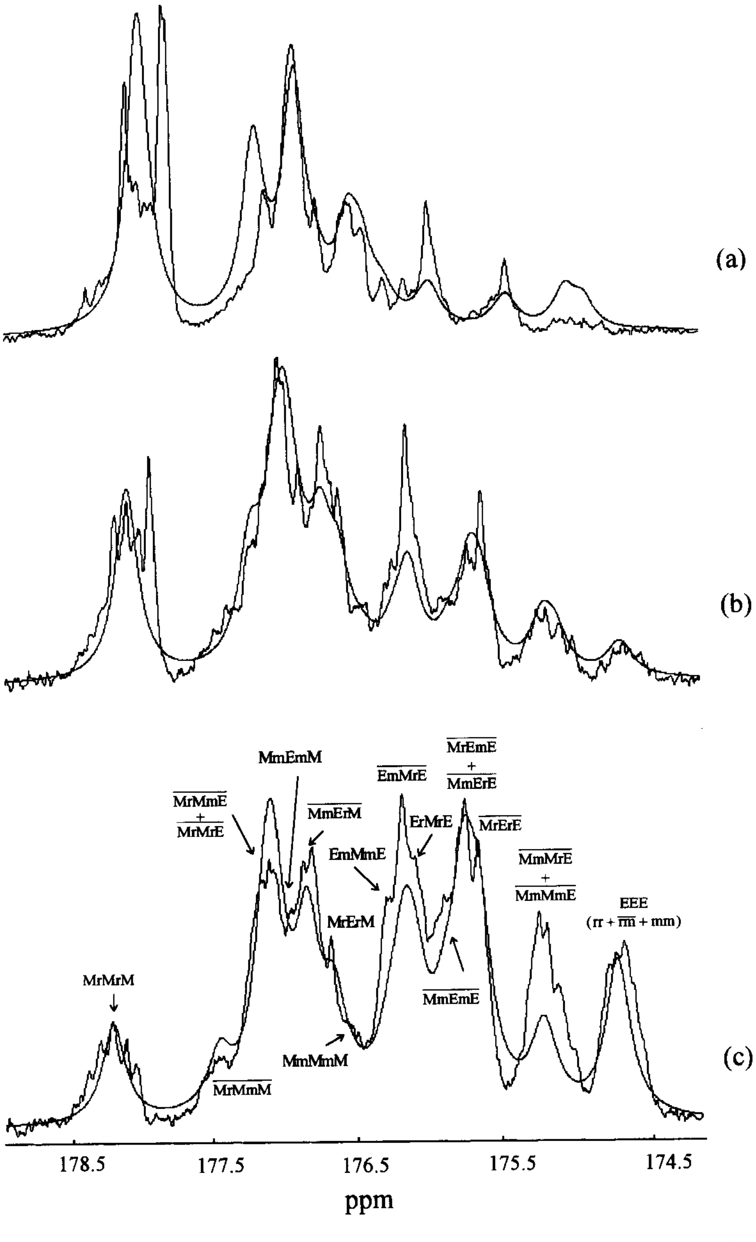

Figure 1 Experimental and simulated spectra for three samples of the PMMA/PEA: 70/30 (a), 50/50 (b), 30/70 (c) applying the literature assignment of the 20 triads[1]

same order and in the same direction, i.e. $\Delta\delta = \delta_{\mathrm{ErMrE}} - \delta_{\mathrm{MrMrE}} = -1.02\,\mathrm{ppm}$. If we consider the E-centred triads we can observe the same regularity but with the direction inversed. When we observe the change from ErErE triad to the ErErM one and then to MrErM, it can be seen that a comparable shift can be observed, $\Delta\delta = \delta_{\mathrm{MrErE}} - \delta_{\mathrm{ErErE}} = +0.96\,\mathrm{ppm}$ and $\Delta\delta = \delta_{\mathrm{MrErM}} - \delta_{\mathrm{MrErE}} = +1.04\,\mathrm{ppm}$, respectively. These observations lead to a conclusion that the chemical shifts of certain triads can be written in an incremental manner, for example

