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Distribution of configurational sequences in poly(*n*-butyl methacrylate) by ^{13}C NMR spectroscopy

Abstract. *Microstructural analysis of macromolecular chain of poly(n-butyl methacrylate) was performed using ^{13}C NMR spectroscopy. The samples of PnBuMA, were synthesized in two ways: free radical polymerization and anionic polymerization. The 100 MHz ^{13}C NMR spectra of this homopolymer were recorded in deutereted chloroform. The carbonyl signal in the region from 175.5 to 178.5 ppm was found to be sensitive to chain configuration at the heptad level, while the β-methylene signal of the carbon chain (49.0–55.0 ppm) was split up to configurational hexads.*

WYKORZYSTANIE SPEKTROSKOPII ^{13}C NMR DO BADANIA ROZKŁADU SEKWENCJI KONFIGURA-CYJNYCH POLI(AKRYLANU N-BUTYLU)

Streszczenie. *Badania mikrostruktury poli(metakrylanu n-butylu) przeprowadzono z wykorzystaniem spektroskopii ^{13}C NMR. Próbki PnBuMA uzyskano na drodze polimeryzacji wolnorodnikowej i anionowej. Widma 100 MHz ^{13}C NMR homopolimeru metakrylanu n-butylu zarejestrowano w deuterowanym chloroformie. Sygnał karbonylowy w zakresie od 175,5 do 178,5 ppm, jest czuły na efekty konfiguracyjne na poziomie heptad, natomiast sygnał węgli metylenowych z łańcucha głównego (49,0 – 55,0 ppm) rozszczepia się na poziomie heksad konfiguracyjnych.*

INTRODUCTION

Chiral carbon in the main chain of acrylic polymers introduces configurational differentiation in the structure of the polymer repeating units enchainment. This phenomenon leads to significant changes in the physical properties of the polymers with different configurational preferences. Nuclear magnetic resonance spectroscopy, NMR, can provide information on different configurations of segments of macromolecular chain expressed in statistical terms of distribution of configurational sequences. From the spectroscopic point of view two signals in the ^{13}C NMR spectra of acrylic polymers are of predominant interest: the carbonyl and methylene (β-CH$_2$) carbons since they are present in all typical acrylic structures.

Precise assignment of individual lines to respective sequences is important in detailed analysis, especially, when longer sequences are taken into account. The correctness of the attribution can be verified by spectral simulation, however, the intensity and exact position of a line representing given sequence has to be known. Relative intensities may be calculated assuming Bernoulli or Markov distribution, while the values of chemical shifts may be determined by incremental calculations, and such an approach has been shown effective in the study of both carbonyl and β-CH$_2$ signals. Information on sequence distribution of a homopolymer is very important in the subsequent analysis of the copolymers containing the same (meth)acrylate repeating units and provide indications on configuration of the macromolecular chain of the respective copolymers and starting parameters in simulation of their spectra [1-4].

EXPERIMENTAL

The first sample of poly(*n*-butyl methacrylate) homopolymer, P*n*BuMA, was prepared by radical polymerization in solution [1, 2]. The monomer was poured into butan-2-one to obtain 40 wt % mixture and was heated up to 78 °C. Then azobisisobutyronitrile (AIBN) was added as radical initiator (0.5 wt % with respect to the total solution). The polymerization mixture was diluted with acetone and poured into a large volume of a water-methanol mixture to precipitate the polymer. It was washed with methanol and vacuum dried to constant weight.

The second sample of isotactic poly(*n*-butyl methacrylate) was prepared by anionic polymerization initiated by *n*-butyllithium (2.5 M in hexane). The monomer/solvent (hexane) weight ratio was 1/2.5 and the monomer initiator molar ratio was 1/50. The polymerization was carried out at -80 °C for 3 hours. After reaction the polymer was precipitated from methanol–water mixture and vacuum dried at 80 °C to constant weight [1].

The 100 MHz ^{13}C NMR spectra were recorded with a Bruker AM 400 spectrometer at 40°C, using sample concentration of 10% (w/v) in CDCl$_3$ as a solvent. Good signal to noise ratio was obtained for about 12000 scans, with a 4 s delay. Simulations of the NMR spectra were performed using our own software written in Matlab environment (*MathWorks, Inc.*). [2-4].

