

Incremental method for determination of sequence distribution of poly(methyl methacrylate) by ^{13}C NMR spectroscopy

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Abstract – A method of incremental calculation of chemical shifts in the ^{13}C NMR spectra for different configurational-compositional sequences, developed for copolymer of methyl methacrylate and ethyl acrylate, PMMA/EA, has been applied to poly(methyl methacrylate) samples of different tacticity. The numerical values of the increments determined for the copolymer can be used in the case of the homopolymer after only minor modifications. A very good agreement between the experimental and simulated spectra was obtained at the triad and pentad level, while the heptad splittings were too small to be decisive.

Keywords. ^{13}C NMR – poly(methyl methacrylate) – sequence distribution.

Introduction

In our previous paper [1] we have shown that it was possible to assign individual configurational sequences of poly(methyl methacrylate), PMMA, up to the heptad level. The method was based on the deconvolution of the carbonyl signal in the ^{13}C NMR spectrum by means of the algorithm of maximum likelihood [2] and then by comparison of the intensities of the individual lines with those calculated according to 1st order Markov statistics. However, in the case of a copolymer, due to the complexity of the spectrum this method permitted only assignment of the predominating sequences as it was shown for the copolymer of methyl methacrylate and ethyl acrylate [3], PMMA/EA. Based on these first results we have developed a new method of incremental calculation of chemical shifts of the carbonyl signal for different configurational-compositional sequences at triad and pentad level. Therefore, having both intensities and respective line positions, we were able to simulate the ^{13}C NMR carbonyl signal for this copolymer [4]. Now, we would like to test if this incremental method is applicable to describe the carbonyl signal observed in the ^{13}C NMR spectrum of the model homopolymer, PMMA.

Experimental

Predominantly syndiotactic PMMA was synthesized by free radical polymerization. The methyl methacrylate monomer was placed in a double-coated reactor under nitrogen and then heated up to 78 °C with azobisisobutyronitrile (AIBN)

as radical initiator. Predominantly isotactic PMMA was prepared by anionic polymerization under argon atmosphere at –78 °C in a mixture of toluene and tetrahydrofuran as a solvent, according to the method described previously [5], using fluorenyllithium as the initiator.

The 100 MHz ^{13}C NMR spectra were recorded on a Bruker DRX 400 for 5 w. % solutions in CDCl_3 at 40 °C. In order to obtain quantitative spectra a gated decoupling sequence was applied even though the nuclear Overhauser effect does not influence the carbonyl signal [6] and the time delay between the pulses has to be set at least 5 times greater than the longest relaxation time. Since $T_{1(\text{C}=\text{O})} \cong 3 \div 6$ sec, the delay was set to 30 sec [7]. A reasonable signal to noise ratio was attained after about 1200 scans. The quantitative nature of the spectra was verified by comparison of the intensities for the $\text{C}=\text{O}$, $\alpha\text{-CH}_3$ and $\alpha\text{-C}$ signals.

Results and discussion

Syndiotactic PMMA

In the previous publication [4] we have shown that the ^{13}C NMR chemical shifts for different configurational sequences of PMMA/EA observed in the carbonyl signal can be described in an empirical manner. For example, the positions of the two symmetric methyl methacrylate triads can be calculated as:

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$$\delta_{MrMmM} = \delta_{0M} + 2\alpha_{rM}^M \quad \text{hence} \quad \alpha_{rM}^M = \frac{\delta_{MrMmM} - \delta_{0M}}{2}$$

$$\delta_{MmMmM} = \delta_{0M} + 2\alpha_{mM}^M \quad \text{hence} \quad \alpha_{mM}^M = \frac{\delta_{MmMmM} - \delta_{0M}}{2}$$

where δ_{0M} is regarded as the position of the carbonyl signal of the methyl methacrylate unit (M) without any influence of its neighbors and $2\alpha_{rM}^M$ represents the incremental change of the chemical shift of this signal on addition of two neighboring units M, both in configuration r . The position of the third asymmetric triad is therefore the linear combination of the two above increments:

