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ORIGINAL PAPER

# Microstructure of methyl methacrylate/*tert*-butyl acrylate copolymer characterized by $^{13}$C NMR spectroscopy

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**Abstract** 100 MHz $^{13}$C NMR spectra of methyl methacrylate/*tert*-butyl acrylate copolymer, PMMA/tBA, reveal configurational effects of both comonomers. The microstructure of the macromolecular chain has been determined utilizing carbonyl and $\beta$-CH$_2$ carbon signals and the spectral assignments were performed in terms of the configurational–compositional sequences. To determine the line positions of individual sequences, the incremental method of the chemical shift calculation has been applied. Based on these data, the analyzed signals were simulated yielding fairly good agreement with the experimental spectra—at the pentad level for the carbonyl signal and at the tetrad level for $\beta$-CH$_2$ signal.

**Keywords** Methyl methacrylate/*tert*-butyl acrylate copolymer · $^{13}$C NMR spectroscopy · Sequence distribution

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## Introduction

Acrylic formulations based on alkyl acrylate copolymers are of practical interest in the preparation of coatings, membranes, adhesives, sealants, and various engineering materials because of the wide range of their glass transition temperatures covered by an appropriate selection of the copolymer system, as well as by their excellent chemical and optical properties. The distribution of monomer sequences along the macromolecular chain and the stereochemical configuration of the monomeric units are the factors of great significance to their physical and chemical properties, hence their industrial applications [1, 2]. Nuclear magnetic resonance spectroscopy is practically the only method providing insight into details of sequence distribution of the polymer chain. For acrylic copolymers two signals in the $^{13}$C NMR spectra are of predominant interest from microstructural point of view—the carbonyl and $\beta$-CH$_2$ carbon—since they are present in all typical acrylic structures. Moreover, they can provide complementary information: the carbonyl signal on distribution of uneven sequences, while the methylene signal from the main chain on distribution of even sequences. Usually, in the acrylate–methacrylate copolymers the configurational effects are introduced only by methacrylate units. No configurational influence of acrylate units was observed for methyl methacrylate–methyl acrylate copolymer [3] and only traces of acrylate splitting were observed for methyl methacrylate–ethyl acrylate copolymer [4]. In the case of methyl methacrylate–butyl acrylate copolymers no configurational effects were reported for acrylate units or they were neglected in the microstructure analysis [5–7]. However, the 100 MHz $^{13}$C NMR spectra of *tert*-butyl acrylate homopolymer, PtBA, show clear splittings of the carbonyl signal up to configurational heptads [8]. Hence, in the detailed analysis of PMMA/tBA, the configurational effects introduced by both comonomers have to be taken into account.

## Experimental

A series of methyl methacrylate/*tert*-butyl acrylate copolymer samples, PMMA/tBA, were synthesized by free radical polymerization. The comonomers taken in respective weight ratio were poured into butan-2-one to obtain 40 wt% mixture. 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). After polymerization for 0.5 h, when the conversion attained about 10%, the reaction mixture was diluted with acetone and poured into a large volume of a water–methanol mixture to precipitate the copolymer. The product was washed with methanol and vacuum dried to constant weight [4]. Respective homopolymers, i.e., poly(methyl methacrylate), PMMA, and poly(*tert*-butyl acrylate), P*t*BA, were synthesized in analogous manner. The reactivity ratios for the PMMA/tBA copolymer calculated according to Tidwell and Mortimer [9] were found to be equal to $r_{\mathrm{M}} = 2.14$ and $r_{\mathrm{tB}} = 0.60$. These values are approximate since they were obtained for only three copolymer samples of different composition but they are comparable to those for another butyl acrylate copolymer, i.e., copolymer of methyl methacrylate and *n*-butyl acrylate [5], equal to $r_M = 2.279$ and $r_{nB} = 0.395$.

The NMR spectra were recorded with a Bruker AM 400 spectrometer at 40 °C, using 10 wt% solutions in bezene-$d_6$. The 400 MHz $^1$H NMR spectra were obtained for sample concentrations of 10% (w/v), applying pulse delay of 5 s and 240 scans [5]. To record the 100 MHz $^{13}$C NMR spectra, a gated decoupling sequence was applied to avoid the nuclear Overhauser effect, and a good signal to noise ratio was achieved after 12,000 scans. The spectra were obtained with a 4 s delay (D1). The DEPT experiments, necessary for generation of $CH_n$ ($n = 1$–3) sub-spectra, were performed using the pulse sequence described by Bendal, Doddrell, and Schenker [10–12]. The $^{13}$C and $^1$H 90° pulse widths were equal to 6.75 and 10.8 μs, respectively. Since we were only interested in the aliphatic region of the spectra, the carbon–hydrogen spin coupling was set to 125 Hz. The DEPT sub-spectra were generated by the appropriate linear combination of the spectra acquired for $\theta = 45°$, 90°, and 135°. The average copolymer composition, $F_M$, (mole fraction of methyl methacrylate) was calculated from the $^1$H NMR spectra using the following equation:

$$F_M = \frac{12 \times A_1}{7 \times A_1 + 3 \times A_2}$$

where $A_1 = 3 \times \mathrm{M}$ and $A_2 = 5 \times \mathrm{M} + 12 \times \mathrm{B}$ (the intensities of the signals from methyl methacrylate units are represented by *M* and those of *tert*-butyl acrylate units by *B*). The respective regions are indicated in Fig. 1, showing 400 MHz $^1$H NMR spectrum of PMMA/*t*BA copolymer of $F_M = 0.31$. Composition of the copolymer samples used, as determined by $^1$H NMR, is given in Table 1.