RESULTS AND DISCUSSION

The carbonyl signal of PnBuMA

In the ^{13}C NMR spectrum of syndiotactic P*n*BuMA homopolymer the carbonyl and the β-methylene signals are present in a well separated regions at about 177.5 ppm and 53.5 ppm, respectively (Fig. 1).

Microstructure analysis of acrylic polymers is usually based on their ^{13}C NMR spectra recorded in CDCl₃. The carbonyl signal of *n*-butyl methacrylate homopolymer exhibit good resolution in CDCl₃ (Fig. 2). The figure 2a shows the carbonyl signal of the polymer obtained by anionic polymerization. This signal indicates that the synthesized polymer is highly isotactic. Integration of the carbonyl band yields high content of *mm* triads, and residual values of *rr* and *rm* triads. Due to high isotactic purity, attribution of the signals, except for the *mmmm* line, cannot be done unequivocally. Therefore, detailed analysis of the carbonyl signal has been carried out for the syndiotactic chain of P*n*BuMA obtained via radical polymerization (Fig. 2b). Tacticity of this P*n*BuMA homopolymer can be determined based on the splitting of the carbonyl signal at about 177.5 ppm. The values of probabilities of configurational triads obtained in this way for the radically synthesized homopolymer are equal to P(*rr*) = 0.63, P(*mm*) = 0.02 and P(*mr*) = 0.35 which confirms its predominantly syndiotactic configuration of macromolecular chain [2-4]. Triad probabilities for the syndiotactic sample can be readily obtained by simple integration since the signals are baseline resolved. Probabilities of some pentads, namely the *rr*-centred ones, could be also obtained in this way, however, Fig. 2b reveals that the carbonyl signals exhibit lines of longer sequences, up to heptads. To attribute individual heptad lines and derive

Table 1. Probabilities of odd configurational sequences of syndiotactic P*n*BuMA according to 1ˢᵗ order Markov statistics and chemical shifts calculated incrementally