$$\delta_{MrMmM} = \delta_{0M} + \alpha_{rM}^M + \alpha_{mM}^M$$

In the case of a homopolymer the notation is commonly simplified and the symbol of the repeating unit is usually omitted. Henceforth, the respective symbols referring to homopolymer will be as follows: rr instead of $MrMmM$, δ_0 instead of δ_{0M} , α_r instead of α_{rM}^M , and so on. Since only the sum of asymmetric sequences can be observed by NMR we will use the following notation [8] for the spectroscopically observable asymmetric sequences: e.g., $\overline{r\overline{m}} = \overline{m\overline{r}} = mr + rm$. It should be noted that in these calculations the α values are dependent of δ_0 , hence, the position of δ_0 could be chosen arbitrarily. If this parameter is defined as the center of the observed signal the chemical shift of the $\overline{m\overline{r}}$ triad was found to be practically identical to that of δ_{0M} for the PMMA/EA copolymer with $\alpha_r = \alpha_{rM}^M \cong |\alpha_{mM}^M| \cong 0.420$ ppm. Nevertheless, we have shown that for the asymmetric $\overline{m\overline{r}}$ -centered sequences, the increment α^M has to be modified, α^1 , taking into account the slight differences with respect to the symmetric sequences. Hence:

$$\delta_{rm} = \delta_0 + \alpha_r^1 + \alpha_m^1$$

with $\alpha_r + \alpha_m \cong 0$.

The individual values of these two increments are in fact unknown but they are incorporated in the positions of the twenty triads of the PMMA/EA copolymer (for example $MrMmE$, $MmMrE$, ...) and they can be arbitrarily assumed. We have found that the best fit of the simulated spectra can be obtained for

$$\alpha_r^{1M} \approx |\alpha_m^{1M}| \approx 0.320 \text{ ppm}$$

For the PMMA homopolymer we observe a small difference between the chemical shifts of identical sequences when compared to respective signals in copolymer. For example, the $\overline{r\overline{m}}$ triad is no longer situated in the middle of the spectral region considered (Fig. 1) with:

$$\alpha_r^1 + \alpha_m^1 = -0.12 \text{ ppm}$$

Only the sum of these two increments is experimentally accessible but the individual value of each increment can be estimated with respect to this shift of ± 0.32 ppm obtained

for the copolymer, hence:

$$\alpha_r^1 = 0.320 - 0.06 = 0.26 \text{ ppm}$$

$$\alpha_m^1 = -0.320 - 0.06 = -0.38 \text{ ppm}$$

Assignment of longer sequences by applying this incremental method requires an initial simulation of the spectrum [1]. The theoretical sequence intensities were calculated from 1st order Markov statistics utilizing the following triad probabilities $P(rr) = 0.598$; $P(mm) = 0.035$ and $P(\overline{m\overline{r}}) = 0.367$, determined from the carbonyl or $\alpha\text{-CH}_3$ signal. These intensities are compared to those for the lines obtained by deconvolution of the experimental spectrum. Then the spectrum can be simulated assuming Lorentzian lineshape. Assignment of the lines found in this way is in accordance with those from the literature [9,10].

The four independent β increments, representing the contribution of the methyl methacrylate units in β position with respect to the considered one are therefore determined based on the attribution of the symmetrical pentads assuming the center of the two triads rr and mm as its origin. The chemical shifts of the six other pentads were obtained by linear combination of the respective increments, for example:

$$\delta_{rrmm} = \delta_0 + 2\alpha_r + \beta_{rm} + \beta_{rr}$$

however, like for the α increments, the measured values of β increments should be modified (β^1) in order to get better position of the four $\overline{m\overline{r}}$ -centered pentads (Tab. I).