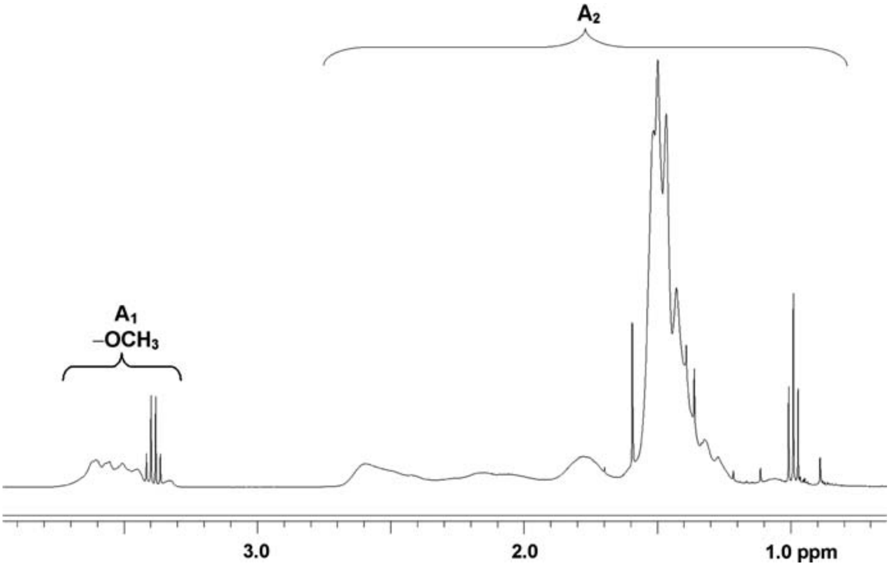

**Fig. 1** 400 MHz $^1$H NMR spectrum of PMMA/*t*BA with $F_M = 0.31$ in benzene-$d_6$

**Table 1** Composition of methyl methacrylate–*tert*-butyl acrylate copolymer samples

| Methyl methacrylate (mol %) | |
|---|---|
| Monomer mixture | Copolymer |
| 50.0 | 31.0 |
| 60.0 | 41.0 |
| 75.0 | 63.0 |

## Results and discussion

In the description that follows, M designates methyl methacrylate units and B the units of *tert*-butyl acrylate in the macromolecular chain. In the 100 MHz $^{13}C$ NMR spectra of PMMA/tBA copolymer samples recorded in $C_6D_6$ at 40 °C (Fig. 2) we can observe a single signal of methyl carbons from acrylate *tert*-butyl group at 28.25 ppm and single signal of $–OCH_3$ carbons from methacrylate units, while the signal of tertiary carbon of *tert*-butyl acrylate unit at 80.2–80.6 display slight splitting. The remaining signals in this spectrum reveal considerable sensitivity to microstructural effects. In the region from 18 to 23 ppm, we can observe $\alpha$-$CH_3$ (M) carbons. The signals of $\beta$-$CH_2$ carbons occupy very large region from 35 to 56 ppm but they are superimposed with the $\alpha$-CH (B) carbons at 42 ppm, the $\alpha$-C(M) signals at about 45 ppm and a single signal at 51.5 ppm of $–OCH_3$ (M) group. The carbonyl signal is split over about 5 ppm and can be observed at 173.5–178.5 ppm. It should be noted that only the carbonyl and $\beta$-$CH_2$ carbons are present both in acrylate and methacrylate units and therefore can provide complete information on distribution of all sequences. The carbonyl signals can be analyzed without further processing while the $\beta$-$CH_2$ signals, superimposed with others, requires their separation applying for example the DEPT technique.

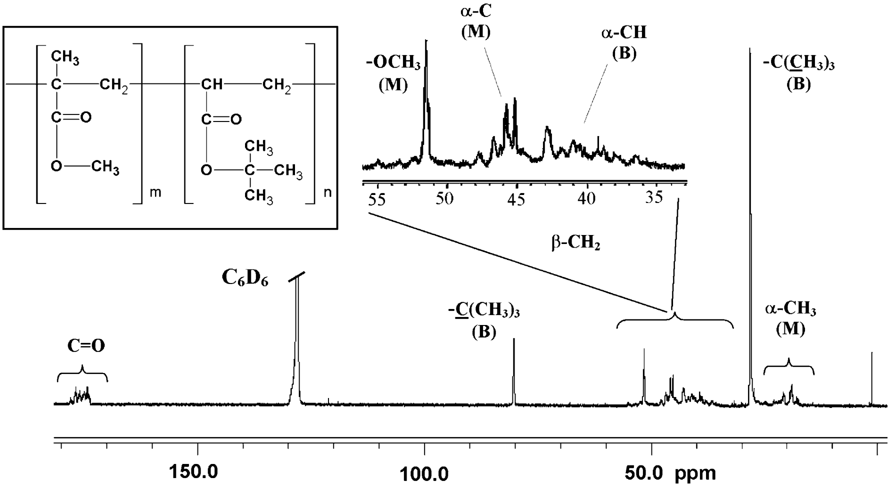

**Fig. 2** 100 MHz $^{13}C$ NMR spectrum of PMMA/*t*BA with $F_M = 0.41$ in benzene-$d_6$

## Carbonyl signal

Figure 3 shows the carbonyl region of the 100 MHz $^{13}$C NMR spectra of PMMA/tBA samples of various composition (Fig. 3b–d) compared with the carbonyl region for respective homopolymers, i.e., PMMA (Fig. 3a) and PtBA (Fig. 3e). As in the case of an analogous copolymer of methyl methacrylate and *n*-butyl acrylate, PMMA-nBA [13] the signal is split at the level of configurational–compositional pentads yielding up to total 272 possible lines.

Microstructural analysis of this signal can be commenced at the triad level. We can utilize the spectral data of carbonyl signals of respective homopolymers, i.e., PMMA [14] and P*t*BA [8]. Based on the data on distribution of configurational sequences in predominantly syndiotactic PMMA [14] (radical polymerization) the following probabilities $P(mm) = 0.02$, $P(\overline{mr}) = 0.34$,. $P(rr) = 0.64$ were used while for the P*t*BA homopolymer [8], the respective values were equal to $P(mm) = 0.19$, $P(\overline{mr}) = 0.45$, $P(rr) = 0.36$. In addition, using the data on copolymer composition (Table 2) obtained from $^{1}$H NMR spectra, the distribution of compositional triads was calculated applying Bernoulli statistics. For the distribution of configurational sequences 1st order Markov as well as Bernoulli statistics was tested. Comparing these two statistics with the experimental values a better fit was found for Bernoullian distribution which is in agreement with observation of de la Fuente et al. [15]; therefore, Bernoulli statistics was finally applied to both composition and configuration. Since the polymerization was carried up to the conversion below 10%, it can be safely assumed that these probabilities can represent the unperturbed proportion of respective sequences in the copolymers obtained. Table 2 lists triad probabilities for all copolymer samples. These values can be used to simulate the spectrum of carbonyl region; however, the position of respective lines in the spectrum should be known. Chemical shifts of all these triads can be calculated incrementally [4], assuming additive influences of neighboring units on the chemical shifts of the carbonyl carbon in a given sequence. Totally, eight independent α-increments should be known as well as two additional parameters, the original positions of respective homopolymer carbonyl signals, $\delta_{0\mathrm{M}}$ and $\delta_{0\mathrm{B}}$ being the centers of carbonyl signals of PMMA and PtBA homopolymers, respectively. They were equal to 177.1 ppm for PMMA [14] and 174.05 ppm for P*t*BA [8], respectively. The values of four α-increments can be obtained from previous studies on the homopolymers, i.e., $\alpha^{\mathrm{M}}_{r\mathrm{M}}$ and $\alpha^{\mathrm{M}}_{m\mathrm{M}}$ for PMMA [14], and $\alpha^{\mathrm{B}}_{r\mathrm{B}}$ and $\alpha^{\mathrm{B}}_{m\mathrm{B}}$ for P*t*BA [8] (Table 3). The remaining four α-increments (Table 3) were derived from the copolymer spectra, for example:

