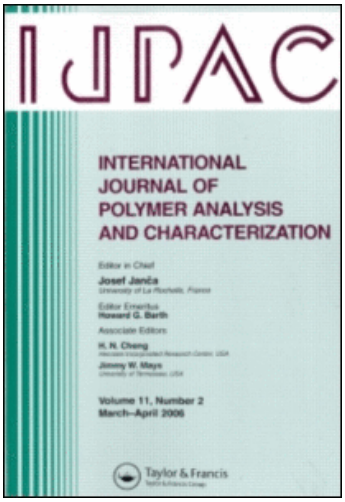

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Incremental Calculation of Sequence Distribution of Poly(Butyl Acrylate)

Piotr Bujak[a]; Marek Matlengiewicz[ab]; Norbert Henzel[c]
[a] Department of Environmental Chemistry and Technology, Silesian University, Katowice, Poland [b] Polish Academy of Sciences, Institute of Coal Chemistry, Gliwice, Poland [c] Institute of Electronics, Silesian Technical University, Gliwice, Poland

Online publication date: 10 June 2010

To cite this Article Bujak, Piotr , Matlengiewicz, Marek and Henzel, Norbert(2007) 'Incremental Calculation of Sequence Distribution of Poly(Butyl Acrylate)', International Journal of Polymer Analysis and Characterization, 12: 2, 95 — 104
To link to this Article: DOI: 10.1080/10236660601136233
URL: http://dx.doi.org/10.1080/10236660601136233

International Journal of Polymer Anal. Charact., 12: 95–104, 2007

ISSN: 1023-666X print
DOI: 10.1080/10236660601136233

Incremental Calculation of Sequence Distribution of Poly(Butyl Acrylate)

Piotr Bujak
Department of Environmental Chemistry and Technology, Silesian University, Katowice, Poland

Marek Matlengiewicz
Department of Environmental Chemistry and Technology, Silesian University, Katowice, Poland, and Polish Academy of Sciences, Institute of Coal Chemistry, Gliwice, Poland

Norbert Henzel
Institute of Electronics, Silesian Technical University, Gliwice, Poland

Abstract: The carbonyl signal in the 100 MHz ^{13}C NMR spectra of both poly(*n*-butyl acrylate) and poly(*t*-butyl acrylate) exhibit configurational sensitivity up to pentads. Since the attribution of respective sequences cannot be performed in a straightforward manner, a method of incremental calculation of chemical shifts of individual sequences has been applied. The simulated spectrum for PnBA obtained in this way required only slight corrections to match the experimental carbonyl signal. This method can therefore be extended to determine the configurational sequences in acrylic copolymers containing *n*-butyl acrylate units.

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

Address correspondence to Marek Matlengiewicz, Department of Environmental Chemistry and Technology, Silesian University, ul. Szkolna 9, 40-006 Katowice, Poland. E-mail: matlen@us.edu.pl

INTRODUCTION

Microstructural effects in the macromolecular chains of acrylic homo- and copolymers can be observed by means of high-resolution ^{13}C nuclear magnetic resonance (NMR) spectroscopy for different carbon signals, however, the carbonyl and the main-chain methylene carbons (β-CH_2) are preferred, since they are present in all acrylic structures. Nevertheless, the configurational effects are not visible in the carbonyl signal of ^{13}C NMR spectra for the simplest homologues of poly(*n*-alkyl acrylates). A single carbonyl line is observed for homopolymers of methyl, ethyl, or propyl acrylates, and there are no splittings due to configurational differences in their C-13 spectra up to 100 MHz.[1] In contrast, the carbonyl regions for poly(*n*-butyl acrylate), PnBA, and poly(*tert*-butyl acrylate), PtBA, are clearly split into configurational pentads, but the attribution of the sequences is not straightforward. For PnBA this splitting was observed by Aerdts et al.[2] at 100 MHz, but they did not analyze the configurational effect for this signal. Recently, Brar and Kaur[3] presented the 75 MHz ^{13}C NMR spectrum of PnBA homopolymer required for detailed 2-D NMR analysis of copolymer of methyl methacrylate and *n*-butyl acrylate, PMMA/nBA, but their carbonyl signal recorded in $CDCl_3$ showed only traces of configurational splittings, hence, their microstructural analysis neglected configurational effects introduced by *n*-butyl acrylate units. Suchopárek and Spěvaček[4] have studied microstructure of *t*-butyl acrylate homopolymer and observed configurational splitting of its carbonyl signal, but they did not analyze this region. Since the splitting of the carbonyl signal of PnBA and PtBA can be clearly observed in the spectra at higher fields and in various solvents, the configurational effects of nBA and PtBA have to be taken into account. For that reason, knowledge of the configurational pentad assignment in the carbonyl signal of butyl acrylate homopolymers can be very useful in the microstructural analysis of more complex spectra of acrylic copolymers containing butyl acrylate units in their macromolecular chain.

