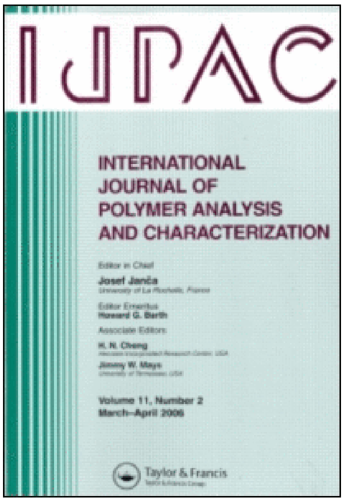

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Microstructure Study of Poly(*tert*-butyl acrylate) by ^{13}C NMR Spectroscopy

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Abstract: Two samples of poly(*tert*-butyl acrylate) (PtBA) of different tacticity, prepared by free radical and anionic polymerization, were investigated by ^{13}C NMR spectroscopy. It was found that the carbonyl signal of the 100 MHz ^{13}C NMR spectrum of PtBA was sensitive to configurational effects and provided sufficient resolution to perform detailed analysis of sequence distribution at the pentad level taking into account some heptads. The line attribution has been verified by positive simulation of the spectrum.

Keywords: ^{13}C NMR spectroscopy; Microstructure; Poly(*tert*-butyl acrylate)

INTRODUCTION

Acrylic polymers exhibit a large variety of physical and chemical properties, leading to their significant industrial importance. The stereochemical configuration of monomeric units is the key factor with respect to their physicochemical properties and industrial applications. For example, the glass transition temperature, T_g, is directly related to the segmental

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motions of the macromolecular chain, and this is a physical value that depends directly on polymer microstructure. Nuclear magnetic resonance (NMR) spectroscopy is a very sensitive method for characterizing the stereochemical structure of polymers because the chemical shift is usually sensitive to configurational sequences. For acrylic polymers the signals of the carbonyl carbons in the ^{13}C NMR spectra yield very precise information about the distribution of uneven sequences, up to configurational heptads.

It has been already shown in a previous article[1] that in the ^{13}C NMR spectra of poly(*n*-butyl acrylate) it was possible to assign individual configurational sequences at the pentad level.The method was based on the calculation of line intensities for different sequences according to Bernoulli or Markov statistics on one hand, and on the other, the chemical shift for each sequence was calculated by a separately developed incremental method. Using these data, the carbonyl signal was simulated. The method of incremental calculation of chemical shifts of the individual lines in the carbonyl signal of the ^{13}C NMR spectra has been developed for a copolymer of methyl methacrylate and ethyl acrylate[2] and was then positively applied to a similar calculation in the case of methyl methacrylate homopolymer, PMMA.[3] The microstructure of *tert*-butyl acrylate homopolymer, PtBA, has already been studied by Suchopárek and Spěvaček,[4] who observed configurational splitting of the carbonyl signal but did not analyze this region. Therefore, the objective of this work is to apply a similar approach to determine sequence distribution in the samples of homopolymers of tert-butyl acrylate of different microstructures.

EXPERIMENTAL SECTION

The first homopolymer sample, predominantly isotactic poly(*tert*-butyl acrylate), PtBA I, was prepared by anionic polymerization initiated by n-butyllithium (2.5 M in hexane (Aldrich). The monomer/solvent (hexane) weight ratio was 1/2.5, and the initiator/monomer molar ratio was 1/50. The anionic polymerization was carried out at −80°C for 2 h. The polymer was then precipitated from methanol and dried at 80°C under vacuum.[5] The second homopolymer sample, PtBA II, was synthesized by free radical polymerization, initiated by 2,2′-azobis(isobutyronitrile) (AIBN). The polymer was prepared by solution polymerization with 5×10^{-3} mol/L AIBN initiator in 60 wt.% 2-butanone at 78°C. After polymerization for 1 h, the polymer was precipitated in methanol and dried at 80°C under vacuum.[5]

The 100 MHz ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 40°C for 5 wt.% solutions in $CDCl_3$ and benzene-d_6 and at 30°C in acetone-d_6. To avoid the nuclear Overhauser effect, a gated decoupling sequence was applied and a good signal-to-noise ratio was achieved after 12000 scans. The spectra were obtained with a 4 s delay (D1). Simulation of the NMR spectra was performed using our own software written in the Matlab environment (Math Works, Inc.).