$$\delta_{\mathrm{B}r\mathrm{M}r\mathrm{B}} = \delta_{0\mathrm{M}} + 2\alpha^{\mathrm{M}}_{r\mathrm{B}} \quad \alpha^{\mathrm{M}}_{r\mathrm{B}} = \frac{\delta_{\mathrm{B}r\mathrm{M}r\mathrm{B}} - \delta_{0\mathrm{M}}}{2}$$

$$\delta_{\mathrm{M}r\mathrm{B}r\mathrm{M}} = \delta_{0\mathrm{B}} + 2\alpha^{\mathrm{B}}_{r\mathrm{M}} \quad \alpha^{\mathrm{B}}_{r\mathrm{M}} = \frac{\delta_{\mathrm{M}r\mathrm{B}r\mathrm{M}} - \delta_{0\mathrm{B}}}{2}.$$

Table 2 shows the chemical shifts of all the configurational–compositional triads calculated incrementally as well as probabilities of individual sequences, representing their relative intensities.

**Fig. 3** 100 MHz $^{13}$C NMR spectra of carbonyl signal of PMMA (**a**) and P*t*BA (**e**) homopolymers and PMMA/*t*BA copolymer in benzene-d$_6$ with $F_M$: 0.63 (**b**), 0.41 (**c**), 0.31 (**d**)

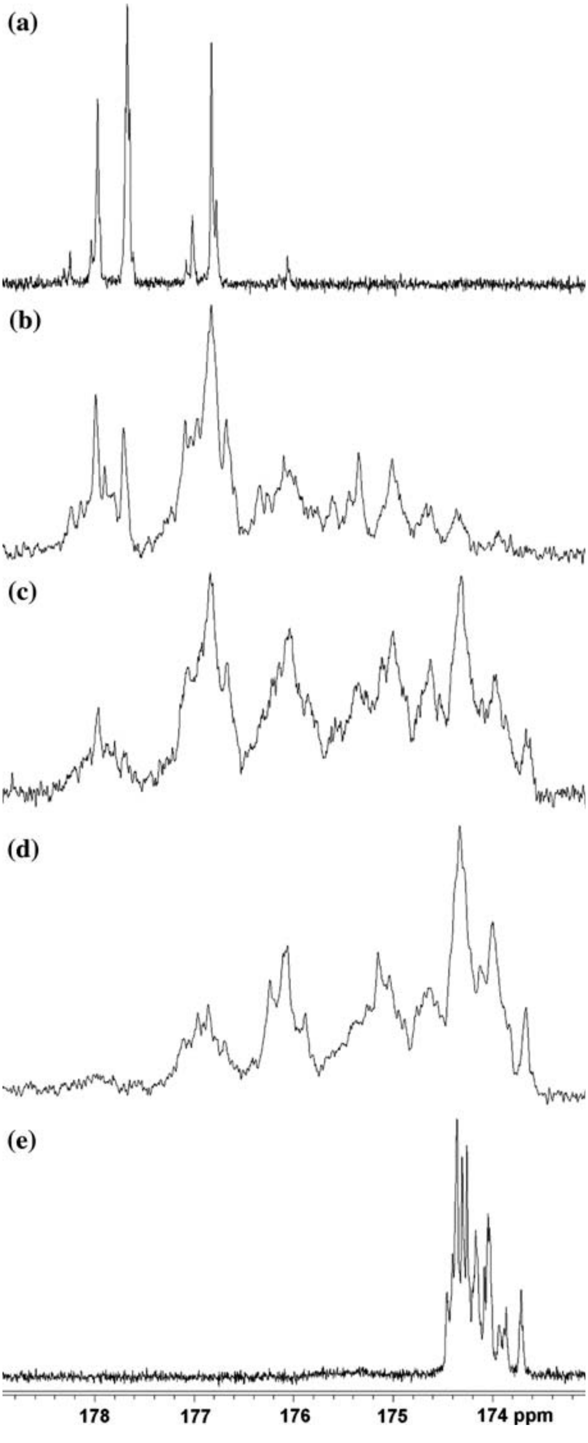

**Table 2** Probabilities of configurational–compositional triads of PMMA/*t*BA calculated according to Bernoulli statistics and chemical shifts calculated incrementally

