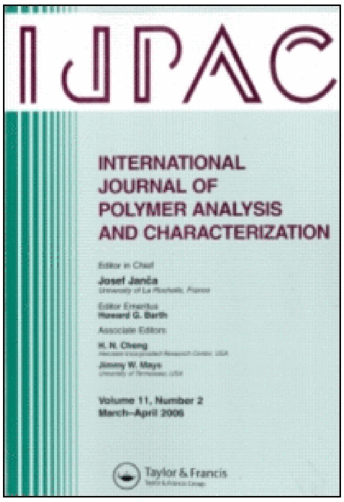

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Computer-Aided Characterization of the Microstructure of Methyl Methacrylate-Ethyl Acrylate Copolymers by ^{13}C-NMR Spectroscopy

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^{13}C-NMR spectra of methyl methacrylate-ethyl acrylate copolymers (PMMA/EA) offer sufficient resolution of the carbonyl signal to observe pentad splitting. The triad distribution can be obtained by spectral simulation, while determination of pentad distribution requires additional semi-empirical calculation of their chemical shifts.

KEY WORDS Methyl methacrylate, ethyl acrylate, copolymer, ^{13}C-NMR, microstructure

INTRODUCTION

Previously, we had developed a method of computer-aided analysis of ^{13}C-NMR spectra of complex carbo- and petrochemical mixtures [1]. The analysis was based on the comparison of chemical shifts and relative intensity data of the experimental spectrum with those collected in a library of pure compounds. In order to obtain information on individual lines in the overlapped zones of the spectrum, two deconvolution algorithms have been developed, based on the digital filtering and maximum likelihood principle [2]. In the case of the analysis of polymer chain microstructure, the problem of superposition of a multitude of lines within a narrow spectral zone is frequently encountered. Despite the increase of the magnet field strength, which provides highly resolved spectra, the problem of overlapped lines still remains since the longer sequences are accessible. The longer sequences contain the precise description of the polymer chain. Moreover, the sequence distribution is usually governed by Bernoulli or Markov statistics, hence, even partial insight into the distribution of longer sequences provided by experimental data may permit the reconstitution of the parameters for the remaining sequences and subsequent ver-

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ification of a particular model applied. The aim of this work is to show that it is possible to apply our method to the analysis of configurational-compositional sequence distribution of methyl methacrylate-ethyl acrylate copolymers.

EXPERIMENT

The industrial samples of the methyl methacrylate-ethyl acrylate copolymer (50/50), PMMA/EA, as well as the respective homopolymers: poly(methyl methacrylate), PMMA and poly(ethyl acrylate), PEA, were synthesized at the Centre de Recherches Elf-Atochem (Carling, France), using azobisisobutyronitrile (AIBN) as a radical initiator; hence, the copolymer obtained was predominantly syndiotactic. The reaction was carried out in butan-2-one at 80°C for 5 h until complete consumption of the comonomers. The solvent was then evaporated under vacuum. The molecular weight of the copolymer was measured on a GPC apparatus in terahydrofuran solution and was found to be 50,100 g/mol.

The 100 MHz ^{13}C-NMR spectra were recorded on a Bruker AM 400 spectrometer for 12 wt % (copolymer) and 5 wt % (homopolymers) solutions in $CDCl_3$ at 40°C. A reasonable signal-to-noise ratio was obtained after 1200 accumulations. In order to obtain quantitative spectra, the time delay between the pulses was five times greater than the longest longitudinal relaxation time [3]. Because $T_{l(c=0)} \approx 3$ s, the delay was set to 15 s. The quantitative nature of the spectra was verified by comparison of the intensities for the carbonyl 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 good agreement (i.e., $I_{c=o} = 100.0$ and $I_{\alpha\text{-}CH3(M)} + I_{O\text{-}CH3(E)} = 100.2$). 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 giving 48.4% of ethyl acrylate, hence, 51.6% of methyl methacrylate. In the case of copolymers, the digital filtering algorithm was chosen for deconvolution of the carbonyl signals because of the presence of a great number of peaks [2].

METHODOLOGY

The analysis of the polymer microstructure was performed in four consecutive steps:

Recording of a quantitative ^{13}C-NMR spectrum and assignment of the principal lines by comparison with the spectra of homopolymers, low-molecular-weight analogues, model compounds, etc..

Deconvolution of the overlapped lines. In the case of microstructure analysis, deconvolution seldom gives the parameters of all the individual lines. It should be regarded as a method yielding primary results for the most intense lines which can be later used as starting parameters for subsequent simulation and assignment.