The eight independent γ increments were estimated in a similar manner but in this case with respect to the center of the respective symmetrical pentads. In the case of the syndiotactic PMMA they can be best observed for the increments involved in the rr -centered heptads. Even though these measurements are approximate due to insufficient resolution at the heptad level, it is revealed from our calculation method (Fig. 1) that:

$$\gamma_{rmm} > 0 \quad \text{and} \quad \gamma_{rmr} < 0$$

$$\text{and} \quad \gamma_{rrm} > 0 \quad \text{and} \quad \gamma_{rrr} < 0$$

If we now examine the chemical shifts of the four heptads with central $\overline{m\overline{r}\overline{r}\overline{r}}$ pentad we can say, according to the assignment performed initially, that:

$$\delta_{rmrrrr} > \delta_{mmrrrr} \quad \text{hence} \quad \gamma_{rmr} > \gamma_{rmm}$$

which is contradictory to the first inequality observed, mentioned above. To satisfy this condition it is possible to inverse the order of the $\overline{m\overline{m}\overline{r}\overline{r}\overline{r}}$ and $\overline{r\overline{m}\overline{r}\overline{r}\overline{m}}$ heptads, since their intensities are nearly the same. But in this case we arrive at:

$$\delta_{rmrrrr} > \delta_{rmrrrm} \quad \text{hence} \quad \gamma_{rrr} > \gamma_{rrm}$$

which is in complete contradiction with the second inequality.

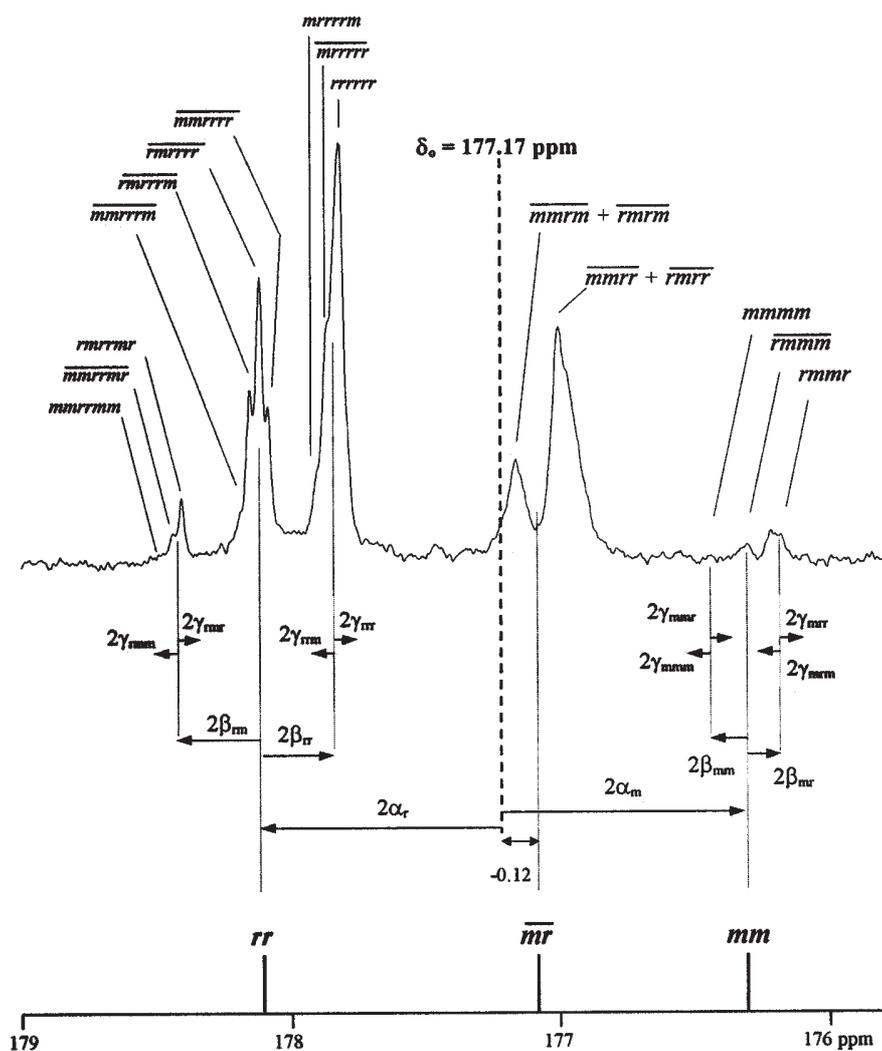


Fig. 1. Determination of the α , β and γ increments in the carbonyl signal of the 100 MHz ^{13}C NMR spectrum of the syndiotactic PMMA.