| Sequence | Probability | | | $\delta$ (ppm) |
|---|---|---|---|---|
| | $F_{\mathrm{M}} = 0.31$ | $F_{\mathrm{M}} = 0.41$ | $F_{\mathrm{M}} = 0.64$ | |
| $P(\mathrm{B}m\mathrm{B}m\mathrm{B})$ | 0.0565 | 0.0353 | 0.0080 | 174.25 |
| $P(\overline{\mathrm{B}m\mathrm{B}r\mathrm{B}})$ | 0.1595 | 0.0997 | 0.0226 | 174.13 |
| $P(\mathrm{B}r\mathrm{B}r\mathrm{B})$ | 0.1124 | 0.0702 | 0.0159 | 174.01 |
| $P(\mathrm{B}m\mathrm{M}m\mathrm{B})$ | 0.0224 | 0.0217 | 0.0126 | 176.15 |
| $P(\overline{\mathrm{B}m\mathrm{M}r\mathrm{B}})$ | 0.0702 | 0.0679 | 0.0394 | 176.00 |
| $P(\mathrm{B}r\mathrm{M}r\mathrm{B})$ | 0.0549 | 0.0531 | 0.0308 | 175.86 |
| $P(\overline{\mathrm{M}m\mathrm{B}m\mathrm{B}})$ | 0.0477 | 0.0461 | 0.0268 | 174.43 |
| $P(\overline{\mathrm{M}m\mathrm{B}r\mathrm{B}})$ | 0.0673 | 0.0651 | 0.0378 | 174.31 |
| $P(\overline{\mathrm{M}r\mathrm{B}m\mathrm{B}})$ | 0.0747 | 0.0722 | 0.0419 | 175.14 |
| $P(\overline{\mathrm{M}r\mathrm{B}r\mathrm{B}})$ | 0.1053 | 0.1018 | 0.0591 | 175.02 |
| $P(\overline{\mathrm{M}m\mathrm{M}m\mathrm{B}})$ | 0.0098 | 0.0146 | 0.0218 | 176.18 |
| $P(\overline{\mathrm{M}m\mathrm{M}r\mathrm{B}})$ | 0.0153 | 0.0229 | 0.0341 | 176.04 |
| $P(\overline{\mathrm{M}r\mathrm{M}m\mathrm{B}})$ | 0.0418 | 0.0626 | 0.0931 | 177.06 |
| $P(\overline{\mathrm{M}r\mathrm{M}r\mathrm{B}})$ | 0.0655 | 0.0980 | 0.1457 | 176.91 |
| $P(\mathrm{M}m\mathrm{B}m\mathrm{M})$ | 0.0100 | 0.0150 | 0.0224 | 174.61 |
| $P(\overline{\mathrm{M}m\mathrm{B}r\mathrm{M}})$ | 0.0315 | 0.0471 | 0.0701 | 175.32 |
| $P(\mathrm{M}r\mathrm{B}r\mathrm{M})$ | 0.0246 | 0.0369 | 0.0548 | 176.00 |
| $P(\mathrm{M}m\mathrm{M}m\mathrm{M})$ | 0.0010 | 0.0024 | 0.0094 | 176.22 |
| $P(\overline{\mathrm{M}m\mathrm{M}r\mathrm{M}})$ | 0.0091 | 0.0212 | 0.0806 | 177.10 |
| $P(\mathrm{M}r\mathrm{M}r\mathrm{M})$ | 0.0195 | 0.0452 | 0.1719 | 177.98 |

On the basis of these data, theoretical spectra of carbonyl signal for each copolymer sample were calculated assuming adequate linewidths of the lines. For relatively small linewidth for polymers spectra, say 2 Hz (Fig. 4), it is possible to show clearly the positions of individual lines, while increase of the linewidth value to about 8 Hz (Fig. 5) gives more realistic accordance between the simulated and experimental spectra. However, comparison between the experimental spectra and those simulated at the triad level shows clearly that further splitting, coming from configurational–compositional pentads, should be taken into account. This conclusion is in agreement with the results obtained for respective homopolymers, synthesized by radical polymerization.

In the carbonyl region of 100 MHz $^{13}$C NMR spectrum of both PMMA [14] and P*t*BA [8], clear splitting into pentads and even some heptads are evidently visible. On the basis of the distribution of configurational triads of the homopolymers and copolymer composition from $^{1}$H NMR spectra, the distribution of configurational–compositional pentads was calculated for the PMMA/tBA copolymer samples of different composition (Table A1, see Supporting Information). Chemical shifts of individual configurational-compositional pentads were obtained by incremental calculation, applying $\alpha$-increments given in Table 3 and additional $\beta$-increments, representing the influence of second neighbors removed from the given carbonyl

**Table 3** Values of $\alpha$ and $\beta$ increments (in ppm) used to calculate the chemical shifts of triads and pentads

| $\delta_{0\mathrm{M}} = 177.1$ | $\delta_{0\mathrm{B}} = 174.05$ |
|---|---|
| $\alpha^{\mathrm{M}}_{r\mathrm{M}} = 0.439$ | $\alpha^{\mathrm{B}}_{r\mathrm{B}} = -0.019$ |
| $\alpha^{\mathrm{M}}_{m\mathrm{M}} = -0.439$ | $\alpha^{\mathrm{B}}_{m\mathrm{B}} = 0.098$ |
| $\alpha^{\mathrm{M}}_{r\mathrm{B}} = -0.620$ | $\alpha^{\mathrm{B}}_{r\mathrm{M}} = 0.995$ |
| $\alpha^{\mathrm{M}}_{m\mathrm{B}} = -0.472$ | $\alpha^{\mathrm{B}}_{m\mathrm{M}} = 0.280$ |
| $\beta^{\mathrm{M}}_{r\mathrm{M}r\mathrm{M}} = -0.149$ | $\beta^{\mathrm{B}}_{r\mathrm{B}r\mathrm{B}} = 0.148$ |
| $\beta^{\mathrm{M}}_{m\mathrm{M}r} = -0.166$ | $\beta^{\mathrm{B}}_{m\mathrm{B}r\mathrm{B}} = 0.106$ |
| $\beta^{\mathrm{M}}_{r\mathrm{M}m\mathrm{M}} = 0.149$ | $\beta^{\mathrm{B}}_{r\mathrm{B}m\mathrm{B}} = -0.148$ |
| $\beta^{\mathrm{M}}_{m\mathrm{M}m\mathrm{M}} = 0.135$ | $\beta^{\mathrm{B}}_{m\mathrm{B}m\mathrm{B}} = -0.106$ |
| $\beta^{\mathrm{M}}_{r\mathrm{B}r\mathrm{M}} = 0.057$ | $\beta^{\mathrm{B}}_{r\mathrm{M}r\mathrm{M}} = -0.098$ |
| $\beta^{\mathrm{M}}_{m\mathrm{B}r\mathrm{M}} = 0.081$ | $\beta^{\mathrm{B}}_{m\mathrm{M}r\mathrm{M}} = -0.045$ |
| $\beta^{\mathrm{M}}_{r\mathrm{B}m\mathrm{M}} = -0.136$ | $\beta^{\mathrm{B}}_{r\mathrm{B}r\mathrm{M}} = -0.002$ |
| $\beta^{\mathrm{M}}_{m\mathrm{B}m\mathrm{M}} = -0.192$ | $\beta^{\mathrm{B}}_{m\mathrm{B}r\mathrm{M}} = 0.003$ |
| $\beta^{\mathrm{M}}_{r\mathrm{M}r\mathrm{B}} = 0.005$ | $\beta^{\mathrm{B}}_{r\mathrm{M}m\mathrm{M}} = 0.235$ |
| $\beta^{\mathrm{M}}_{m\mathrm{M}r\mathrm{B}} = -0.005$ | $\beta^{\mathrm{B}}_{m\mathrm{M}m\mathrm{M}} = 0.108$ |
| $\beta^{\mathrm{M}}_{r\mathrm{B}r\mathrm{B}} = -0.007$ | $\beta^{\mathrm{B}}_{r\mathrm{B}m\mathrm{M}} = 0.004$ |
| $\beta^{\mathrm{M}}_{m\mathrm{B}r\mathrm{B}} = -0.010$ | $\beta^{\mathrm{B}}_{m\mathrm{B}m\mathrm{M}} = -0.008$ |
| $\beta^{\mathrm{M}}_{r\mathrm{M}m\mathrm{B}} = 0.050$ | $\beta^{\mathrm{B}}_{r\mathrm{M}r\mathrm{B}} = 0.013$ |
| $\beta^{\mathrm{M}}_{m\mathrm{M}m\mathrm{B}} = -0.054$ | $\beta^{\mathrm{B}}_{m\mathrm{M}r\mathrm{B}} = 0.006$ |
| $\beta^{\mathrm{M}}_{r\mathrm{B}m\mathrm{B}} = -0.076$ | $\beta^{\mathrm{B}}_{r\mathrm{M}m\mathrm{B}} = 0.131$ |
| $\beta^{\mathrm{M}}_{m\mathrm{B}m\mathrm{B}} = -0.108$ | $\beta^{\mathrm{B}}_{m\mathrm{M}m\mathrm{B}} = 0.060$ |