EXPERIMENTAL SECTION

The samples of poly(*n*-butyl acrylate) and poly(*t*-butyl acrylate) were prepared by radical polymerization in solution. The monomer was mixed with butan-2-one to obtain 40 wt% solution and was heated up to 80°C. Then azobisisobutyronitrile (AIBN) was added as radical initiator (0.5 wt% with respect to the whole solution). The polymerization mixture was diluted with acetone and poured into a large volume of a water-methanol mixture to precipitate the polymer, which was then washed with methanol and vacuum dried to constant weight.

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. Simulation of the NMR spectra were performed using our own software written in the Matlab environment (MathWorks, Inc.).

RESULTS AND DISCUSSION

Carbonyl Signal of Poly(*n*-Butyl Acrylate)

In the 100 MHz ^{13}C NMR spectrum of PnBA recorded in $CDCl_3$ the carbonyl signal occupies the region from about 174.0 to 174.7 ppm. The signal is noticeably split into several lines due to configurational effects, however, this effect is not very strong. The use of acetone-d_6 as a solvent yields substantial enhancement in resolution but with simultaneous and considerable downfield shift of about 1.6 ppm with respect to that recorded in $CDCl_3$, due to the polar character of acetone. Even better resolution, without significant shift of the whole region, can be observed in benzene-d_6. Different resolution in these three solvents is due to different solubility.

Although in all these solvents the carbonyl signal is clearly split into configurational pentads (Figure 1), only for signals recorded in deuterated chloroform and acetone can a rough attribution of configurational pentads be performed based on relative intensities of the pentads assuming Bernoullian or first-order Markov statistics. The carbonyl signal recorded in C_6D_6 does not yield clear splitting, since probably the lines of *rr* and $\overline{mr}$ triads are intermixed, so it seems that the spectrum recorded in deuterated acetone offers the best choice for further analysis.

For the PnBA homopolymer, the triad distribution can be calculated from the CH signal at about 41.7 ppm by simple integration of the well-resolved lines, assuming the triad assignment, according to Aerdts et al.[2] This calculation yields the values of $P(rr) = 0.54$, $P(\overline{mr}) = 0.38$, and $P(mm) = 0.08$ for our predominantly syndiotactic PnBA sample. Respective probabilities for Bernoullian and first-order Markov probabilities can be then readily calculated and used to verify the propagation statistics by simulation of the carbonyl signal (Table I). As can be seen for such triad distribution of a slightly predominantly syndiotactic chain, there is no significant difference between Bernoullian and first-order Markov statistics and there is no need to differentiate them. For the sake of simplicity we will henceforth use the Bernoullian distribution. The correctness of sequence attribution can be verified by spectral simulation. The sequence probabilities can be used as line intensities, but to calculate simulated