Table I. Values (in ppm) of increments α , α^1 , β , β^1 and γ used to calculate the chemical shifts of the configurational sequences of syndiotactic PMMA.

| | | | |
|----------------|----------------|--------------------|-------------------|
| α_m | | α_r | |
| -0.455 | | 0.455 | |
| α_m^1 | | α_r^1 | |
| -0.38 | | 0.26 | |
| β_{mm} | β_{mr} | β_{rm} | β_{rr} |
| 0.065 | -0.05 | 0.15 | -0.145 |
| β_{mm}^1 | β_{mr}^1 | β_{rm}^1 | β_{rr}^1 |
| 0.035 | -0.03 | 0.09 | -0.09 |
| γ_{mmm} | γ_{mrm} | γ_{rmm} | γ_{rrr} |
| 0.015 | -0.01 | 0.025 ^c | -0.005 |
| | | γ_{mrr} | γ_{rrm} |
| | | -0.01 ^b | 0.04 ^e |
| | | | -0.005 |

a. -0.02 ppm in the \overline{mrmrrr} and \overline{mrmrmr} heptads

b. +0.01 ppm in the \overline{rmrrr} heptad

c. -0.025 ppm in the \overline{mmrrrr} heptad

d. +0.005 ppm in the \overline{rmrrrr} heptad

e. -0.04 ppm in the \overline{mrmrrm} and \overline{rmrmm} heptads

The same phenomenon is observed for the heptads with central \overline{rmrr} pentad. These contradictions show that due to very small values for γ increments their values could be slightly different, depending on the particular heptad, and some of them should be modified, even to invert their sign (Tab. I and notes below). In other words the γ increments are not independent and each increment can be influenced by the adjacent increment in the heptad considered. The new increments introduced in this way are of such values that they correspond to the initial assignments performed and those of Moad *et al.* [10] for the ^{13}C enriched PMMA. They lead to the assignment of the heptads with the central \overline{mr} triad and satisfying final simulation (Tab. II, Fig. 2).

Table II. Intensities and chemical shifts for the 36 heptads of the syndiotactic PMMA.