group. From the previously presented pentad analysis of carbonyl signal of PMMA [14], the following $\beta$-increments were utilized: $\beta^{\mathrm{M}}_{r\mathrm{M}r\mathrm{M}}$, $\beta^{\mathrm{M}}_{m\mathrm{M}r\mathrm{M}}$, $\beta^{\mathrm{M}}_{r\mathrm{M}m\mathrm{M}}$, $\beta^{\mathrm{M}}_{m\mathrm{M}m\mathrm{M}}$, while the analysis of pentads in P*t*BA [8] provided next four $\beta$-increments: $\beta^{\mathrm{B}}_{r\mathrm{B}r\mathrm{B}}$, $\beta^{\mathrm{B}}_{m\mathrm{B}r\mathrm{B}}$, $\beta^{\mathrm{B}}_{r\mathrm{B}m\mathrm{B}}$, $\beta^{\mathrm{B}}_{m\mathrm{B}m\mathrm{B}}$. The remaining $\beta$-increments (Table 3) were calculated from copolymer spectra utilizing well-defined lines, for example:

$$\delta_{\mathrm{B}r\mathrm{B}r\mathrm{M}r\mathrm{B}r\mathrm{B}} = \delta_{0M} + 2\alpha^{\mathrm{M}}_{r\mathrm{B}} + 2\beta^{\mathrm{M}}_{r\mathrm{B}r\mathrm{B}} \quad \beta^{\mathrm{M}}_{r\mathrm{B}r\mathrm{B}} = \frac{\delta_{\mathrm{B}r\mathrm{B}r\mathrm{M}r\mathrm{B}r\mathrm{B}} - \delta_{0\mathrm{M}} - 2\alpha^{\mathrm{M}}_{r\mathrm{B}}}{2}$$

$$\delta_{\mathrm{M}r\mathrm{M}r\mathrm{B}r\mathrm{M}r\mathrm{M}} = \delta_{0\mathrm{B}} + 2\alpha^{B}_{r\mathrm{M}} + 2\beta^{B}_{r\mathrm{M}r\mathrm{M}} \quad \beta^{\mathrm{B}}_{r\mathrm{M}r\mathrm{M}} = \frac{\delta_{\mathrm{M}r\mathrm{M}r\mathrm{B}r\mathrm{M}r\mathrm{M}} - \delta_{0\mathrm{B}} - 2\alpha^{\mathrm{B}}_{r\mathrm{M}}}{2}.$$

The values of some $\beta$-increments were estimated based on comparison with analogous increments determined for analogous copolymer of methyl methacrylate and ethyl acrylate, PMMA-EA [16] (Table 3). Table A1 (see Supporting Information) lists the probabilities of configurational–compositional pentads and chemical shifts of individual sequences, calculated using increments listed in Table 3. These data were used to simulate the carbonyl region of $^{13}$C NMR spectra of PMMA/*t*BA copolymer (Fig. 6). Application of the linewidth of 8 Hz provided very good agreement between simulated and experimental spectra of all copolymer samples of different composition (Fig. 6). The observed discrepancies are probably due to slight conformational differences between individual sequences leading to