$$\delta_{\mathrm{MrMrM}} = \delta_{0\mathrm{M}} + 2\alpha^{\mathrm{M}}_{\mathrm{rM}} \quad \text{or} \quad \alpha^{\mathrm{M}}_{\mathrm{rM}} = \frac{\delta_{\mathrm{MrMrM}} - \delta_{0\mathrm{M}}}{2}$$

and

$$\delta_{\mathrm{ErMrE}} = \delta_{0\mathrm{M}} + 2\alpha^{\mathrm{M}}_{\mathrm{rE}} \quad \text{or} \quad \alpha^{\mathrm{M}}_{\mathrm{rE}} = \frac{\delta_{\mathrm{ErMrE}} - \delta_{0\mathrm{M}}}{2}$$

where $\delta_{0\mathrm{M}}$ is the chemical shift of the carbonyl signal for the PMMA homopolymer (regarded as a position of the M-centred sequence without any influence of its neighbours). Therefore, the measurement of different α increments requires initial assignment of the symmetrical triads (*Figure 2a*). There are eight triads symmetrical with respect to both their configuration and composition, i.e. four triads of mixed composition (EmMmE, ErMrE, MmEmM and MrErM) and four homo-triads (MrMrM, MmMmM, ErErE and EmEmE); the chemical shifts of the latter being well known from the spectra of the respective homopolymers. The chemical shifts of the remaining 12 triads can be obtained as a linear combination of the increments:

$$\delta_{\mathrm{MrMrE}} = \delta_{0\mathrm{M}} + \alpha^{\mathrm{M}}_{\mathrm{rM}} + \alpha^{\mathrm{M}}_{\mathrm{rE}}$$

It can be noted that even if the values of α^{M} depend on $\delta_{0\mathrm{M}}$, the chemical shifts of asymmetric sequence like MrMrE are independent of this parameter, hence it can be chosen arbitrarily but it is reasonable to assume it as the chemical shift of the methyl methacrylate carbonyl signal, corresponding approximately to triads MrMmM, i.e. $\delta_{0\mathrm{M}} = 177.42\,\mathrm{ppm}$. Respective value for the E-centred sequences was assumed to be