| sequence | probability | chemical shift (ppm) |
|-----------------------|-------------|----------------------|
| \overline{mmrrmm} | 0.00085 | 178.43 |
| \overline{mmrrmr} | 0.00887 | 178.40 |
| \overline{rmrrmr} | 0.02325 | 178.37 |
| \overline{mmrrrm} | 0.00808 | 178.15 |
| \overline{rmrrrm} | 0.04237 | 178.12 |
| \overline{rmrrrr} | 0.13809 | 178.08 |
| \overline{mmrrrr} | 0.02634 | 178.05 |
| \overline{mrrrrm} | 0.01930 | 177.87 |
| \overline{mrrrrr} | 0.12582 | 177.83 |
| \overline{rrrrrr} | 0.20502 | 177.78 |
| \overline{mmmrmm} | 0.00035 | 177.22 |
| \overline{rmmrmm} | 0.00186 | 177.19 |
| \overline{mmmrmr} | 0.00186 | 177.19 |
| \overline{rmmrmr} | 0.00974 | 177.16 |
| \overline{mrmrmm} | 0.00272 | 177.16 |
| \overline{mrmrmr} | 0.01427 | 177.13 |
| \overline{rrmrmm} | 0.00887 | 177.13 |
| \overline{rrmrmr} | 0.04651 | 177.10 |
| \overline{mmmrmm} | 0.00169 | 177.05 |
| \overline{rmmrmm} | 0.00887 | 177.03 |
| $\overline{mmmr rr}$ | 0.00551 | 177.01 |
| $\overline{rmmr rr}$ | 0.02891 | 176.98 |
| $\overline{rrmr rr}$ | 0.13809 | 176.94 |
| \overline{mrmrmm} | 0.01300 | 176.91 |
| \overline{mrmrmr} | 0.04237 | 176.91 |
| \overline{rrmrmm} | 0.04237 | 176.88 |
| \overline{mmmmmm} | 0.00002 | 176.43 |
| \overline{mmmmmr} | 0.00024 | 176.40 |
| \overline{rmmmmr} | 0.00063 | 176.37 |
| \overline{mmmmrm} | 0.00035 | 176.30 |
| $\overline{rmmmrmm}$ | 0.00186 | 176.28 |
| \overline{mmmmrr} | 0.00115 | 176.27 |
| $\overline{rmmmr rr}$ | 0.00605 | 176.25 |
| $\overline{mrmmrmm}$ | 0.00136 | 176.20 |
| $\overline{mrmmr rr}$ | 0.00887 | 176.17 |
| \overline{rrmmrr} | 0.01445 | 176.14 |

Isotactic PMMA

In the case of isotactic PMMA the carbonyl signal exhibits a reversed spectral pattern with respect to the syndiotactic sample, *i.e.*, the signals in the highest field are of the greatest intensity, especially the line of the \overline{mmmm} pentad. On the other hand, the resolution of the heterotactic \overline{mr} triad band is better than for the syndiotactic sample and as a result it permits to observe four pentad bands in this region (Fig. 3). At first, for this polymer sample obtained by anionic polymerization it was necessary to verify the statistics governing the stereosequences propagation.

The probabilities of the configurational triads were determined in the same manner as for the syndiotactic PMMA, based on the intensities of respective lines for both carbonyl and $\alpha\text{-CH}_3$ signals, which lead to the following triad probabilities: $P(rr) = 0.133$; $P(mm) = 0.659$ and $P(\overline{mr}) = 0.208$. The second order Markov statistics required determination of the following four conditional probabilities, found to be:

$$P(mm/m) = 0.915$$

$$P(mr/m) = 0.538$$

$$P(rm/m) = 0.528$$

$$P(rr/m) = 0.330$$

where the pentad probabilities were calculated by integration or deconvolution of the spectrum, while those of tetrads were derived from the relations between tetrads and pentads. The results listed in table III show the theoretical pentad probabilities for the 1st and 2nd order Markov statistics; after comparison with the deconvolution results it was revealed that the latter statistics is more adequate to represent the tacticity of such a polymer. The respective calculations show that the difference between these two statistics is even more evident at the heptad level.

The distance between the signals of homo-triads mm and rr (1.72 ppm, *i.e.*, from 176.30 to 178.02 ppm) is a little smaller than in the case of syndiotactic PMMA (1.82 ppm) while the band for the heterotactic triad is larger (0.55 ppm with respect to 0.48 ppm) and better resolved, especially for the increments involved in the \overline{mm} -centered heptads yielding better line separation in the isotactic sample. The values calculated for the α and α^1 increments are therefore slightly smaller (Tab. IV). The values for the β and γ increments were left practically identical as for the syndiotactic PMMA since they are virtually independent of the total width of this region. Slight corrections of the same increments were introduced for the same sequences as in the case of the syndiotactic PMMA. Using the intensities and chemical shifts calculated in this way it is possible to simulate the entire carbonyl region (Fig. 3a,b). The simulation of the four \overline{mrrr} -centered heptads shows that the initial assignment of the sequences was correct in the case of the syndiotactic PMMA (Fig. 3c). On the other hand, the simulation of the signals of the heterotactic \overline{mr} triad allowed for more precise determination of chemical shifts and assignment of the four pentads and numerous heptads.