RESULTS AND DISCUSSION

The ^{13}C NMR spectroscopy has been used for the investigation of the microstructure of two PtBA samples prepared by different methods, i.e., anionic and radical polymerization, which should provide different

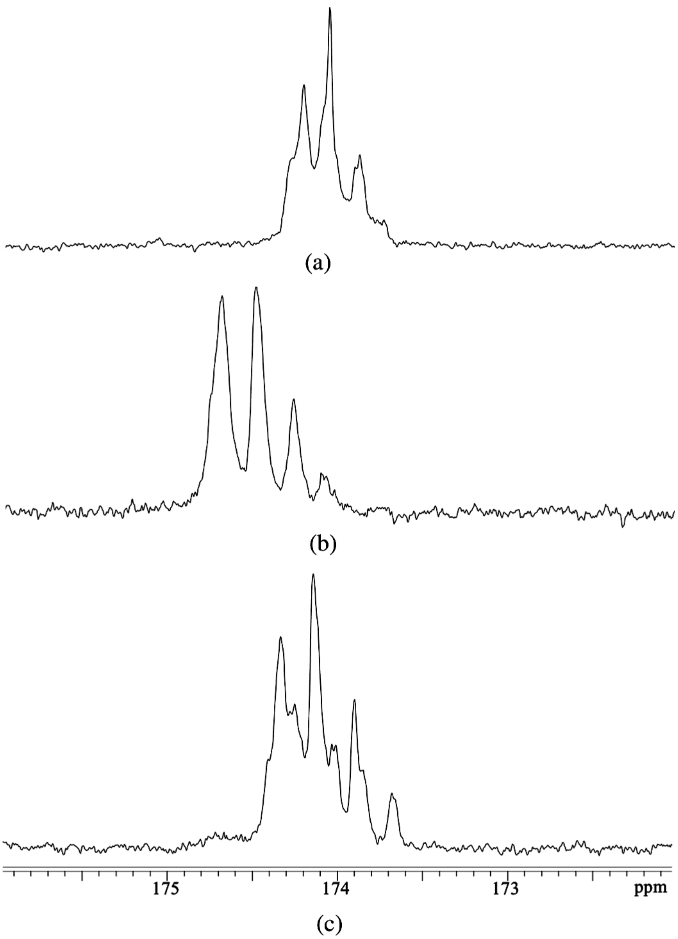

Figure 1. 100 MHz ^{13}C NMR spectrum of carbonyl signal of PtBA I in (a) $CDCl_3$, (b) acetone-d_6, and (c) benzene-d_6.

tacticity of the polymer chain. In the previous publication[1] the carbonyl region of 100 MHz ^{13}C NMR spectra of PnBA homopolymer recorded in $CDCl_3$, acetone-d_6 and benzene-d_6 has been examined. In general, the spectra of PtBA samples studied here follow the same general pattern, and the solvent effects are of the same character for both homopolyacrylates. When the carbonyl region of PtBA I obtained in ionic conditions and recorded in different solvents (Figure 1) is compared with the same carbonyl region for the second homopolymer sample, PtBA II synthesized by radical polymerization (Figure 2), much broader lines and less