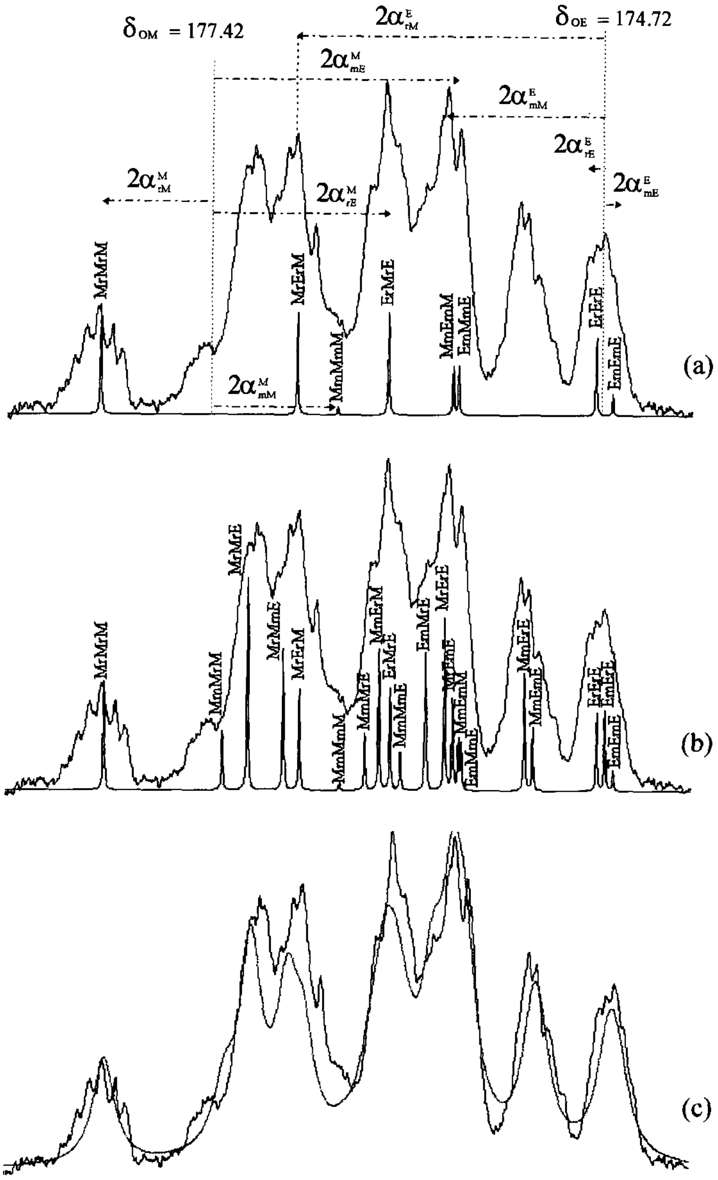

Figure 2 Principle of the calculation of increments α (a) and spectrum simulation utilizing linewidth of 1 Hz (b) and 18 Hz (c) for each triad

$\delta_{0E} = 174.72\,\text{ppm}$, as a centre of the carbonyl signal for the PEA homopolymer.

For the triads of lower intensity there are some anomalies hence their assignment may be uncertain. For example, substitution of one outer unit M by E in sequence MmMmM leads to a decrease of the chemical shift for this sequence, while the exchange of the second outer M unit by E shifts this sequence towards the

Table 3 α and β increments for the calculation of the triad and pentad chemical shifts

$\alpha_{\mathrm{rM}}^{\mathrm{M}}$	$\alpha_{\mathrm{mM}}^{\mathrm{M}}$	$\alpha_{\mathrm{mE}}^{\mathrm{E}}$	$\alpha_{\mathrm{rE}}^{\mathrm{E}}$	$\alpha_{\mathrm{mM}}^{\mathrm{E}}$	$\alpha_{\mathrm{rM}}^{\mathrm{E}}$	$\alpha_{\mathrm{mE}}^{\mathrm{M}}$	$\alpha_{\mathrm{rE}}^{\mathrm{M}}$
0.405	**−0.435**	**−0.038**	**0.020**	**0.490**	**1.060**	**−0.870**	**−0.615**
$\alpha_{\mathrm{rM}}^{\mathrm{1M}}$	$\alpha_{\mathrm{mM}}^{\mathrm{1M}}$					$\alpha_{\mathrm{mE}}^{\mathrm{1M}}$	$\alpha_{\mathrm{rE}}^{\mathrm{1M}}$
0.315	**−0.330**					**−0.835**	**−0.570**
$\beta_{\mathrm{rMrM}}^{\mathrm{M}}$	$\beta_{\mathrm{mMrM}}^{\mathrm{M}}$	$\beta_{\mathrm{mErM}}^{\mathrm{E}}$	$\beta_{\mathrm{rErM}}^{\mathrm{E}}$	$\beta_{\mathrm{mMrM}}^{\mathrm{E}}$	$\beta_{\mathrm{rMrM}}^{\mathrm{E}}$	$\beta_{\mathrm{mErM}}^{\mathrm{M}}$	$\beta_{\mathrm{rErM}}^{\mathrm{M}}$
−0.075	0.081	0.007	−0.004	−0.091	−0.197	0.162	0.114
$\beta_{\mathrm{rMrE}}^{\mathrm{M}}$	$\beta_{\mathrm{mMrE}}^{\mathrm{M}}$	$\beta_{\mathrm{mErE}}^{\mathrm{E}}$	$\beta_{\mathrm{rErE}}^{\mathrm{E}}$	$\beta_{\mathrm{mMrE}}^{\mathrm{E}}$	$\beta_{\mathrm{rMrE}}^{\mathrm{E}}$	$\beta_{\mathrm{mErE}}^{\mathrm{M}}$	$\beta_{\mathrm{rErE}}^{\mathrm{M}}$
0.010	−0.011	−0.0009	0.0004	0.012	0.026	−0.021	−0.015
$\beta_{\mathrm{rMmM}}^{\mathrm{M}}$	$\beta_{\mathrm{mMmM}}^{\mathrm{M}}$	$\beta_{\mathrm{mEmM}}^{\mathrm{E}}$	$\beta_{\mathrm{rEmM}}^{\mathrm{E}}$	$\beta_{\mathrm{mMmM}}^{\mathrm{E}}$	$\beta_{\mathrm{rMmM}}^{\mathrm{E}}$	$\beta_{\mathrm{mEmM}}^{\mathrm{M}}$	$\beta_{\mathrm{rEmM}}^{\mathrm{M}}$
0.179	−0.193	−0.017	0.009	0.217	0.470	−0.385	−0.272
$\beta_{\mathrm{rMmE}}^{\mathrm{M}}$	$\beta_{\mathrm{mMmE}}^{\mathrm{M}}$	$\beta_{\mathrm{mEmE}}^{\mathrm{E}}$	$\beta_{\mathrm{rEmE}}^{\mathrm{E}}$	$\beta_{\mathrm{mMmE}}^{\mathrm{E}}$	$\beta_{\mathrm{rMmE}}^{\mathrm{E}}$	$\beta_{\mathrm{mEmE}}^{\mathrm{M}}$	$\beta_{\mathrm{rEmE}}^{\mathrm{M}}$
0.100	−0.108	−0.009	0.005	0.120	0.263	−0.216	−0.152