Calculation of the line intensities. Deconvolution can provide the parameters, but for the major lines, it is generally possible to verify if these values follow a certain statistical model, usually Bernoulli or Markov of different orders. If so, the parameters of the remaining minor lines can be reconstituted. For the PMMA/EA copolymer 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 the respective homopolymers, while the co-isotacticity parameters, postulated to be indistinguishable [4], $\sigma_{EM} = \sigma_{ME} = \sigma^*$, were assumed to be equal to 0.41, according to San Román [5]. Since the copolymerization was performed until the complete disappearance of the comonomers, the first-order Markovian conditional probabilities for the compositional triads cannot be calculated from respective reactivity ratios since these calculations are valid only for low conversions; therefore, they were estimated from the NMR spectrum. Since

$$P(E/M) = \frac{P(\overline{EM})}{2P(E)} \quad \text{and} \quad P(M/E) = \frac{P(\overline{EM})}{2P(M)},$$

we had to determine $P(\overline{EM})$, where $\overline{EM} = EM + ME$ [6]. For acrylic polymers, only β-CH_2 signals can provide direct information on distibution of even sequences. We know from the respective homopolymers spectra that: (a) β-CH_2 diads from PMMA and PEA can be observed at 50.80–54.90 ppm and 31.15–36.90 ppm, respectively. The signals of $\overline{ME}$ diads are situated between these two regions. (b) The signals of α-CH (PEA), α-C and O-CH_3 (PMMA) are also present in the region between 40 and 52 ppm and their lines overlap with those of β-CH_2 signals (Figure 1). Therefore, in order to obtain the intensities of respective β-CH_2 signals by simple integration, it is necessary to substract the intensities of intervening signals calculated from the signals outside this region (since $I_{OCH2} = I_{\alpha\text{-}CH}$ for PEA and $I_{\alpha\text{-}CH3} = I_{\alpha\text{-}C} = I_{OCH3}$ for PMMA). P(E/M) and P(M/E) were found to be equal to 0.62 and 0.58, respectively.

Simulation of a copolymer spectrum. To simulate a copolymer spectrum, the intensities and the line positions are used as starting parameters of the simulation algorithm using the Lorentzian line-shape model. As stated above, the intensity values can be derived from deconvolution and subsequent verification of a particular statistical model, while the positions of the lines have to be estimated separately [7]. They are usually obtained by calculations of the possible different statistical configurations (γ-gauche effect [8,9]) or semi-empirical incremental calculations [10,11].

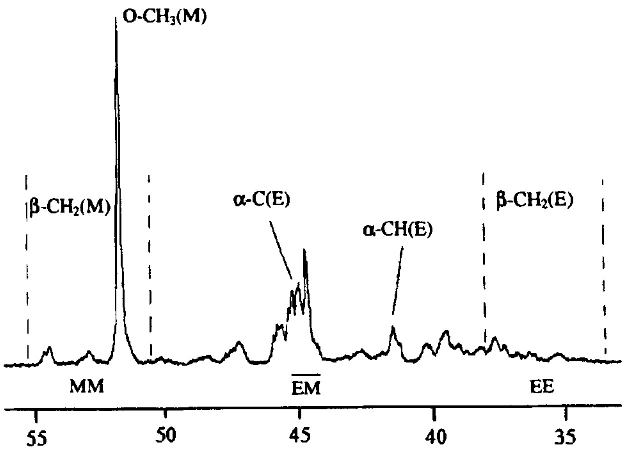

FIGURE 1 100 MHz ^{13}C-NMR spectrum of the region containing the β-CH_2 signals of the PMMA/EA copolymer.

RESULTS AND DISCUSSION

The methodology presented here for a copolymer has been already positively tested for a sample of a model homopolymer, syndiotactic PMMA [12]. The carbonyl signal if this sample in the 100 MHz ^{13}C-NMR spectrum exhibited traces of the heptad lines. Application of the deconvolution with the maximum likelihood algorithm can provide deeper insight into the heptad distribution using first-order Markov statistics.

The carbonyl region of the PMMA/EA copolymer and respective PMMA and PEA homopolymers is presented in Figure 2. It can be seen that strong configurational effect is introduced by the M units, while E units give rather slight effects. At first, assignment of the lines at the triad level can be accomplished based on the results published by Cheng [13] and San Román and Valero [5] who have assigned 12 triads considering only the conformation effect of the M unit.