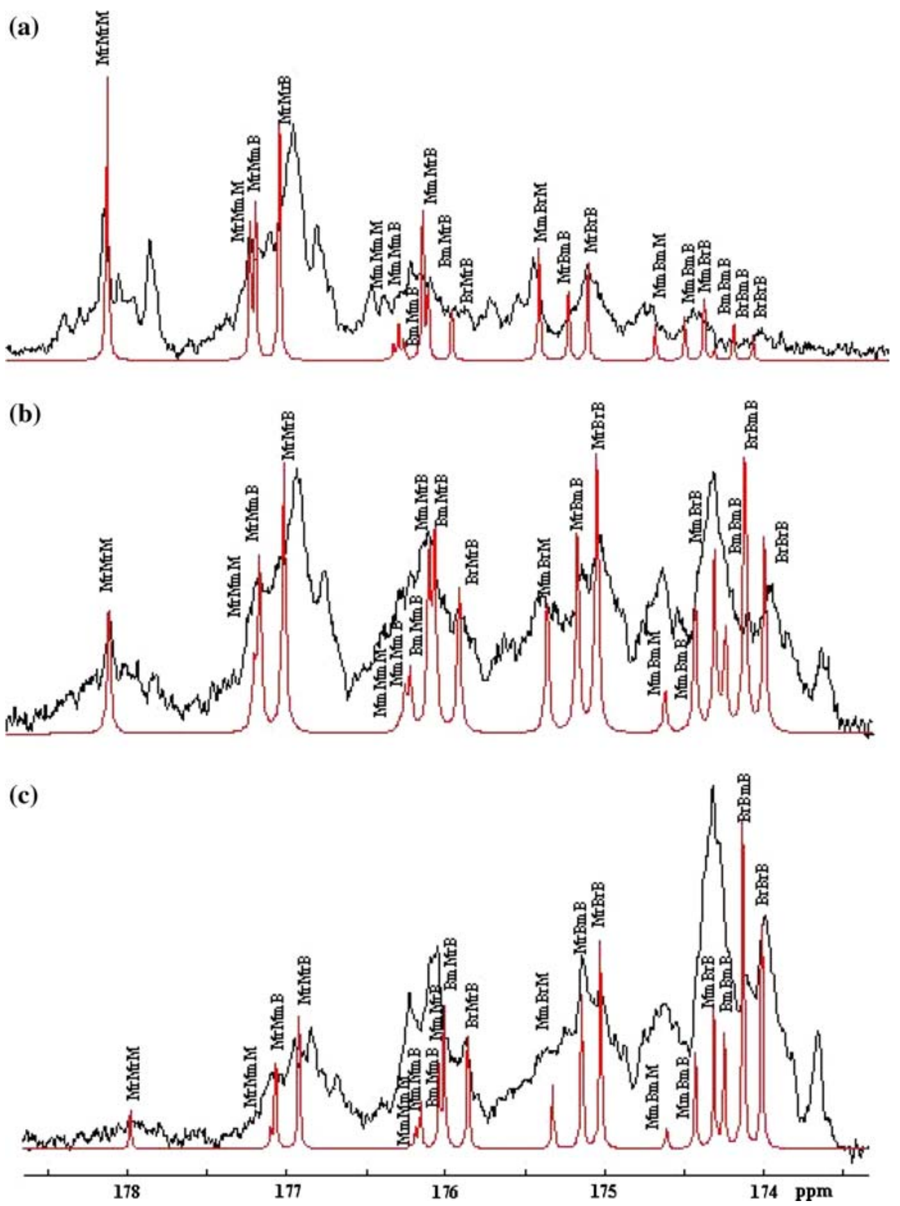

**Fig. 4** Simulation of the carbonyl signal of PMMA/*t*BA at the triad level using Bernoullian statistics and 2 Hz linewidth, $F_{\mathrm{M}}$: 0.64 (**a**), 0.41 (**b**), and 0.31 (**c**)

nonlinearity of the incremental calculations. In this way, based on the analysis of carbonyl region in the 100 MHz $^{13}$C NMR spectra of PMMA/*t*BA copolymer, it was possible to determine distribution of odd sequences at the level of configurational–compositional pentads.

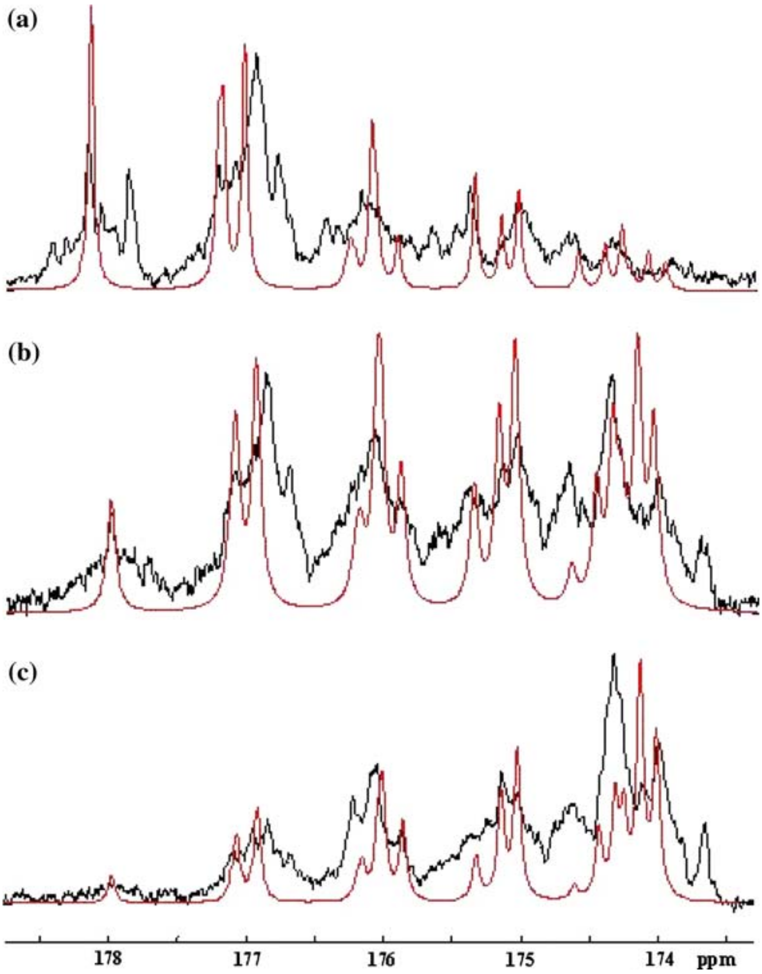

**Fig. 5** Simulation of the carbonyl signal of PMMA/*t*BA at the triad level for linewidth of 8 Hz, $F_M$: 0.64 (**a**), 0.41 (**b**), and 0.31 (**c**)

## Methylene carbon $\beta$-$CH_2$

In the 100 MHz $^{13}C$ NMR spectrum of PMMA/*t*BA recorded in deuterated benzene at 40 °C, the lines of $\beta$-$CH_2$ carbons are distributed over very large region of about 20 ppm from 35 to 56 ppm. These signals are, however, superimposed with the signals of the *tert*-butyl $\alpha$-CH carbons of the acrylate units at about 42 ppm, with $\alpha$-C carbons of the methyl methacrylate units at about 45 ppm and with the $-OCH_3$ carbons of the methyl methacrylate units at about 51.5 ppm (Fig. 2). Microstructural analysis of $\beta$-$CH_2$ signals requires separate recording of these signals alone, for example by means of DEPT technique. Therefore, for the sample of PMMA/*t*BA with $F_M = 0.41$ the DEPT 45 (Fig. 7a) and DEPT 135 (Fig. 7b) spectra were