The numerical values obtained experimentally are indicated in bold

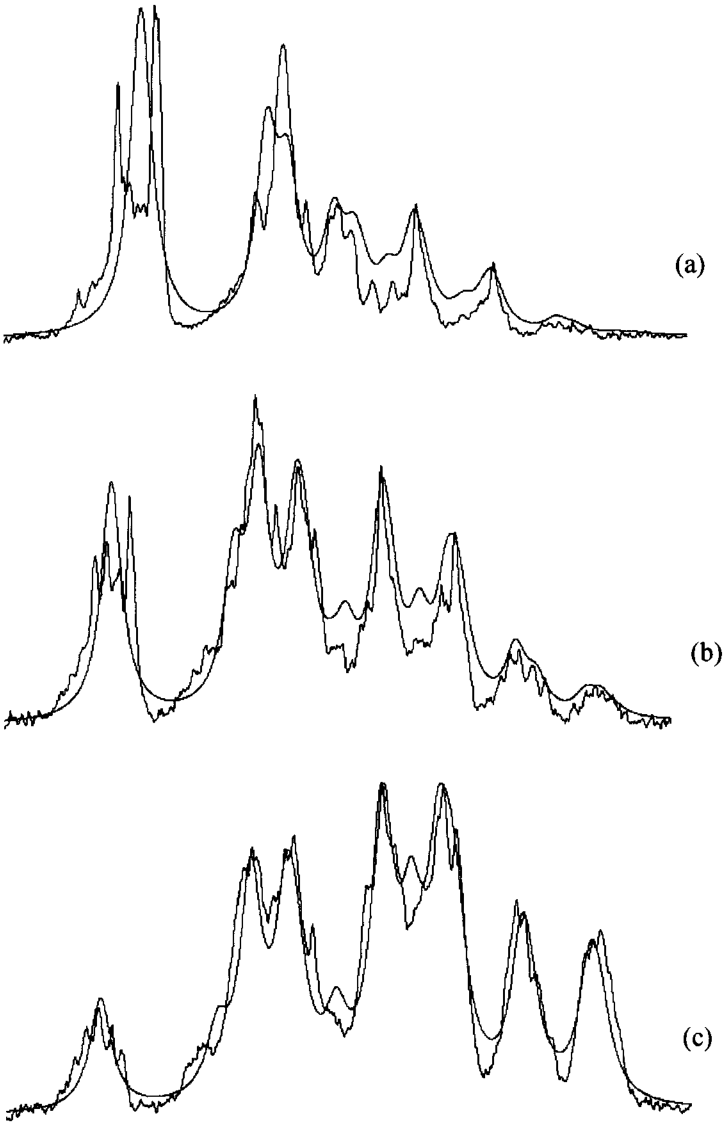

Figure 3 Simulation of the spectra for three samples of the PMMA/PEA copolymer applying modified α increments (α^1): 70/30 (a), 50/50 (b) and 30/70 (c)

opposite direction.