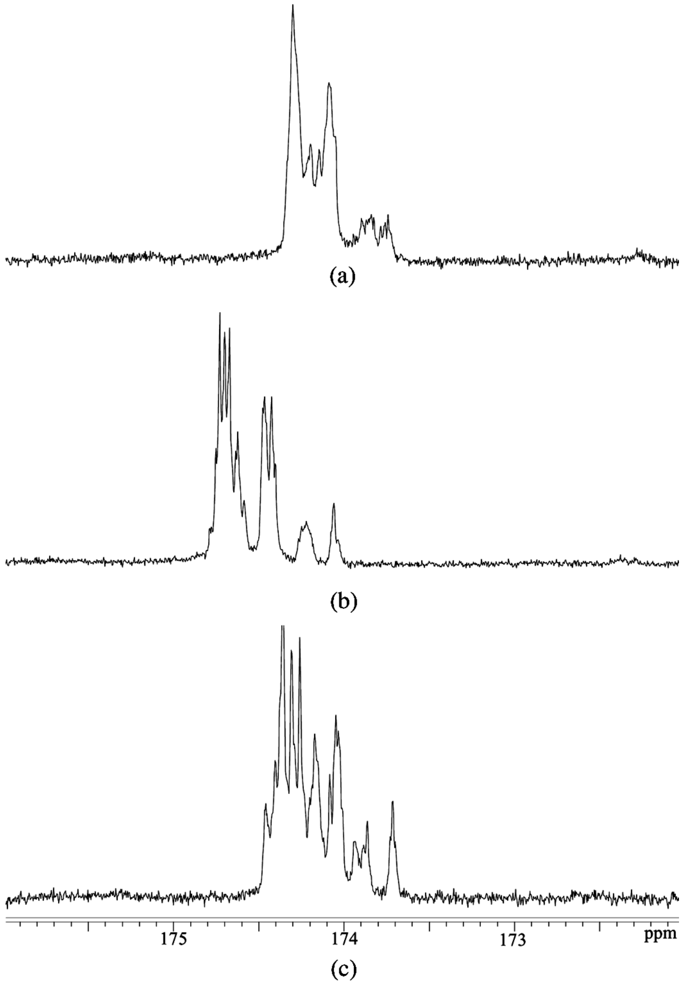

Figure 2. 100 MHz ^{13}C NMR spectrum of carbonyl signal of PtBA II in (a) $CDCl_3$, (b) acetone-d_6, and (c) benzene-d_6.

splitting is observed for the first sample. Nevertheless, in both cases, in all solvents applied configurational splitting can be observed at least at the pentad level. Analysis of the methine signal at about 42 ppm for 100 MHz ^{13}C NMR spectra in $CDCl_3$ (Figure 3) made it possible to determine the triad probabilities by simple integration of well-resolved peaks according to Suchopárek and Spěvaček.[4] For PtBA I (ionic polymerization) the following triad probabilities were obtained: P(*mm*) = 0.46, P($\overline{mr}$) = 0.38, and P(*rr*) = 0.16. For PtBA II (radical polymerization) the triad probabilities were as follows: P(*mm*) = 0.19, P($\overline{mr}$) = 0.45, and P(*rr*) = 0.36. It can be therefore concluded that PtBA I is predominantly isotactic. Radical polymerization carried out under the conditions used for *t*-butyl acrylate usually leads to a predominantly syndiotactic chain for most acrylate and methacrylate monomers; for the sample PtBA II the triad distribution is nearly atactic, with significant