| Probability	First-order Markov	Chemical shift, δ [ppm]
P($\overline{mmmmmm}$)	0.00001	176.28
P($\overline{rmmmrr}$)	0.00270	176.09
P($\overline{mrmmrr}$)	0.00551	175.91
P($\overline{rrmmrr}$)	0.01007	175.96
P($\overline{rmmrmr}$)	0.00627	177.16
P($\overline{mmmmrr}$)	0.00237	176.86
P($\overline{rmmrrm}$)	0.00551	176.88
P($\overline{rmmrrr}$)	0.02013	176.83
P($\overline{mrmrmr}$)	0.01279	176.98
P($\overline{rrmrmm}$)	0.00551	177.09
P($\overline{rrmrmr}$)	0.04676	176.91
P($\overline{mrmrrm}$)	0.01123	176.64
P($\overline{mrmrrr}$)	0.04104	176.59
P($\overline{rrmrrm}$)	0.04104	176.75
P($\overline{rrmrrr}$)	0.15003	176.70
P($\overline{mmmrmr}$)	0.00551	178.16
P($\overline{rmrrmr}$)	0.02338	178.10
P($\overline{mrrrmm}$)	0.00483	177.88
P($\overline{rrrrmm}$)	0.01767	177.83
P($\overline{mrrrmr}$)	0.04104	177.82
P($\overline{rrrrmr}$)	0.15003	177.77
P($\overline{mrrrrm}$)	0.01801	177.54
P($\overline{mrrrrr}$)	0.13169	177.49
P($\overline{rrrrrr}$)	0.24071	177.44
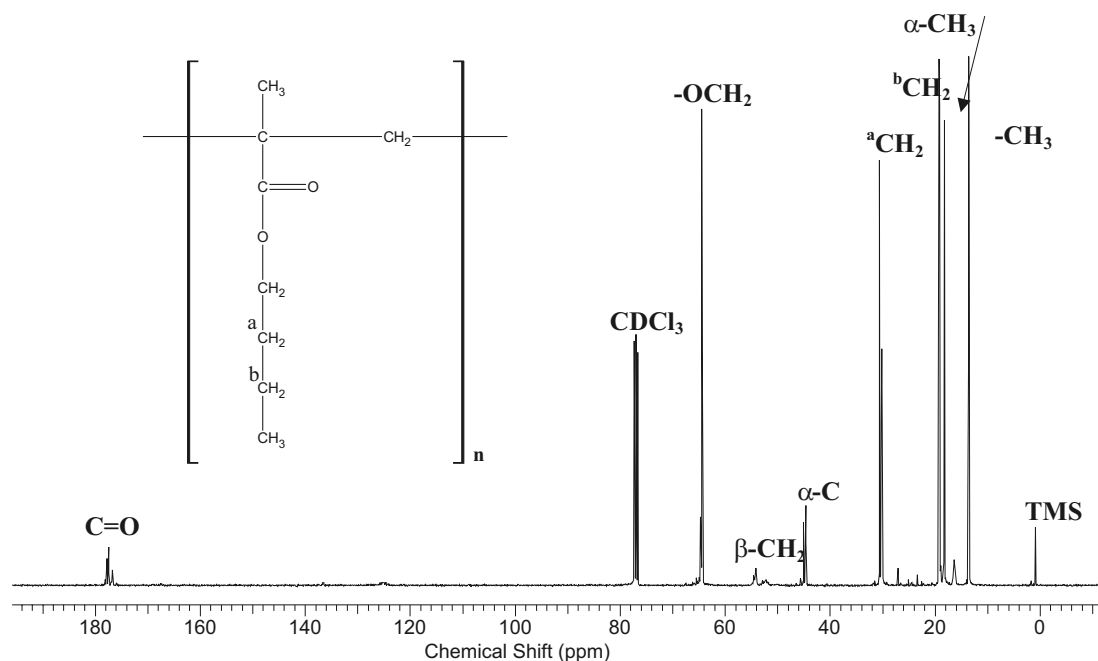
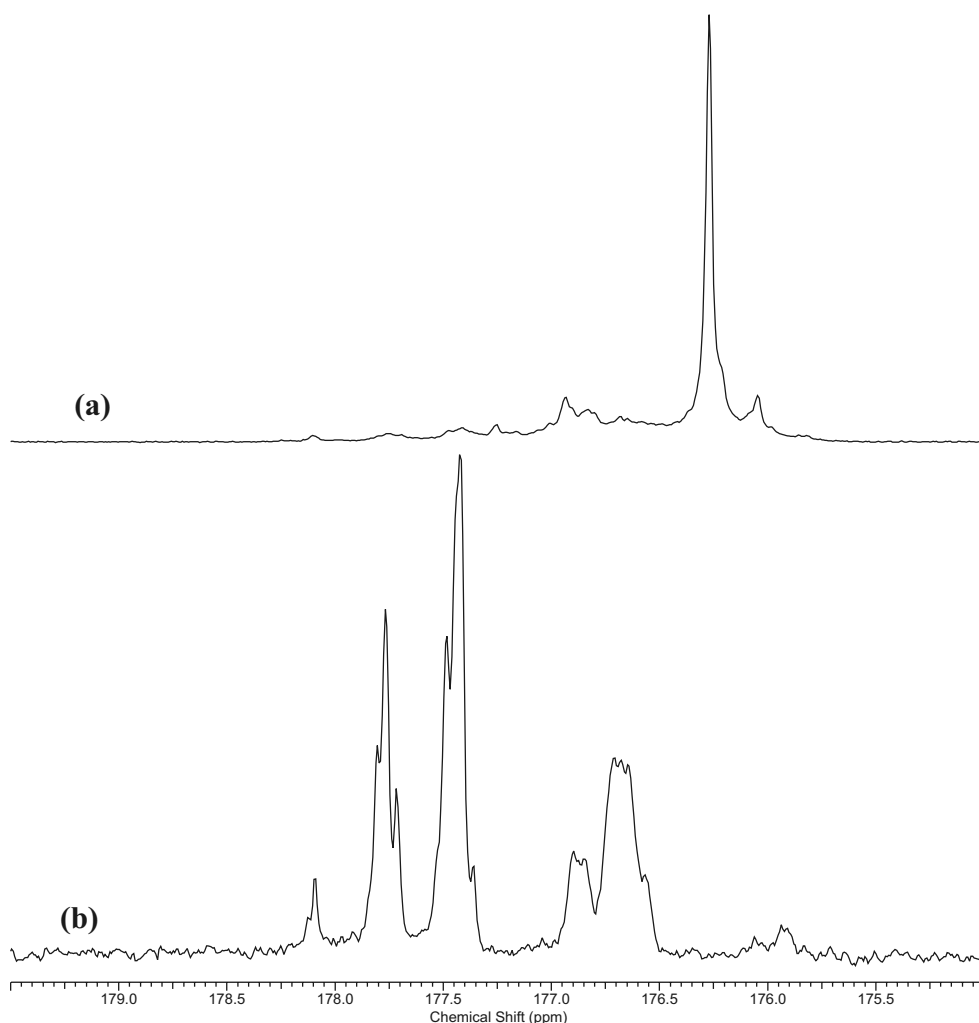*Figure 1. 100 MHz ^{13}C NMR spectrum of syndiotactic PnBuMA homopolymer in CDCl₃*