Table III. Probabilities and chemical shifts of the configurational sequences of the isotactic PMMA.

| Sequence | Probability | δ C=O [ppm] | Experimental | | Calculated |
|---------------------------------------|--|-----------------------|---------------|------------------------|------------------------|
| | | | Deconvolution | Markov 1 st | Markov 2 nd |
| triads | P(<i>mm</i>) | 176.30 | 0.6590 | 0.659 | 0.659 |
| | P(<i>m\bar{r}</i>) | 177.02 | 0.2080 | 0.208 | 0.208 |
| | P(<i>rr</i>) | 178.02 | 0.1330 | 0.133 | 0.133 |
| pentads | P(<i>mmmm</i>) | 176.46 | 0.5711 | 0.4916 | 0.5518 |
| | P(<i>mmmr</i>) | 176.31 | 0.0638 | 0.1551 | 0.1015 |
| | P(<i>rmmr</i>) | 176.12 | 0.0231 | 0.0122 | 0.0046 |
| | P(<i>m\bar{m}rm</i>) | 177.19 | 0.0600 | 0.0788 | 0.0597 |
| | P(<i>r\bar{m}rm</i>) | 177.10 | 0.0508 | 0.0124 | 0.0527 |
| | P(<i>m\bar{m}rr</i>) | 176.95 | 0.0500 | 0.1008 | 0.0491 |
| | P(<i>r\bar{m}rr</i>) | 176.86 | 0.0473 | 0.0159 | 0.0433 |
| | P(<i>mrrm</i>) | 178.34 | 0.0186 | 0.0256 | 0.0159 |
| | P(<i>m\bar{r}rr</i>) | 178.02 | 0.0518 | 0.0655 | 0.0615 |
| P(<i>rrrr</i>) | 177.73 | 0.0631 | 0.0418 | 0.0595 | |
| heptads | P(<i>mmmmmm</i>) | 176.49 | - | 0.3667 | 0.4619 |
| | P(<i>mmmmmr</i>) | 176.46 | - | 0.1157 | 0.0850 |
| | P(<i>rmmmmr</i>) | 176.43 | - | 0.0091 | 0.0039 |
| | P(<i>mmmmrm</i>) | 176.34 | - | 0.0588 | 0.0500 |
| | P(<i>m\bar{m}mmrr</i>) | 176.31 | - | 0.0752 | 0.0411 |
| | P(<i>r\bar{m}mmrm</i>) | 176.30 | - | 0.0092 | 0.0046 |
| | P(<i>rmmmrr</i>) | 176.29 | - | 0.0118 | 0.0037 |
| | P(<i>mrrmmrm</i>) | 176.15 | - | 0.0023 | 0.0013 |