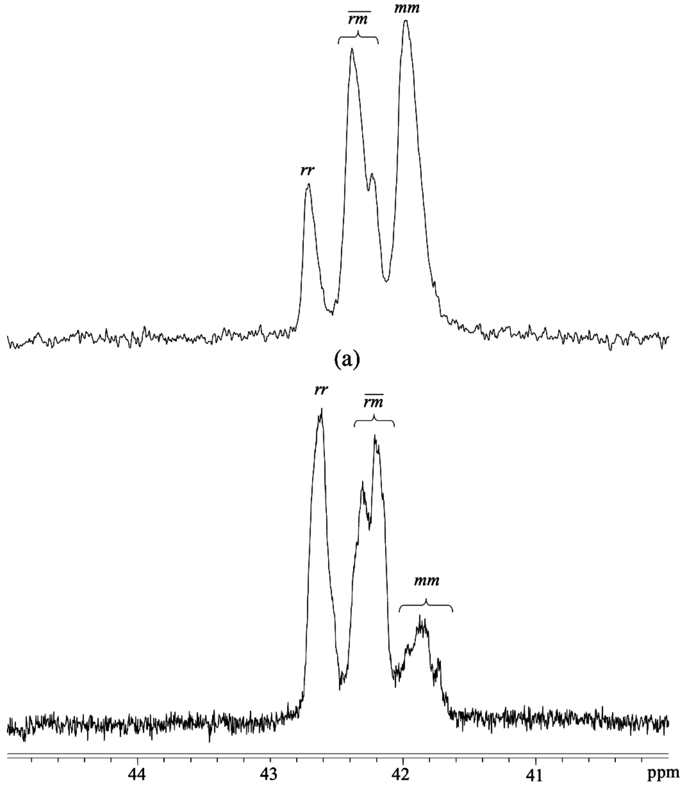

Figure 3. 100 MHz ^{13}C NMR spectrum of methine signal of (a) PtBA I and (b) PtBA II in $CDCl_3$.

Table I. Probabilities of configurational pentads of PtBA I calculated according to Bernoulli and first-order Markov statistics and chemical shifts calculated incrementally

Probability	Bernoulli	First-order Markov	δ [ppm]
P(*mmmm*)	0.178	0.230	174.14
P($\overline{mmmr}$)	0.192	0.190	174.32
P(*rmmr*)	0.052	0.039	174.50
P($\overline{mmrm}$)	0.192	0.146	173.91
P($\overline{mmrr}$)	0.103	0.123	174.24
P($\overline{rmrm}$)	0.103	0.060	174.09
P($\overline{rmrr}$)	0.056	0.051	174.42
P(*mrrm*)	0.052	0.047	173.68
P($\overline{rrrm}$)	0.056	0.079	174.01
P(*rrrr*)	0.015	0.033	174.34

syndiotactic fraction. Triad distribution comparable to that of PtBA I was obtained by Suchopárek and Spěvaček[4] for their ionic sample.

The carbonyl region of PtBA I, recorded in C_6D_6 (Figure 1), offers sufficient resolution to perform analysis of pentad distribution. The proposed attribution of the lines can be verified by spectrum simulation. The respective line intensities can be obtained based on Bernoullian or first-order Markov statistics. The data for triad probabilities from methine signal integration were used to calculate pentad probabilities according to these two statistics (Table I). Chemical shifts of each line were determined by incremental calculations. The influence of the neighboring monomeric units closest to the central unit is described as α increments, and the effect of subsequent units is described by β increments. Therefore, for example, the position of *rmrr* pentad can be calculated as:

$$\delta_{rmrr} = \delta_0 + \alpha_m + \alpha_r + \beta_{mr} + \beta_{rr}$$

Table II. Values of α and β increments (in ppm) used to calculate the chemical shifts of configurational sequences of PtBA I

Parameter	Value
δ_0	174.05
α_m	0.1365
β_{mm}	−0.091
β_{mr}	0.091
α_r	−0.02
β_{rr}	0.1655
β_{rm}	−0.1655

In order to determine the positions of 10 pentads, it is necessary to know seven independent parameters: two α increments, four β increments, and starting chemical shift δ_0. The value of δ_0 can be assumed as the center of