Figure 2. *The carbonyl signal of PnBuMA homopolymer of the 100 MHz ^{13}C NMR spectra recorded in chloroform-d (a) isotactic polymer (b) syndiotactic polymer*

their intensities we have applied computer simulation of the spectrum.

The values of chemical shifts of individual heptads are listed in Table 1. The sequence probabilities and line positions can be used as starting parameters to calculate the simulated spectrum of the carbonyl region. Figure 3a presents the simulated spectrum obtained for relatively narrow lines of 1 Hz, just to show the positions of individual lines. It can be seen from this figure that incremental calculations of chemical shifts yields fairly good positions of the lines, however, the line intensities taken from 1st order Markov statistics do not provide exact match. Figure 3b shows the position of the heptads with the correction of the position of some of the individual lines. To obtain a better fit of the simulated spectrum to the experimental spectrum three heptads: *rrmrrr, rrrrmr* and *rrrrrr* separated into several nonads: *rrrmrrrr, rrrmrrrm + mrrmrrrr, rrrrrmrr, rrrrrmrm + mrrrrrmrr* and *rrrrrrrr, rrrrrrrm + mrrrrrrr* (Fig. 3c). Nevertheless, general agreement between the experimental and simulated spectra can be re-

garded as a confirmation of the proposed sequence attribution. The increase of the linewidth of the individual simulated lines to 2.5 Hz give quite good match between the experimental and simulated spectra (Fig. 3d).

Attribution of the individual heptad/nonads resulting from the final simulation of the carbonyl signal is presented in Figure 4.

The β-methylene signal of PnBuMA

The signal of the backbone β-CH$_2$ carbon in the (meth)acrylate chain is also of great interest in microstructure determination, especially for acrylate-methacrylate copolymers [1]. The chemical shift of β-CH$_2$ signals in acrylate unit (at about 35 ppm) and methacrylate one (at about 53.5 ppm) observed in the homopolymers are separated by about 8 ppm.