| | P(<i>m\bar{r}mmrr</i>) | 176.13 | - | 0.0060 | 0.0022 |
| | P(<i>rrmmrr</i>) | 176.11 | - | 0.0038 | 0.0009 |
| | P(<i>m\bar{m}mmrm</i>) | 177.22 | - | 0.0588 | 0.0291 |
| | P(<i>mmmmrmr</i>) | 177.19 | - | 0.0092 | 0.0257 |
| | P(<i>rmmmrmm</i>) | 177.19 | - | 0.0092 | 0.0026 |
| | P(<i>r\bar{m}mmrmr</i>) | 177.16 | - | 0.0014 | 0.0023 |
| | P(<i>mrrmmmm</i>) | 177.13 | - | 0.0047 | 0.0151 |
| | P(<i>m\bar{r}mmrmr</i>) | 177.07 | - | 0.0007 | 0.0133 |
| | P(<i>rrmmrmm</i>) | 177.10 | - | 0.0060 | 0.0124 |
| | P(<i>rrmmrmr</i>) | 177.09 | - | 0.0009 | 0.0109 |
| | P(<i>m\bar{m}mmrrm</i>) | 177.00 | - | 0.0382 | 0.0155 |
| | P(<i>m\bar{m}mmrrr</i>) | 176.96 | - | 0.0488 | 0.0300 |
| | P(<i>r\bar{m}mmrrm</i>) | 176.98 | - | 0.0060 | 0.0014 |
| | P(<i>rmmmrrr</i>) | 176.93 | - | 0.0077 | 0.0027 |
| | P(<i>mrrmmrm</i>) | 176.85 | - | 0.0030 | 0.0080 |
| | P(<i>m\bar{r}mmrrr</i>) | 176.83 | - | 0.0039 | 0.0156 |
| | P(<i>rrmmrrm</i>) | 176.82 | - | 0.0039 | 0.0066 |
| | P(<i>rrmmrrr</i>) | 176.87 | - | 0.0128 | 0.1381 |
| | P(<i>m\bar{m}rrmm</i>) | 178.37 | 0.0056 | 0.0191 | 0.0045 |
| P(<i>m\bar{m}rrmr</i>) | 178.34 | 0.0074 | 0.0060 | 0.0079 | |
| P(<i>rmrrmr</i>) | 178.31 | 0.0056 | 0.0004 | 0.0035 | |
| P(<i>mmrrrm</i>) | 178.07 | 0.0061 | 0.0248 | 0.0113 | |
| P(<i>mmrrrr</i>) | 178.00 | 0.0117 | 0.0317 | 0.0219 | |
| P(<i>rmrrrm</i>) | 178.04 | 0.0250 | 0.0039 | 0.0100 | |
| P(<i>r\bar{m}rrrr</i>) | 178.03 | 0.0090 | 0.0050 | 0.0194 | |
| P(<i>mrrrrm</i>) | 177.81 | 0.0202 | 0.0080 | 0.0071 | |
| P(<i>m\bar{r}rrrr</i>) | 177.76 | 0.0403 | 0.0206 | 0.0276 | |
| P(<i>rrrrrr</i>) | 177.72 | 0.0026 | 0.0131 | 0.0266 | |