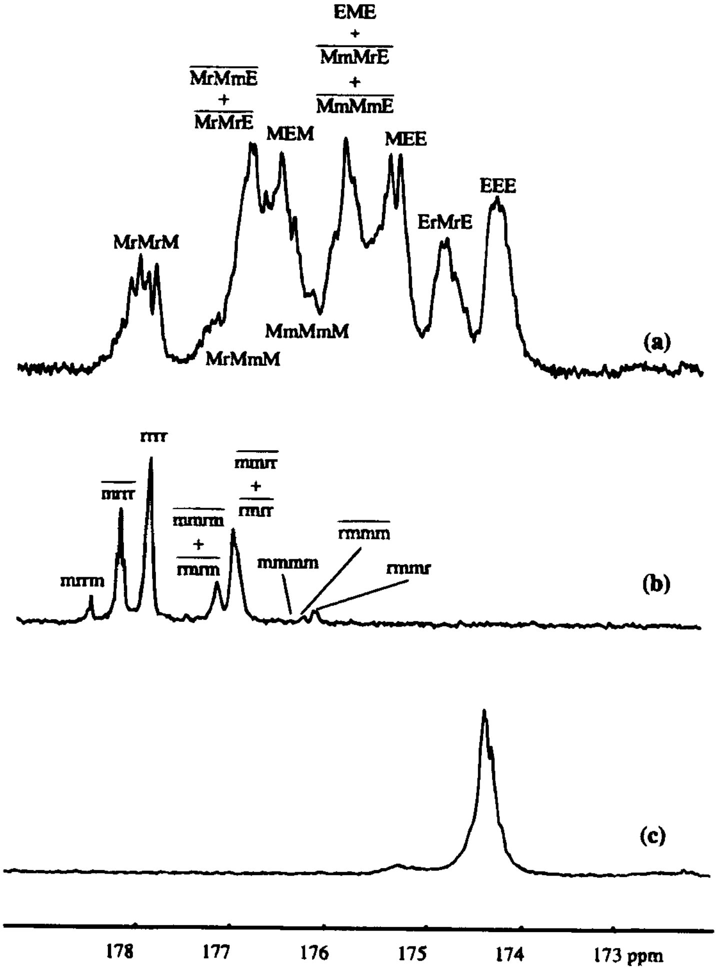

FIGURE 2 100 MHz ^{13}C-NMR spectra of the carbonyl signal of the PMMA/EA copolymer (a), PMMA (b) and PEA (c) homopolymers. Lines assignments according to San Román [5].

From these data, the simulation of the carbonyl spectrum of the copolymer with 12 Hz linewidths can provide substantial agreement between the experimental and simulated spectra. The results of these simulations (from data of Table I) performed according to different statistical models for configurational and compositional sequences, that is, for the 20 theoretically triads, show that the Markov-Bernoulli model (Figure 3b) fits better than the Bernoulli-Bernoulli model (Figure 3a). Since the investigated industrial copolymer sample was prepared by high-conversion polymerization, the values of the isotacticity parameters taken from homopolymer measurements and especially the compositional conditional probabilities calculated from the ^{13}C-NMR spectrum were not quite adequate; there was visible discrepancy for the outermost signals of the two homotriads. Moreover, according to the assignments proposed by San Román and Valero [5] there was significant discrepancy between the lines at about 174.9 and 175.9 ppm, ascribed to be the ErMrE and $[EME + \overline{MrMmE} + \overline{MmMmE}]$ triads, respectively. If we reverse these two lines instead, we arrive at a much better fit which suggests the change in the assignment. The new assignments are presented in Figure 3c.

Nevertheless, it is obvious that precise pentad assignment is essential to obtain better agreement between the experimental and the simulated spectra, since numerous pentads having identical central triad can significantly overlap and contribute to different triads. It indicates that a more sophisticated statistical model could be necessary to further increase the precision of the sequence distribution determination. Theoretically, there are 272 pentads observable in the NMR spectrum for a copolymer which reflect both configurational and sequence effects. The spectrum resolution of the carbonyl signal recorded at 100 MHz makes it possible to observe the pentad splitting; nevertheless, the overlapping of pentad lines is so prevalent that deconvolution can yield not more than 100 lines (Figure 4).

TABLE I

Calculated and experimental (see Figure 4) probabilities for methyl methacrylate ethyl acrylate copolymer. Assignment of the resonance pattern of carbonyl carbons.