$$\delta_{\mathrm{MmMmE}} - \delta_{\mathrm{MmMmM}} = -1.30\,\mathrm{ppm}$$

and

$$\delta_{\mathrm{EmMmE}} - \delta_{\mathrm{MmMmE}} = +0.88\,\mathrm{ppm}$$

If we assume that this behaviour does not come from the incremental method itself it can be supposed that the triads EmMmE and $\overline{\mathrm{MmMmE}}$ were incorrectly attributed. This conclusion is not surprising since it was already observed that the band at 175.25 ppm, which contains in particular the $\overline{\mathrm{MmMmE}}$ triad was imperfectly simulated. On the other hand, this M-centred sequence containing only one E unit should be situated near MmMmM triad than the EEE one. Based on these observations we have proposed to assign this band to $\overline{\mathrm{EmEmM}}$ and $\overline{\mathrm{ErEmM}}$ triads which should be situated close to each other since the configurational effects are rather small for the PEA homopolymer. The same relationship was observed for the two following triads $\overline{\mathrm{ErErM}}$ and $\overline{\mathrm{EmErM}}$ at 175.74 and 175.80 ppm, respectively. These corrections made it possible to calculate the chemical shifts of all the 20 triads (*Table 3*) based on the values of the eight independent α increments. Simulation of the spectrum for the copolymer of $f = 0.50$ (*Figures 2b* and *2c*) revealed however that certain sequences, mainly in the methacrylic part, i.e. $\overline{\mathrm{MrMrE}}$ or $\overline{\mathrm{MrMmE}}$, exhibit small deviations of the chemical shifts with respect to the experimental values. This is probably due to the fact that each α increment is a weight mean between the increment for the substitution of the first unit (α_1) and that for the second substitution (α_2), which are not exactly identical. This difference should be essentially observed for PMMA due to the steric interactions of methyl group as it was already observed in other systems. These interactions are responsible for the failure of the γ-*gauche*[14–16] calculations for predicting the chemical shifts for stereosequences of PMMA. If we introduce such corrected values for the triads containing only one diad MM ($\alpha_{r\mathrm{M}}^{1\mathrm{M}} = 0.315$ and $\alpha_{\mathrm{mM}}^{1\mathrm{M}} = -0.330$) and even for one diad EM ($\alpha_{\mathrm{mE}}^{1\mathrm{M}} = -0.835$ and $\alpha_{r\mathrm{E}}^{1\mathrm{M}} = -0.570$) the