The β-CH$_2$ signal of poly(*n*-butyl methacrylate) displays good resolution in CDCl$_3$ (Fig. 5). The figure 5a shows the carbonyl signal of the isotactic polymer. Inte-
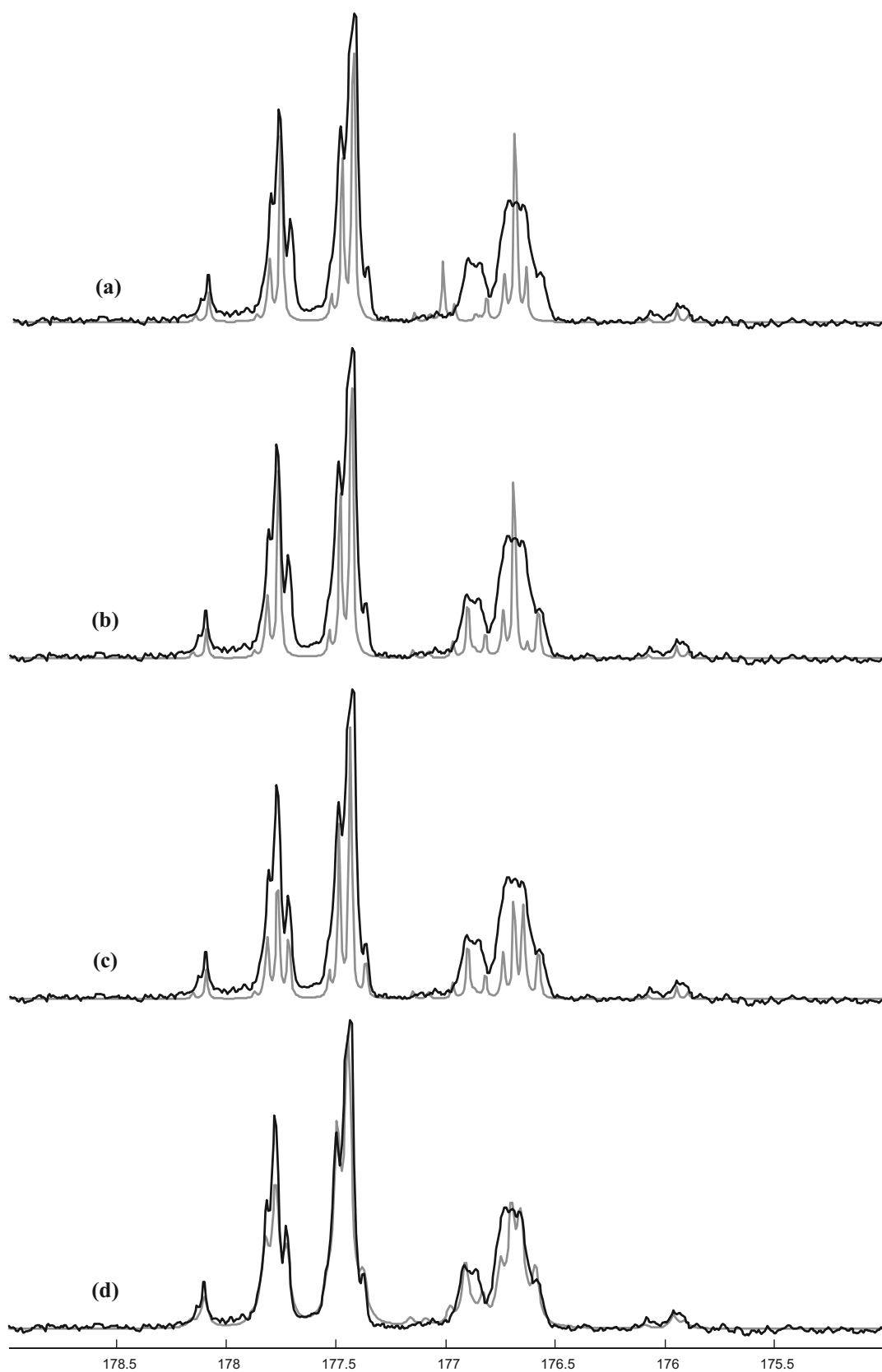
Figure 3. *Simulation of the carbonyl signal of syndiotactic PnBuMA in CDCl$_3$ using 1st order Markov statistics and incremental calculation of chemical shifts (linewidth 1 Hz) (a), with the correction