Chemical shift	Copolymer sequence	Bernoulli/ Bernoulli	Bernoulli/ Markov first order	Experimental (deconvolution)
177.87	MrMrM	0,0703	0,0453	0.0920
177.20	$\overline{\text{MrMmM}}$	0,0393	0,0253	0.0266
176.87	$\overline{\text{MrMrE}}$	0,1120	0,1068	0.2998
176.81	$\overline{\text{MrMmE}}$	0,0779	0,0742	
176.68	MmEmM	0,0204	0,0288	
176.53	$\overline{\text{MmErM}}$	0,0588	0,0829	
176.38	MrErM	0,0423	0,0596	
176.22	MmMmM	0,0055	0,0035	0.0151
176.05	EmMmE	0,0216	0,0304	0.1618
175.90	$\overline{\text{EmMrE}}$	0,0621	0,0875	
175.80	ErMrE	0,0447	0,0630	
175.65	$\overline{\text{MmEmE}}$	0,0360	0,0352	0.1699
175.55	$\overline{\text{MrEmE}}$	0,0518	0,0506	
175.47	$\overline{\text{MmErE}}$	0,0692	0,0676	
175.35	$\overline{\text{MrErE}}$	0,0996	0,0972	
174.90	$\overline{\text{MmMrE}}$	0,0313	0,0298	0.0972
174.80	$\overline{\text{MmMmE}}$	0,0218	0,0207	
174.48	EmEmE	0,0159	0,0107	0.1376
174.41	$\overline{\text{ErEmE}}$	0,0610	0,0413	
174.36	ErErE	0,0586	0,0396	

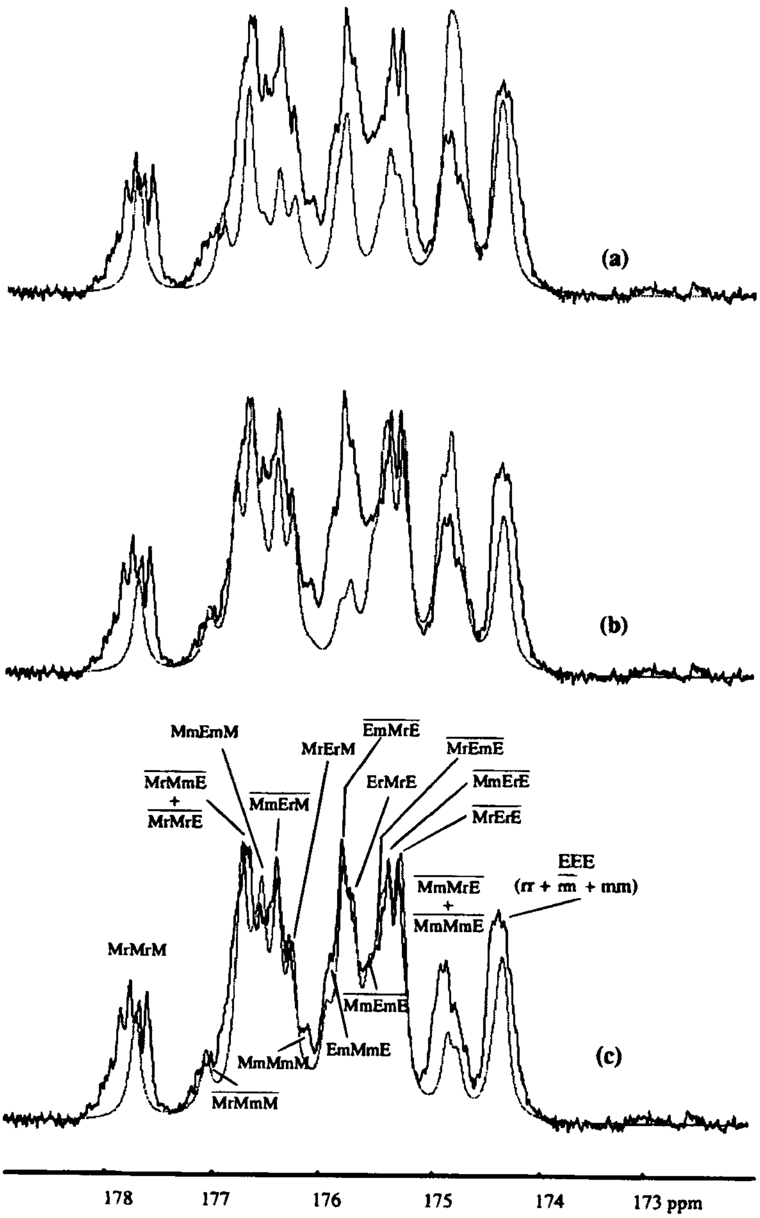

FIGURE 3 Simulation of the PMMA/EA carbonyl signal at the triad level.
a) Bernoulli distribution for both configurational and compositional triads
b) First-order Markov model for compositional triads and Bernoulli model for configurational triads and assignments according to San Román [5] and Cheng [11].
c) First order Markov model for compositional triads and Bernoulli model for configurational triads, but with reversed assignments for the EME and MmME sequences.