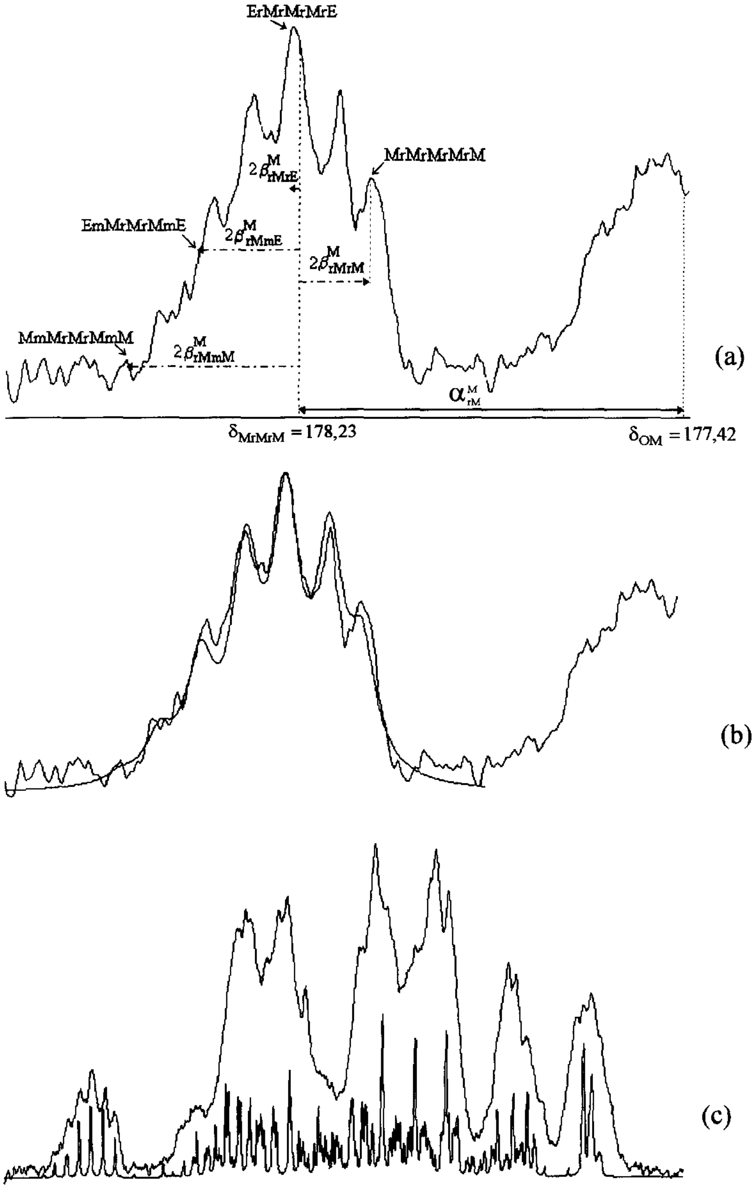

Figure 4 Principle of the calculation of increments β for the MrMrM triad (a) and spectrum simulation using linewidth of 7 Hz for each pentad (b). Spectrum simulation of 272 pentads with a linewidth of 1 Hz (c)

chemical shifts obtained are in very good agreement with the experimental ones (*Figure 3*).

Determination of the 272 pentads was accomplished by means of β-increments, representing the contribution of the comonomers in β-position with respect to the monomer unit considered. These increments can be derived from the signal of the MrMrM triad, where the pentad splitting was the most pronounced. The chemical shift of each pentad can be therefore written in the following form, for example

$$\delta_{\mathrm{MmMrMrMmM}} = \delta_{0\mathrm{M}} + 2\alpha^{\mathrm{M}}_{\mathrm{rM}} + 2\beta^{\mathrm{M}}_{\mathrm{rMmM}}$$

$$\delta_{\mathrm{EmMrMrMrE}} = \delta_{0\mathrm{M}} + 2\alpha^{\mathrm{M}}_{\mathrm{rM}} + \beta^{\mathrm{M}}_{\mathrm{rMrE}} + \beta^{\mathrm{M}}_{\mathrm{rMmE}}$$

As in the case of α increments, the four independent β-increments can be calculated from the symmetrical sequences (*Figure 4a*, *Table 3*), the two of pure methacrylate composition being calculated from the methyl methacrylate signal and the two other being found considering the intensities of the respective lines according to the Markov–Bernoulli statistics. Based on these β-increments the positions of the next six pentads can be calculated. Very good agreement between this simulated and experimental spectrum indicates reliability of this incremental approach (*Figure 4b*). The results concerning the signal of MrMrM triad show that if we compare the absolute values, the β-increments are about four times smaller than the respective α-increment:

$$\frac{|\beta^{\mathrm{M}}_{\mathrm{rMrM}}| + |\beta^{\mathrm{M}}_{\mathrm{rMrE}}| + |\beta^{\mathrm{M}}_{\mathrm{rMmE}}| + |\beta^{\mathrm{M}}_{\mathrm{rMmM}}|}{|\alpha^{\mathrm{M}}_{\mathrm{rM}}|} = 0.90$$

On the other hand, for the same configuration, the influence of comonomer M in β-position is always greater than that of comonomer E

$$\frac{|\beta^{\mathrm{M}}_{\mathrm{rMrM}}|}{|\beta^{\mathrm{M}}_{\mathrm{rMrE}}|} = 7.50 \quad \text{and} \quad \frac{|\beta^{\mathrm{M}}_{\mathrm{rMmM}}|}{|\beta^{\mathrm{M}}_{\mathrm{rMmE}}|} = 1.80$$

Finally, for the same compositional sequence, the influence of a comonomer in configuration *r* is smaller than that in configuration *m*

$$\frac{|\beta^{\mathrm{M}}_{\mathrm{rMrM}}|}{|\beta^{\mathrm{M}}_{\mathrm{rMmM}}|} = 0.42 \qquad \text{and} \qquad \frac{|\beta^{\mathrm{M}}_{\mathrm{rMrE}}|}{|\beta^{\mathrm{M}}_{\mathrm{rMmE}}|} = 0.10$$