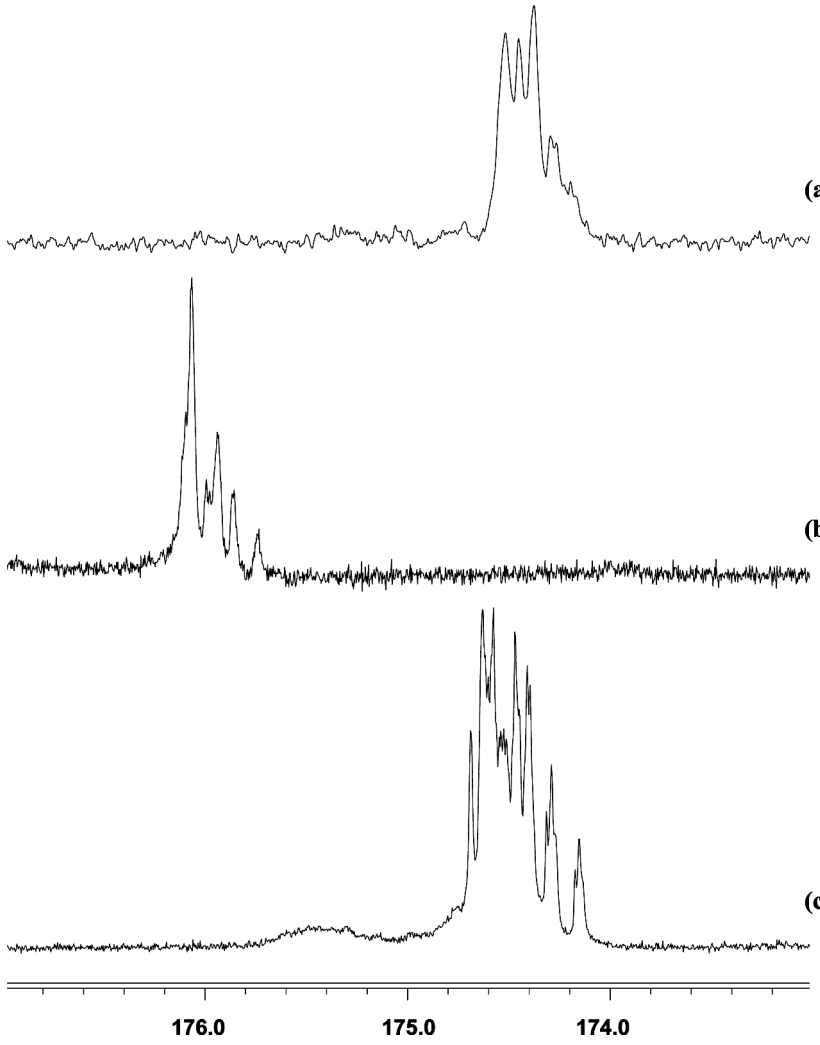

Figure 1. 100 MHz ^{13}C NMR spectrum of carbonyl signal of PnBA in (a) $CDCl_3$, (b) acetone-d_6, and (c) benzene-d_6.

spectrum it is also necessary to know the chemical shifts for individual pentads. They can be estimated applying an incremental procedure described previously.[5] To start the incremental calculation, the symmetric triads have to be assigned, as is shown in Figure 2 for the carbonyl signal recorded in acetone-d_6.

Then, the positions of the two symmetric *n*-butyl acrylate triads can be calculated as:

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

PnBA pentad	Bernoulli	First-order Markov	δ [ppm]
P(*mmmm*)	0.005	0.007	175.64
P($\overline{mmmr}$)	0.029	0.033	175.72
P(*rmmr*)	0.039	0.040	175.80
P($\overline{mmrm}$)	0.029	0.029	175.87
P($\overline{mmrr}$)	0.0775	0.083	175.85
P($\overline{rmrm}$)	0.0775	0.070	175.96
P($\overline{rmrr}$)	0.210	0.198	175.93
P(*mrrm*)	0.039	0.037	176.11
P($\overline{rrrm}$)	0.210	0.208	176.08
P(*rrrr*)	0.284	0.295	176.05

$$\delta_{\mathrm{ArArA}} = \delta_{0\mathrm{A}} + 2\alpha^{\mathrm{A}}_{\mathrm{rA}} \quad \text{hence} \quad \alpha^{\mathrm{A}}_{\mathrm{rA}} = \frac{\delta_{\mathrm{ArArA}} - \delta_{0\mathrm{A}}}{2}$$

$$\delta_{\mathrm{AmAmA}} = \delta_{0\mathrm{A}} + 2\alpha^{\mathrm{A}}_{\mathrm{mA}} \quad \text{hence} \quad \alpha^{\mathrm{A}}_{\mathrm{mA}} = \frac{\delta_{\mathrm{AmAmA}} - \delta_{0\mathrm{A}}}{2}$$

where $\delta_{0\mathrm{A}}$ is regarded as the position of the carbonyl signal of the *n*-butyl acrylate unit (A) without any influence of its neighbors and $2\alpha^{\mathrm{A}}_{\mathrm{rA}}$ represents the incremental change of the chemical shift of this signal on addition of two neighboring units A, both in configuration *r*. The position of the third asymmetric triad is therefore the linear combination of the two above increments:

$$\delta_{\mathrm{ArAmA}} = \delta_{0\mathrm{A}} + \alpha^{\mathrm{A}}_{\mathrm{rA}} + \alpha^{\mathrm{A}}_{\mathrm{mA}}$$

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 A$\bar{r}$A$\bar{r}$A, δ_0 instead of $\delta_{0\mathrm{A}}$, α_{r} instead of $\alpha^{\mathrm{A}}_{\mathrm{rA}}$, and so on. Since NMR spectroscopy cannot distinguish the asymmetric sequences like *mr* and *rm* and can provide only the sum of their intensities, we will use the following notation[6] for the spectroscopically observable asymmetric sequences: e.g., $\overline{rm} = \overline{mr} = mr + rm$. It should be noted that in these calculations that the α values are dependent of δ_0, hence, the position of δ_0 could be chosen arbitrarily. Further splitting of the lines is due to the influence of the subsequent repeating unit described by β increments and leading to configurational pentads. Figure 2 shows the assignment of the α and β increments for the symmetric sequences.