of heptad positions (linewidth 1 Hz) (b), with the correction of heptad-nonad positions (linewidth 1 Hz) (c), with the correction of heptad-nonad positions (linewidth 2.5 Hz) (d)*
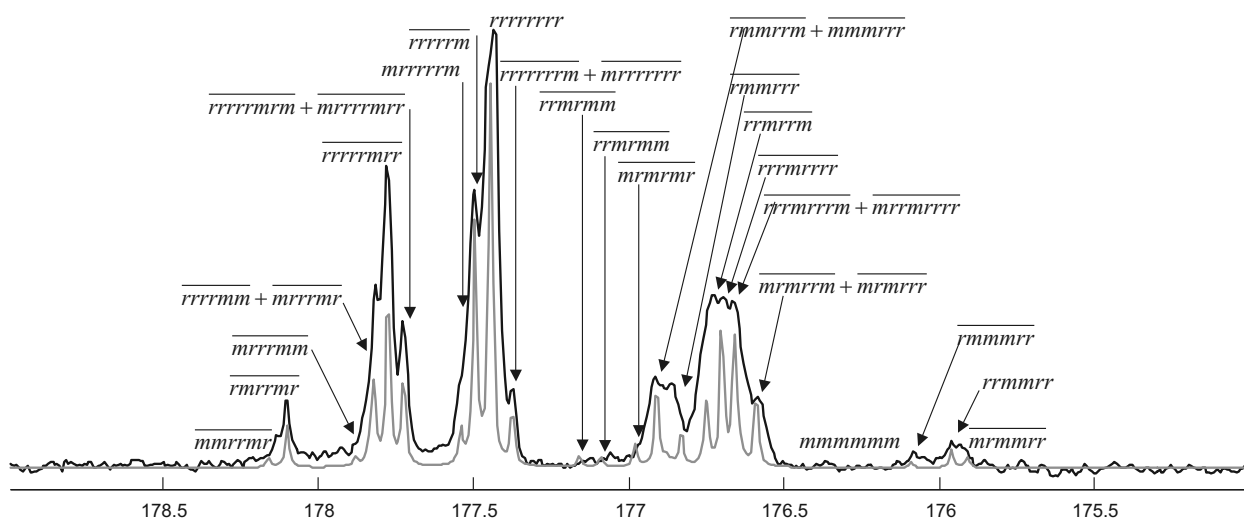
Figure 4. *Attribution of the individual heptad/nonads resulting from the final simulation of the carbonyl signal of syndiotactic PnBuMA polymer*
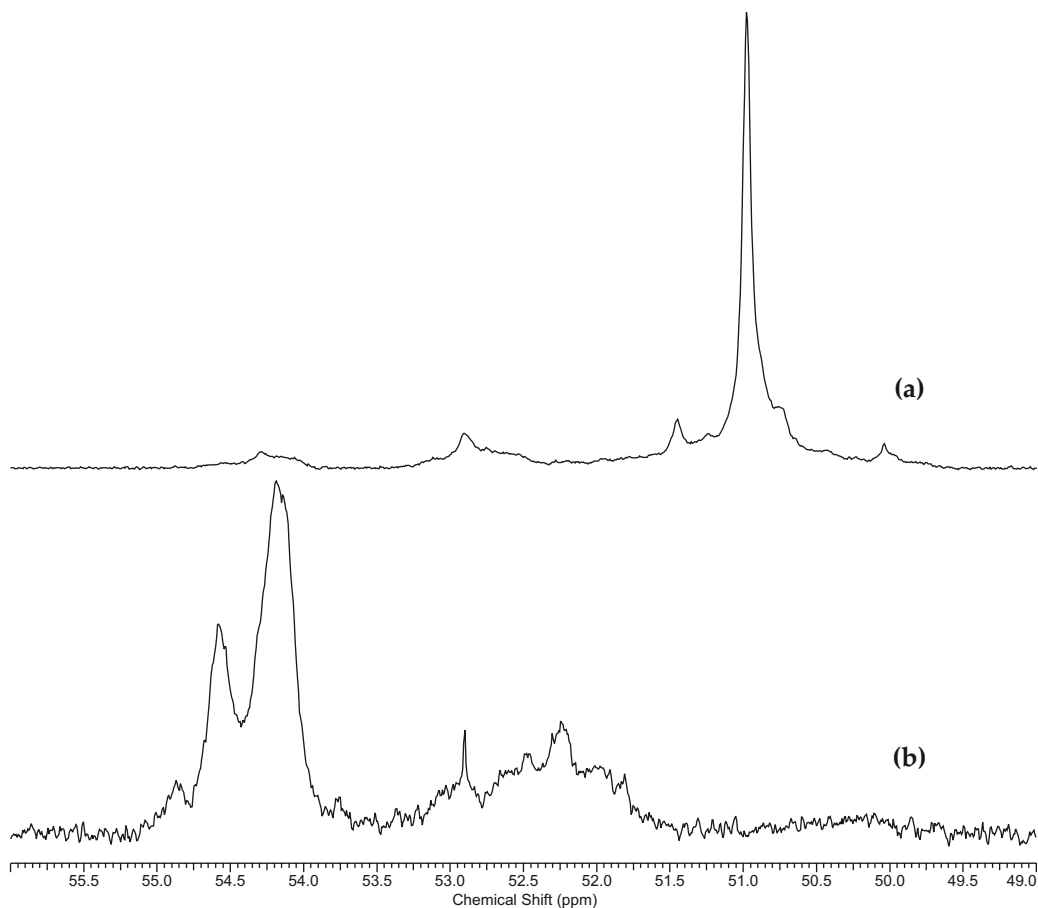