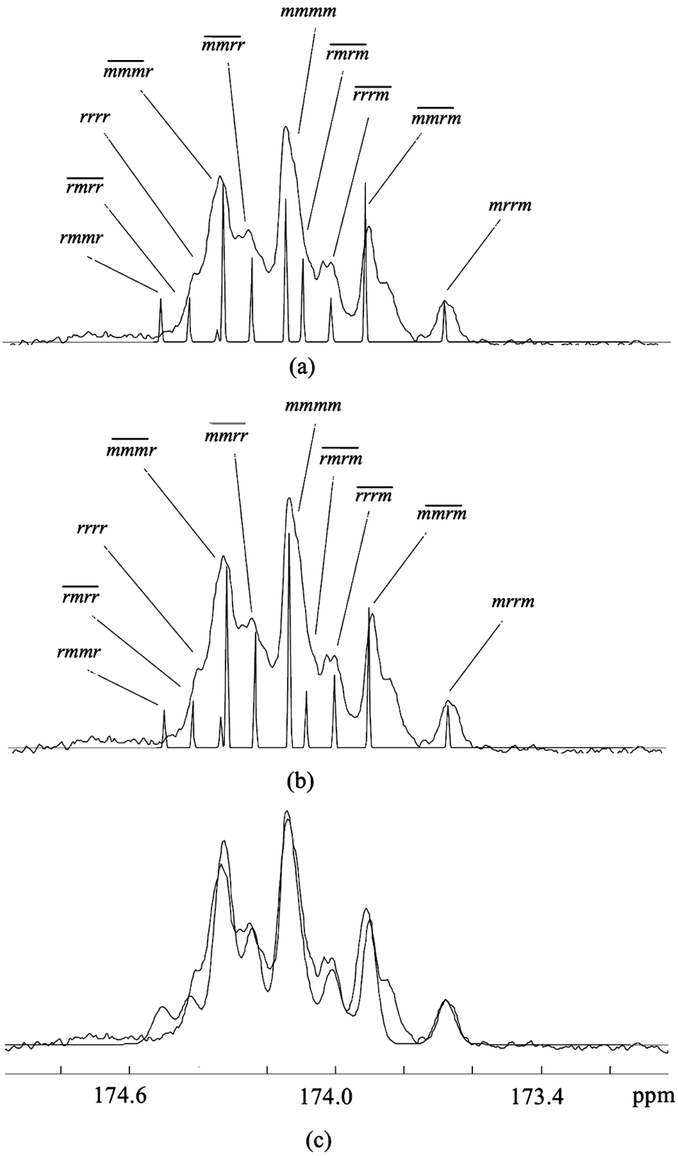

Figure 4. Simulation of the carbonyl signal of PtBA I in benzene-d$_6$ at the pentad level using (a) Bernoullian statistics and 1 Hz line width, (b) first-order Markov statistics and 1 Hz line width, and (c) 10 Hz line width.

the carbonyl signal, which can be estimated to 174.05 ppm for PtBA homopolymer. Some of the α and β increments can be determined experimentally directly from the ^{13}C NMR spectrum, while the rest can be estimated. Based on the previously calculated intensities of the individual pentads (Table I), the positions of symmetric triads can be assumed, which allows for determination of respective α increments:

$$\delta_{rr} = \delta_0 + 2\alpha_r \qquad \text{hence} \qquad \alpha_r = \frac{\delta_{rr} - \delta_0}{2}$$

and

$$\delta_{mm} = \delta_0 + 2\alpha_m \qquad \text{hence} \qquad \alpha_m = \frac{\delta_{mm} - \delta_0}{2}$$

The values of β increments were determined by attribution of respective pentads within the given triad, for example:

$$\delta_{rrrr} = \delta_0 + 2\alpha_r + 2\beta_{rr} \qquad \text{hence} \qquad \beta_{rr} = \frac{\delta_{rrrr} - \delta_0 - 2\alpha_r}{2}$$

The values of respective increments determined in this manner are listed in Table II. The values of chemical shifts obtained, as well as line intensities (Table I), made it possible to simulate the region of carbonyl signal

Table III. Probabilities of configurational pentads of PtBA II calculated according to Bernoulli and first-order Markov statistics and chemical shifts calculated incrementally