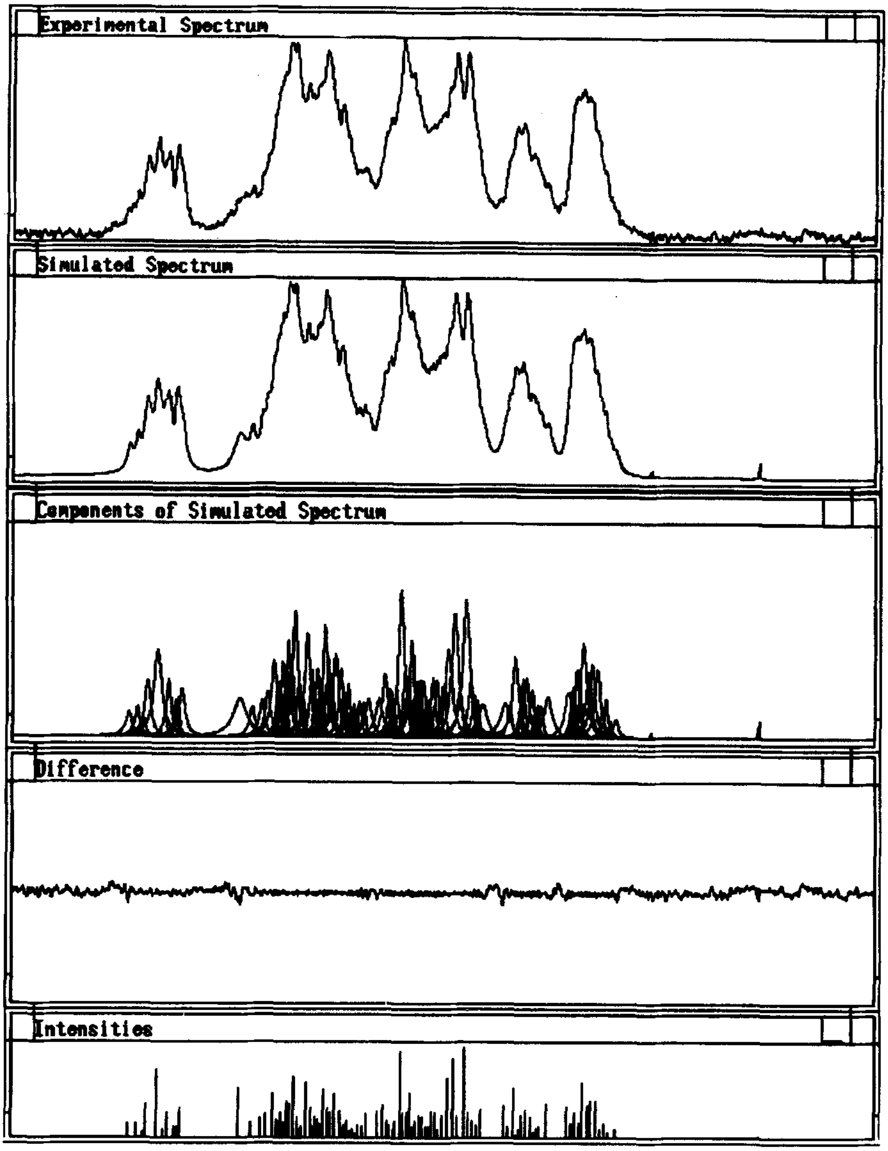

FIGURE 4 Deconvolution of the PMMA/EA carbonyl signal by means of the digital filtering algorithm.

Moreover, the deconvolution results yield many lines larger than a single line, indicating that several groups of two, and three peaks are not resolved into individual lines. Therefore, deconvolution can provide only the starting parameters for separate calculations of line intensities (verification of different statistical models) and positions (incremental calculations of chemical shifts [10,11]), which is currently being investigated.

CONCLUSIONS

The method developed for the analysis of complex petrochemical mixtures has proved useful for the analysis of copolymer microstructure. Also, the spectrum simulation at the triad level can provide fast results for an approximate analysis. Complete distribution of the configurational-compositional pentads can be achieved by spectral simulation which necessities accurate data for 272 lines. Full pentad analysis, in progress, can result in establishing a library of their chemical shifts that can be very useful in rapid determination of sequence distribution at pentad level for samples of PMMA/EA copolymers of different tacticity and composition.

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