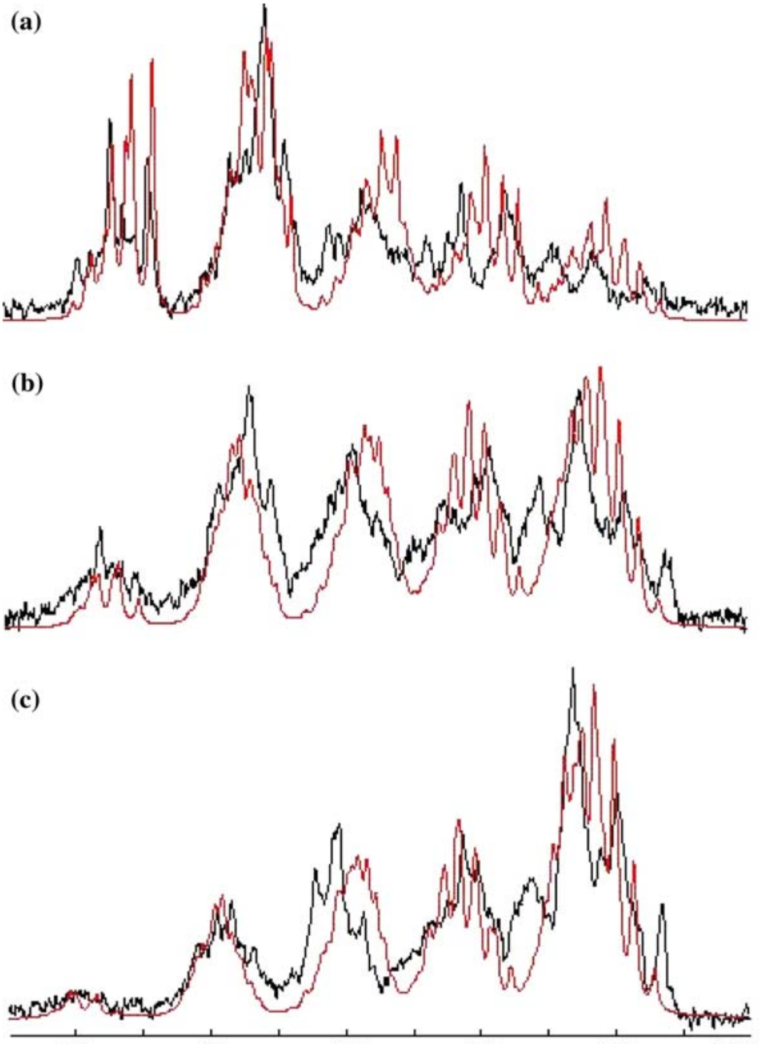

**Fig. 6** Simulation of the carbonyl signal of PMMA/*t*BA at the pentad level using 8 Hz linewidth, $F_M$: 0.64 (**a**), 0.41 (**b**), and 0.31 (**c**)

recorded with subsequent edition applying subtraction of DEPT135 spectrum from DEPT45 yielding a spectrum containing only positive $\beta$-$CH_2$ signals (Fig. 7c). Figure 7 shows clear splitting of these signals coming from the microstructural effects at the level of configurational–compositional tetrads. As in the case of carbonyl signal, the analysis of $\beta$-$CH_2$ splittings can be performed by attribution of respective sequences to individual lines aided by incremental calculation of their chemical shifts and sequence probabilities derived from Bernoulli statistics, subsequently verified by spectra simulation.

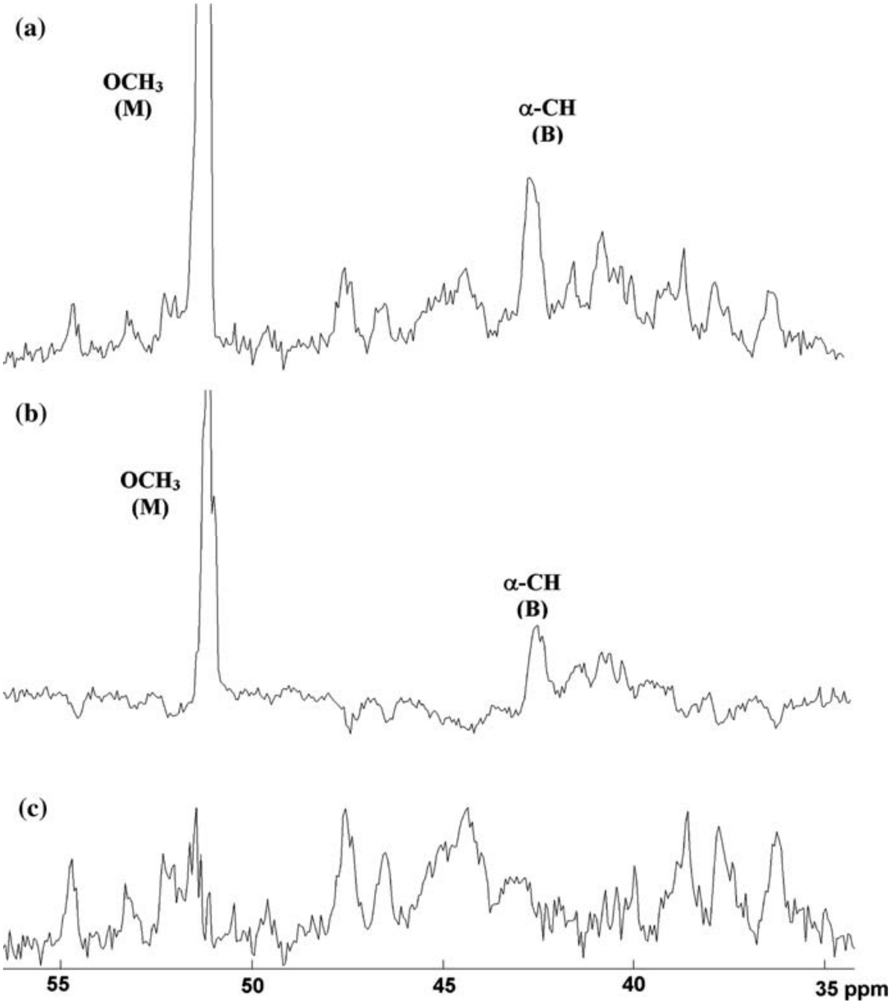

**Fig. 7** DEPT spectra of the methylene carbons of PMMA/*t*BA with $F_{\mathrm{M}} = 0.41$. (**a**) All signals positive, (**b**) $CH_3$ and CH positive, $CH_2$ negative, and (**c**) $\beta$-$CH_2$ sub-spectrum