Probability		Bernoulli	First-order Markov	δ [ppm]
P($mmmm$)		0.030	0.040	174.03
P($\overline{mmmr}$)		0.084	0.094	174.25
P($rmmr$)		0.059	0.056	174.46
P ($\overline{mmrm}$)	P($\overline{mmmrmm}$)	0.014	0.016	173.94
	P($\overline{mmmrmr}$)	0.020	0.019	173.92
	P($\overline{rmmrmm}$)	0.020	0.019	173.87
	P($\overline{rmmrmr}$)	0.028	0.023	173.86
P($\overline{mmrr}$)		0.118	0.127	174.17
P($\overline{rmrm}$)		0.118	0.094	174.09
P($\overline{rmrr}$)		0.166	0.150	174.38
P($mrrm$)		0.059	0.053	173.71
P($\overline{rrrm}$)	P($\overline{mrrrmm}$)	0.028	0.030	174.01
	P($\overline{rrrrmm}$)	0.040	0.048	174.05
	P($\overline{mrrrmr}$)	0.040	0.035	174.00
	P($\overline{rrrrmr}$)	0.056	0.056	174.03
P($rrrr$)		0.117	0.136	174.31

for both statistics. Figure 4 shows simulation of carbonyl signal for Bernoulli (a) and first-order Markov distribution (b), with assumed line-width of 1 Hz. Significant differences between these two statistics can be seen for *mmmm* and $\overline{mmrm}$ pentads, with much better agreement for the first-order Markov distribution (Figure 4(b)). Subsequent simulations were therefore performed using first-order Markov statistics, for line widths of 1 Hz (Figure 4(b)) and 10 Hz (Figure 4(c)). The presence of sequences longer than pentads cannot be directly observed as individual lines, but they significantly influence the width of the observed lines,

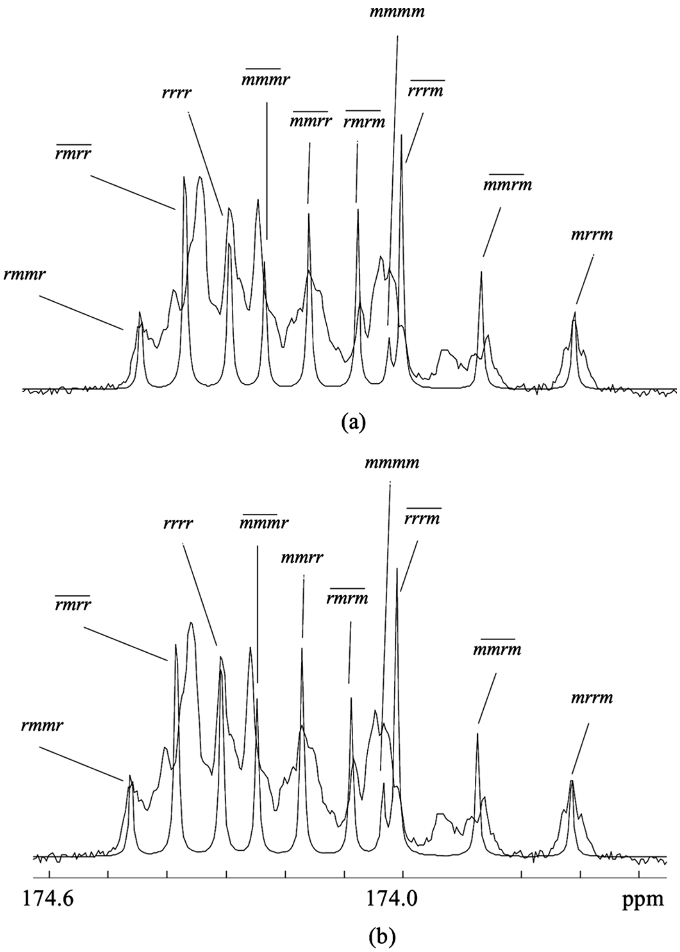

Figure 5. Simulation of the carbonyl signal of PtBA II in benzene-d_6 at the pentad level using (a) Bernoullian statistics and 1 Hz line width and (b) first-order Markov statistics and 1 Hz line width.

therefore application of line width of 10 Hz gives very good agreement between the experimental spectrum and that simulated at the pentad level.