Figure 5. *The β-CH$_2$ signal of PnBuMA homopolymer in the 100 MHz ^{13}C NMR spectra recorded in chloroform-d (a) isotactic polymer (b) syndiotactic polymer*

gration of this signal gives vestigial value for *r* dyad, hence again, further analysis of the backbone β-CH$_2$ carbon signal will be carried out for the syndiotactic polymer chain of P*n*BuMA (Fig. 5b).

The probabilities of individual hexads as well as the values of their chemical shifts calculated by incremental method [2-4] used to simulate the β-CH$_2$ signal of P*n*BuMA homopolymer are collected in Table 2.
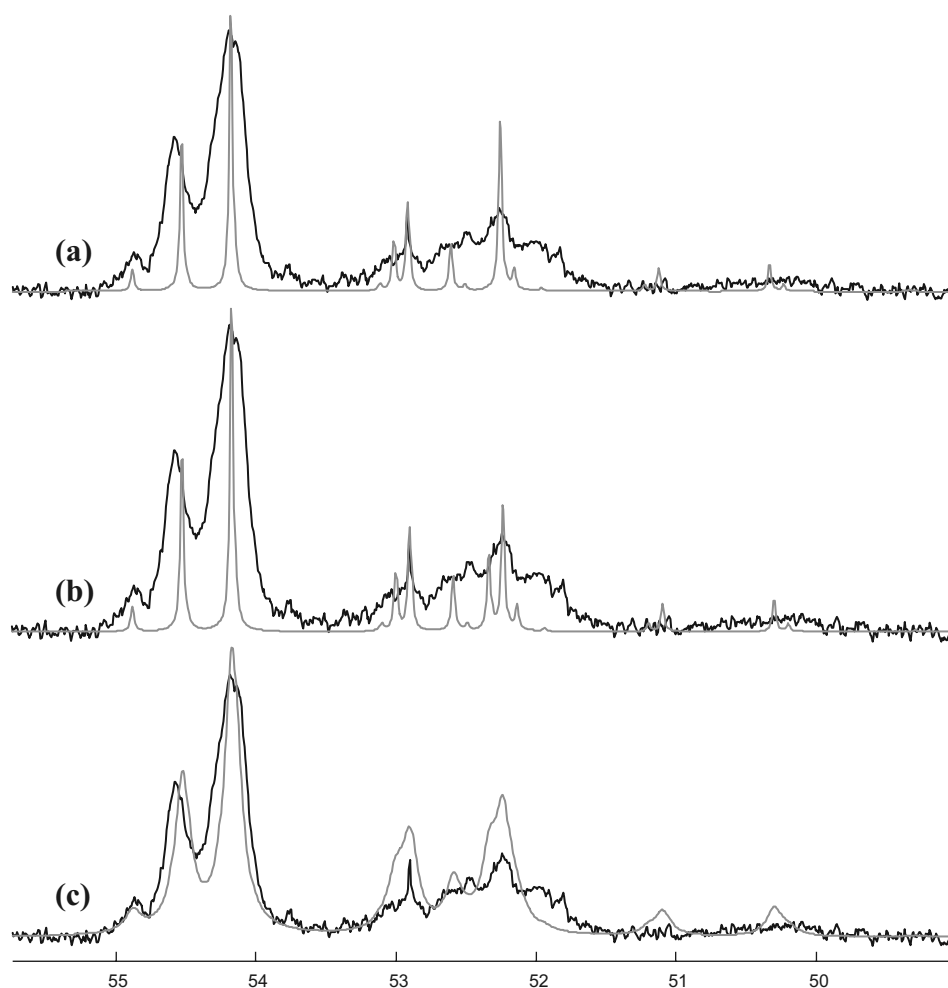
Figure 6. *Simulation of the β-CH$_2$ signal of PnBuMA in CDCl$_3$ using 1st order Markov statistics and incremental calculation of chemical shifts (linewidth 2 Hz) (a), with the incremental of hexad-octad positions (linewidth 2 Hz) (b), with the incremental of hexad-octad positions (linewidth 9 Hz) (c)*

Table 2. Probabilities of even configurational sequences of syndiotactic PMA calculated for 1st order Markov statistics and respective chemical shifts calculated incrementally