The values of the α and β increments can be estimated from the experimental spectrum (Table II), and then the chemical shifts of the

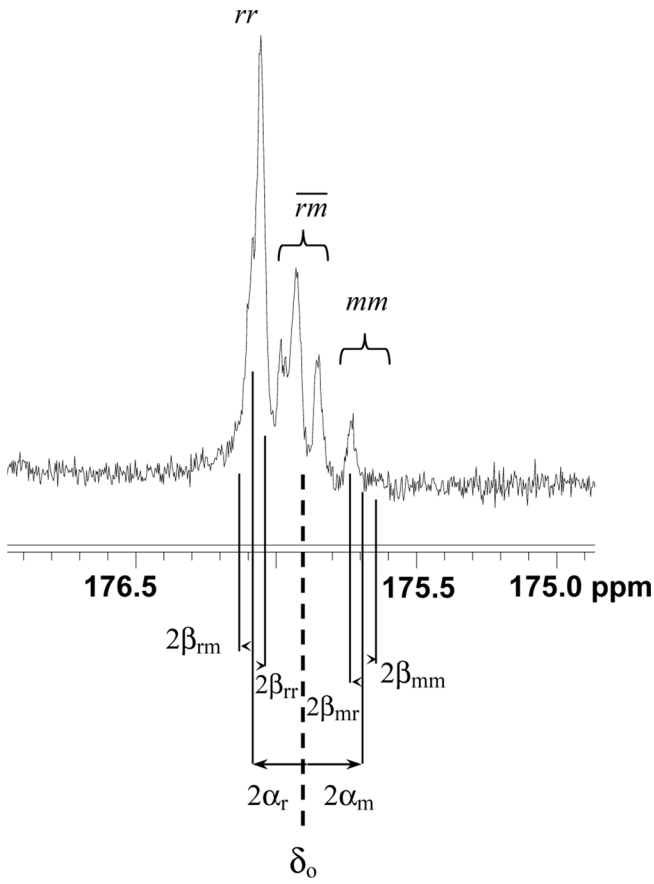

Figure 2. Assignment of the α and β increments for the symmetric sequences of the carbonyl signal of PnBA in acetone-d_6.

remaining pentads can be calculated as the linear combination of respective increments, for example:

$$\delta_{mmmr} = \delta_0 + 2\alpha_m + \beta_{mm} + \beta_{mr}$$

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

$\delta_0 = 175.9$
$\alpha_m = -0.08$, $\alpha_r = +0.09$
$\beta_{mm} = -0.05$, $\beta_{rr} = -0.015$
$\beta_{mr} = +0.03$, $\beta_{rm} = +0.015$

The obtained values of chemical shifts of individual pentads are listed in Table I. The sequence probabilities and line positions can be used as starting parameters to calculate the simulated spectrum of the carbonyl region. Figure 3(a) represents the spectrum obtained for relatively narrow lines of 3 Hz, just to show the positions of individual lines. It can be seen from this figure that all the lines match very well with the experimental signals, except for that of *rmmr*. Assuming that the chemical shift for this pentad is governed by an additional influence, we can slightly shift this line upfield to match the experimental pattern. Figure 3(b) compares the experimental trace with the spectrum simulated with a line width of 5 Hz and applying a correction of −0.06 ppm for the *rmmr* pentad with respect to the previous value.