Microstructural analysis of the predominantly syndiotactic sample, PtBA II, seems to be more difficult since there are no dominating symmetrical *mm* or *rr* triads. Moreover, in the case of deuterated benzene used as a solvent, additional lines appear, indicating splittings at higher level, i.e., configurational heptads. To describe this sample the results from a previous analysis of PtBA I were used. Once again, the pentad distributions for Bernoulli and first-order Markov statistics were calculated based on triad probabilities obtained from integration of a well-resolved methine signal at about 42 ppm; these values are given in Table III. Figure 5 presents simulation of the carbonyl signal at the pentad level for Bernoulli (a) and first-order Markov (b) statistics, with a line width of 1 Hz. Again, as in the case of the isotactic sample, better agreement between simulated and experimental spectra was obtained for Markov statistics. By comparing the carbonyl signals of both homopolymer samples it can be seen that in the predominantly syndiotactic sample, PtBA II, the $\overline{rrrm}$ and $\overline{mmrm}$ pentads are further split into heptad lines. This was taken into account in the calculation of heptad splitting for these two pentads, and the respective heptad intensities are listed in Table III. Chemical shifts of sequences presented in Table III were calculated incrementally for the values of α, β, and γ increments given in Table IV. It can be seen that the values of α and β increments are very close to those for the predominantly isotactic sample, PtBA I. A small difference between chemical shifts, not exceeding 0.1 ppm, can be observed for the same

Table IV. Values of α, β, and γ increments (in ppm) used to calculate the chemical shifts of configurational sequences of PtBA II

Parameter	Value
δ_0	174.05
α_m	0.09875
α_r	−0.01925
β_{mm}	−0.10675
β_{rr}	0.14825
β_{mr}	0.10675
β_{rm}	−0.14825
γ_{mmm}	0.0550
γ_{rrr}	0.0280
γ_{mmr}	−0.0050
γ_{rrm}	−0.005
γ_{rmm}	0.0065
γ_{rmr}	−0.0065