Probability	First-order Markov	Chemical shift, δ [ppm]
P($mmmmm$)	0.00002	50.98
P($\overline{mmmmr}$)	0.00041	50.14
P($rmmmr$)	0.00172	49.29
P($\overline{mmmrm}$)	0.00083	52.04
P($\overline{rmmrm}$)	0.00701	51.20
P($\overline{mmmrr}$)	0.00302	51.94
P($\overline{rmmrr}$)	0.02564	51.09
P($mrmrm$)	0.00715	53.10
P($\overline{mrmrr}$)	0.05226	53.00
P($rrmrr$)	0.09554	52.90
P($mmrmm$)	0.00041	50.10
P($\overline{mmrmr}$)	0.00701	50.20
P($rmrmr$)	0.02977	50.30
P($\overline{mrrmm}$)	0.00616	52.49

P($\overline{mrrmr}$)	0.05226	52.59
P($rrrmm$)	0.02251	52.14
P($\overline{rrrmr}$)	0.19107	52.24
P($\overline{mrrrm}$)	0.02294	54.88
P($\overline{mrrrr}$)	0.16771	54.52
P($rrrrr$)	0.30656	54.17

Simulation of the signal based on incremental approach gave a spectrum presented in Figure 6a. In order to better fit the simulated spectrum to the experimental one the *rrrmr* hexad has been split into three dominating octads: *rrrrmrr, rrrrmrm + mrrrmrr*. The first two spectra were simulated with relatively narrow width of 2 Hz just to exhibit the line positions, and the increase of the linewidth of the individual component lines to 9 Hz give quite good agreement between the experimental and simulated spectra (Fig. 6c).

Attribution of the individual hexad/octads resulting from the final simulation of the β-methylene signal is presented in Figure 7.
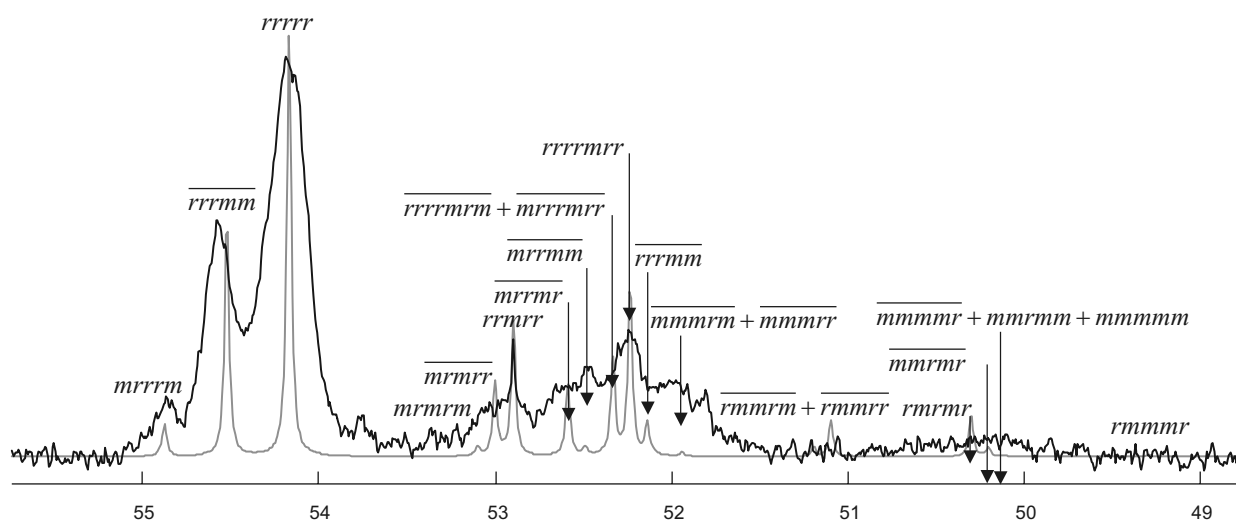
Figure 7. Attribution of the individual hexad/octads resulting from the final simulation of the β-methylene signal of syndiotactic PnBuMA polymer

CONCLUSIONS

The analysis of carbonyl signal of 100 MHz ^{13}C NMR spectrum of P*n*BuMA homopolymer can provide information about distribution of odd configurational sequences and the β-methylene signal on even configurational sequences. The splitting in the carbonyl signal recorded in deuterated chloroform can be assigned to configurational heptads and even some nonads, while the β-methylene signal can be positively simulated at hexad level with additional splitting of some lines into octads. The knowledge on distribution of the homopolymer configurational sequences can be vital in the analysis of sequence distribution of the acrylate copolymers obtained from *n*-butyl methacrylate.

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