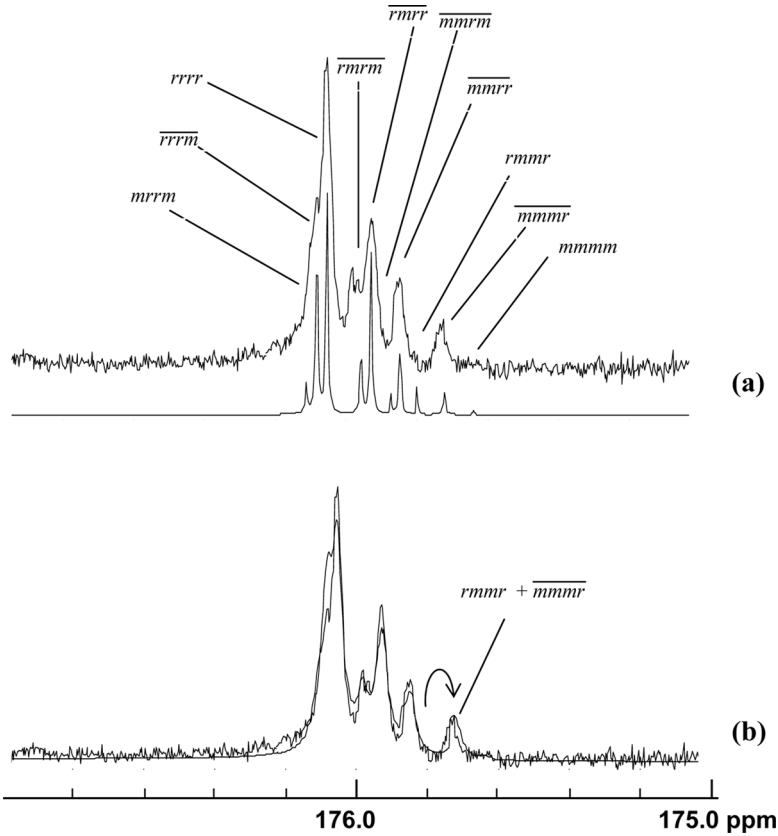

Figure 3. Simulation of the carbonyl signal of PnBA using Bernoullian statistics and incremental calculation of chemical shifts (line width 3 Hz) (a) and with the correction of *rmmr* pentad position (line width 5 Hz) (b).

Very good agreement between the experimental and simulated spectra can be regarded as a confirmation of the proposed sequence attribution.

The same elements of the spectral pattern can be observed for the carbonyl signal of PnBA recorded in deuterated benzene, but, in this case, it can be seen that the downfield part of the *mr*-centered pentads is intermixed with that of *rr*-centered sequences. Therefore, despite

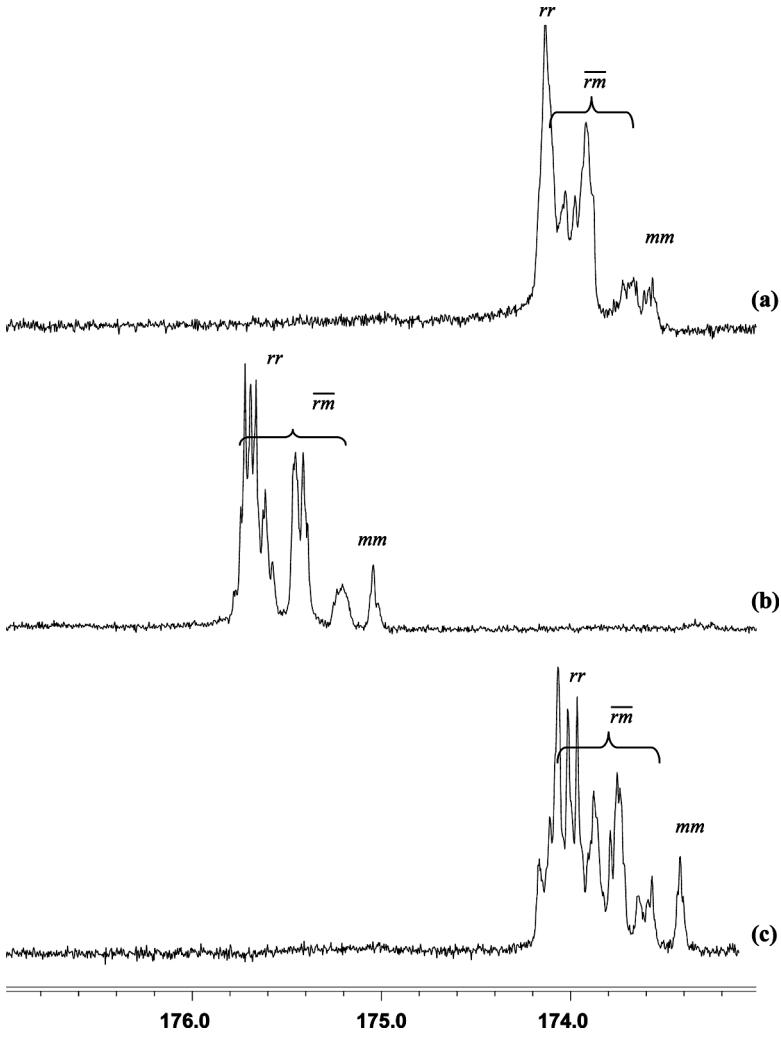

Figure 4. 100 MHz ^{13}C NMR spectrum of carbonyl signal of PtBA in (a) $CDCl_3$, (b) acetone-d_6, and (c) benzene-d_6.