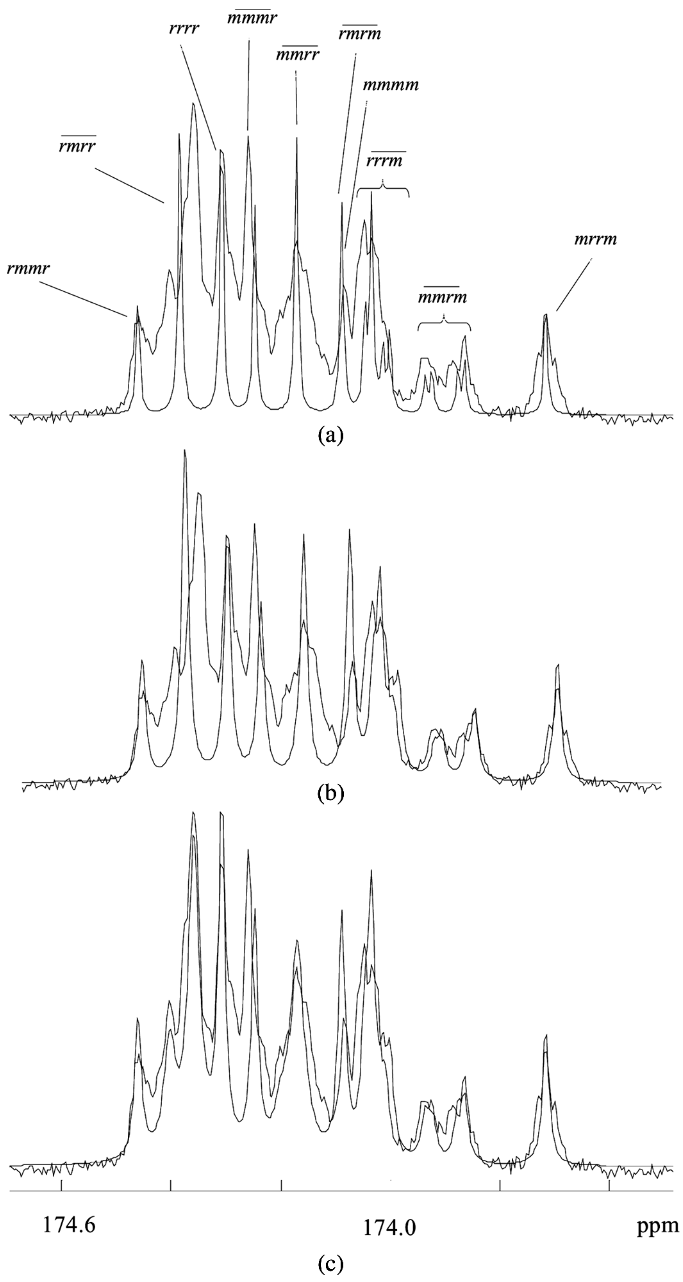

Figure 6. Simulation of the carbonyl signal of PtBA II in benzene-d_6 taking account of the heptad splitting. Line width of (a) 1 Hz and (b), (c) 5 Hz.

pentads in different samples, but it does not change the overall shape of the carbonyl region.

The same phenomenon, which is probably due to different preferred conformation of the isotactic and syndiotactic chains, was also observed for poly(methyl methacrylate).[3] Figure 6 shows the simulation of the carbonyl signal of the PtBA II sample for Markov statistics assuming line widths of 1 Hz (a) and 5 Hz (b), the latter representing a value comparable to experimental data. Good agreement between experimental and simulated spectra is observed, however, two pentads, $\overline{rmrr}$ and $\overline{mmrr}$, exhibit further splitting into heptads, but in this case simple splitting of these lines into respective heptads calculated incrementally do not provide a good match. The $\overline{rmrr}$ pentad is roughly separated into two components and the $\overline{mmrr}$ pentad into three groups of signals. When the spectrum simulation is performed with such a distribution of components, the overall intensities of these two pentads are in good agreement with the experimental spectrum, which confirms the correct line assignment at the pentad level. The simulation, taking into account such separation of the components of these two pentads, shown in Figure 6(c) provided a spectrum very close to the experimental one.

It can be concluded from these simulations that first-order Markov statistics describes quite correctly sequence probabilities of PtBA homopolymer. Application of incremental calculation to obtain chemical shifts of respective pentads provides good agreement between the positions of the experimental and simulated lines. Linear combination of the influences of the α and β neighboring units is therefore sufficient to describe the position of lines of configurational pentads in the carbonyl region of the ^{13}C NMR spectrum of PtBA homopolymer. Even in the case of differences in exact position of the pentads the incremental method can provide reliable guidance on how to assign the lines to individual pentads.

CONCLUSION

Microstructural characterization of poly(*tert*-butyl acrylate), PtBA, can be performed by means of ^{13}C NMR spectroscopy, focusing on the carbonyl signal region of the spectrum. Application of first-order Markov statistics to describe the probabilities of sequence distribution and incremental calculation of chemical shifts of the individual sequences can be used to positively simulate the carbonyl signal for both predominantly isotactic and predominantly syndiotactic samples of the PtBA homopolymer at the pentad level. In the case of the predominantly syndiotactic sample, it can be seen that some pentads exhibit further splitting into heptad lines. Taking into account the separation into heptads only for these selected pentads can significantly augment the agreement of the simulated spectra with the experimental ones.

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