Conclusion

The method of incremental calculation of chemical shifts of the carbonyl signal in the ¹³C NMR spectra, developed for a copolymer of methyl methacrylate and ethyl acrylate, can

be positively applied to the similar calculations in the case of a homopolymer. However, to obtain better standardization it is preferred to take the center of respective signals as the origin of increment calculations. It was shown that for PMMA it was sufficient to slightly modify the numerical

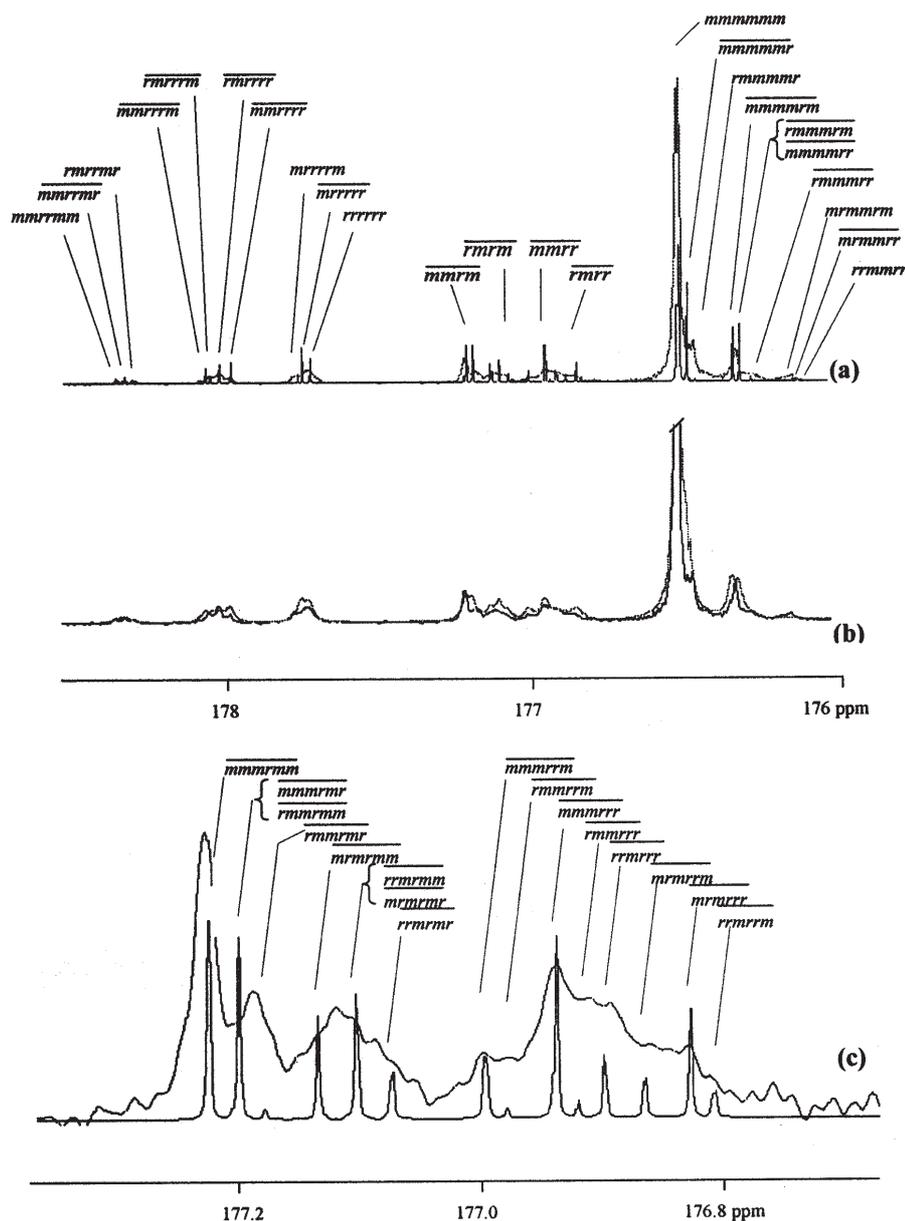


Fig. 3. Simulation of the carbonyl signal of the 100 MHz ^{13}C NMR spectrum of the isotactic PMMA at the heptad level. Linewidth of 1 Hz (a); 5 Hz (b); \overline{rm} -centered sequences, 1 Hz (c).

values of the increments used previously for the copolymer but the methodology remains intact.

References

1. Matlengiewicz, M. *Analysis* **1996**, 24(2), 60
2. Matlengiewicz, M.; Henzel, N.; Czachowska, D.; Schmit-Quilès, F.; Nicole, D.; Lauer J-C. *Fuel* **1994**, 73(6), 843
3. Schmit, F.; Matlengiewicz, M.; Nicole, D. *Int. J. Polymer Analysis & Characterization* **1996**, 2, 95
4. Nguyen, G. Nicole, D. Swistek, M. Matlengiewicz, M. Wiegert, B. *Polymer* **1997**, 38(14), 3455
5. Glusker, D.L.; Gallucio, R.A.; Evans, R.A. *J. Am. Chem. Soc.* **1964**, 86, 187
6. Inoue, Y.; Nishioka, A.; Chûjô, R. *Polymer J.* **1971**, 4, 535
7. Hatada, K.; Kitayama, T.; Okamoto, Y.; Ohta, K.; Umemura, Y.; Yuki, H. *Makromol. Chem.* **1978**, 179, 487
8. Klesper E.; Sielaff, G. in *Polymer Spectroscopy*, Hummel, D.O., Ed.; Verlag Chemie: Weinheim, 1974, p. 192
9. Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, 14, 1359
10. Moad, G.; Solomon, D.H.; Spurling, T.H.; Johns S.R.; Willing, R.I. *Aust. J. Chem.* **1986**, 39, 43