The remaining β-increments cannot be measured directly, due to complexity of the middle part of the carbonyl signal where the mixed sequences occur. Therefore, in the first approximation we have used the same relations as those found previously. For example, the increments related to the MmMmM-centred pentads can be expressed with respect to only one β-increment, say $\beta^{\mathrm{M}}_{\mathrm{mMrE}}$

$$|\beta^{\mathrm{M}}_{\mathrm{mMmE}}| = 10|\beta^{\mathrm{M}}_{\mathrm{mMrE}}|; \quad |\beta^{\mathrm{M}}_{\mathrm{mMrM}}| = 7.5|\beta^{\mathrm{M}}_{\mathrm{mMrE}}|;$$

$$|\beta^{\mathrm{M}}_{\mathrm{mMmM}}| = 17.86|\beta^{\mathrm{M}}_{\mathrm{mMrE}}|$$

with $\Sigma|\beta|/|\alpha| = 0.9$.

The absolute values of the increments calculated in this way are identical, whether the signs of the previous β-values be taken into account or not, but the chemical shifts are slightly different. We have observed however that the fit is better when the signs are taken into consideration (*Figure 4c*, *Table 3*). Therefore, it is difficult to perform very good simulation based only on the small variations of increments β. Nevertheless, it is conceivable to increase the precision of the increment β determination by iterative modification of the estimated values for the mixed sequences and the study of the copolymer samples synthesized in different experimental conditions.

CONCLUSION

The methodology developed, based on one hand on the intensity calculations and on the other on incremental calculation of chemical shifts, offers very good accuracy of triad simulation and approximative simulation at the pentad level for the PMAM/PEA copolymer. The method seems to be applicable to other acrylic copolymers provided that their ^{13}C n.m.r. spectrum offers sufficient resolution of the carbonyl signal to distinguish the lines of individual pentads. The chemical shifts determined for this copolymer synthesized in a radical way may be utilized for determination of sequence distribution of the anionic copolymers where a simple statistics cannot be applied. The method seems to be quite general for determination of sequence distribution of acrylic copolymers of significant industrial importance.

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REFERENCES

1. Schmit, F., Matlengiewicz, M. and Nicole, D., *Int. J. Polymer Analysis & Characterization*, 1996, **2,** 95.
2. Cheng, H. N. and Bennett, M. A., *Anal. Chem.*, 1984, **56,** 2320.
3. Cheng, H. N., *J. Chem. Inf. Comput. Sci.*, 1987, **27,** 8.
4. Cheng, H. N., *Trends in Analytical Chemistry*, 1994, **13,** 95.
5. Johnsen, A., Klesper, E. and Wirthlin, T., *Makromol. Chem.*, 1976, **177,** 2397.
6. Klesper, E., Gronski, A. and Johnsen, A., *NMR Basic Principles and Progress*, 1971, **4,** 47.
7. Matlengiewicz, M., *Macromolecules*, 1984, **17,** 473.
8. Hatada, K., Kitayama, T., Okamoto, Y., Ohta, K., Umemura, Y. and Yuki, H., *Makromol. Chem.*, 1978, **179,** 485.
9. Yuki, H., Okamoto, Y., Shimada, Y., Ohta, K. and Hatada, H., *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17,** 1215.
10. Hatada, K., Kitayama, T., Ochi, T. and Yuki, H., *Polym. J.*, 1987, **19,** 1105.
11. San Román, J. and Valero, M., *Polymer*, 1990, **31,** 1216.
12. Klesper, E. and Sieglaff, G., *Polymer Spectroscopy*, ed. D. O. Hummel. Verlag Chemie, Weinheim, 1974.
13. Grassie, N., Torrance, B. J. D., Fortune, J. D. and Gemmeil, J. D., *Polymer*, 1965, **6,** 653.
14. Tonelli, A. E., *NMR Spectroscopy and Polymer Microstructure. The Conformational Connection.* V.C.H. Publishers, New York, 1989.
15. Tonelli, A. E., *Macromolecules*, 1991, **24,** 3065.
16. Tonelli, A. E. and Schilling, F. C., *Acc. Chem. Res.*, 1981, **14,** 233.