On the basis of the distribution of configurational sequences in PMMA [14]: $P(mm) = 0.02$, $P(\overline{mr}) = 0.34$, $P(rr) = 0.64$ as well as P*t*BA [8] (obtained by radical polymerization): $P(mm) = 0.19$, $P(\overline{mr}) = 0.45$, $P(rr) = 0.36$ for the sample PMMA/tBA featuring $F_{\mathrm{M}} = 0.41$ the diad and tetrad probabilities were calculated applying the Bernoullian statistics both to configurational and compositional sequences and these values are presented in Table A2 (see Supporting Information). To calculate incrementally the chemical shifts of possible 72 individual configurational–compositional tetrads, it is necessary to determine 4 α-increments and 16 $\beta$-increments. The additional necessary parameter, the origin of the methylene signal, $\delta_0$, was assumed to be the centre of the $\beta$-$CH_2$ region equal to 45.0 ppm. The α-increments (Table 4) were determined from the copolymer spectra inspecting

**Table 4** Values of $\alpha$ and $\beta$ increments (in ppm) used to calculate the chemical shifts of diads and tetrads

| $\delta_0 = 45.0$ | |
|---|---|
| $\alpha_{mB} = -2.75$ | $\alpha_{mM} = 3.50$ |
| $\alpha_{rB} = -3.30$ | $\alpha_{rM} = 3.70$ |
| $\beta_{mBmB} = -1.15$ | $\beta_{mMmB} = -0.55$ |
| $\beta_{mBrB} = -0.95$ | $\beta_{mMrB} = -1.40$ |
| $\beta_{mBmM} = 0.50$ | $\beta_{mMmM} = 0.90$ |
| $\beta_{mBrM} = 0.40$ | $\beta_{mMrM} = 0.08$ |
| $\beta_{rBmB} = -2.25$ | $\beta_{rMmB} = -0.40$ |
| $\beta_{rBrB} = -1.40$ | $\beta_{rMrB} = -1.70$ |
| $\beta_{rBmM} = 0.60$ | $\beta_{rMmM} = 1.35$ |
| $\beta_{rBrM} = 1.01$ | $\beta_{rMrM} = 1.16$ |

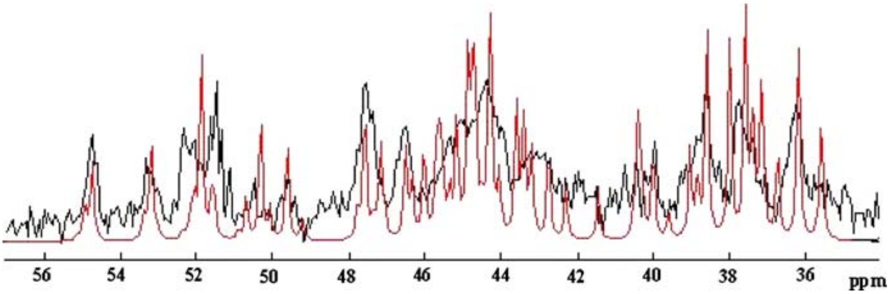

**Fig. 8** Simulation of the $\beta$-CH$_2$ signal of PMMA/*t*BA at the tetrad level using Bernoullian statistics and 8 Hz linewidth, $F_M = 0.41$

the outermost parts of the methylene region and identifying the homosequences by comparison with the spectra of respective homopolymers, for example:

$$\delta_{BmB} = \delta_0 + 2\alpha_{mB} \quad \alpha_{mB} = \frac{\delta_{BmB} - \delta_0}{2}$$

$$\delta_{MrM} = \delta_0 + 2\alpha_{rM} \quad \alpha_{rM} = \frac{\delta_{MrM} - \delta_0}{2}.$$

The $\beta$-increments (Table 4) were determined from the copolymer spectra employing the distribution of configurational–compositional tetrads, for example:

$$\delta_{BmBmBmB} = \delta_0 + 2\alpha_{mB} + 2\beta_{mBmB} \quad \beta_{mBmB} = \frac{\delta_{BmBmBmB} - 2\alpha_{mB} - \delta_0}{2}$$

$$\delta_{MrMrMrM} = \delta_0 + 2\alpha_{rM} + 2\beta_{rMrM} \quad \beta_{rMrM} = \frac{\delta_{MrMrMrM} - 2\alpha_{rM} - \delta_0}{2}$$

Since unequivocal determination of positions of some tetrads was difficult to achieve based on the copolymer spectrum alone, the values of them were estimated using literature data for analogous increments in analogous copolymer of methyl methacrylate and ethyl acrylate, PMMA-EA [4] (Table 4). The tetrad probabilities calculated according to Bernoulli statistics for both configurational and compositional sequences and chemical shifts calculated using thus obtained increments (Table A2, see Supporting Information) were used to simulate the spectrum of $\beta$-$CH_2$ methylene region. Applying linewidth of 8 Hz gave good agreement between the experimental and simulated spectra (Fig. 8) and confirmed the proposed line assignment. It may be observed that fitting of carbonyl signals was better to that of $\beta$-$CH_2$ methylene ones and moreover the presence of some additional lines may be explained in terms of further hexad splitting of some tetrads.

## Conclusions

Splittings of the carbonyl signal in the 100 MHz $^{13}C$ NMR spectrum of the PMMA/*t*BA copolymer can be attributed to the odd configurational–compositional sequences at the pentad level. The configurational effects of both comonomers, methyl methacrylate and *tert*-butyl acrylate, can be observed at the pentad level. The splittings of the methylene $\beta$-$CH_2$ signal can be attributed to the even configurational–compositional sequences and the configurational effects of both comonomers can be observed at the tetrad level. It was shown that for these signals the attribution of the lines of individual sequences can be performed based on the incremental calculations of chemical shifts which were confirmed by spectral simulation yielding quite good agreement between the experimental and simulated spectra.

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