much better resolution in C_6D_6, even at the heptad level for some lines, the signals of individual sequences cannot be assigned in a straightforward manner because the lines are not only overlapped but also intermixed, and the simple incremental model cannot be applied. To confirm the eventual atypical attribution, it is necessary to perform 2-D NMR experiments and/or deconvolution of the overlapped lines, and this work is in progress.

Carbonyl Signal of Poly(Tert-Butyl Acrylate)

Figure 4 presents the carbonyl region of the 100 MHz ^{13}C NMR spectra of PtBA homopolymer recorded in $CDCl_3$, acetone-d_6, and benzene-d_6. The spectra follow the general pattern observed for PnBA, and the solvent effects are of the same character for both homopolymers (compare Figures 1 and 4), i.e., the resolution is lowest in chloroform and the signal is shifted downfield in acetone. Again, all three solvents provide the splitting of the carbonyl signal into configurational pentads.

The signal in acetone is also significantly shifted about 1.4 ppm downfield with respect to those recorded in $CDCl_3$ and benzene-d_6 at about 173.5–174.3 ppm. The best resolution is offered in C_6D_6, but for this polymer in all three solvents, the lines of the downfield part of the *mr*-centered pentads are visibly intermixed with those of *rr*-centered sequences, and the correct line assignment requires confirmation by 2-D NMR experiments and/or deconvolution of the overlapped lines. The work in this direction is also in progress.

CONCLUSION

Determination of sequence distribution of acrylic copolymers containing *n*-butyl acrylate, e.g., copolymer of methyl methacrylate and *n*-butyl acrylate, PMMA/nBA, does not usually take into account the configurational effects introduced by *n*-butyl acrylate units, since its splitting of carbonyl signals is either insufficient or too complicated. It was observed that the splittings in the carbonyl signal of the 100 MHz ^{13}C NMR spectrum of homopolymer of *n*-butyl acrylate, PnBA, recorded in deuterated acetone can be assigned in terms of configurational pentads, applying incremental calculation of chemical shifts of individual pentads. This attribution was verified by spectrum simulation yielding very good agreement with the experimental signals. Since the configurational splittings of carbonyl signal in PnBA in acetone-d_6 follow the simple additivity rules, this opens the possibility of extending such an approach to determine distribution of compositional-configurational sequences in *n*-butyl acrylate copolymers, like PMMA/nBA.

REFERENCES

[1] Brandolini, A. J. and D. D. Hills. (2000). *NMR Spectra of Polymers and Polymer Additives*, New York: Marcel Dekker, pp. 188–192.

[2] Aerdts, A. M., A. L. German, and G. P. M. van der Velden. (1994). Determination of the reactivity ratios, sequence distribution and stereoregularity of butyl acrylate-methyl methacrylate copolymers by means of proton and carbon-13 NMR. *Magn. Reson. Chem.* **32**, S80–S88.

[3] Brar, A. S. and S. Kaur. (2005). Microstructure determination of methyl methacrylate and *n*-butyl acrylate copolymers synthesized by atom transfer radical polymerization with two-dimensional NMR spectroscopy. *J. Polym. Sci. Part A Polym. Chem.* **43**, 1100–1118.

[4] Suchopárek, M. and J. Spěvaček. (1993). Characterization of the stereochemical structure of poly(*tert*-butyl acrylate) by one- and two-dimensional NMR spectroscopy. *Macromolecules* **26**, 102–106.

[5] Nguyen, G., D. Nicole, M. Swistek, M. Matlengiewicz, and B. Wiegert. (1997). Sequence distribution of the methyl methacrylate-ethyl acrylate copolymer by ^{13}C NMR spectroscopy. *Polymer* **38**, 3455–3461.

[6] Klesper, E. and G. Sielaff. (1974). *Polymer Spectroscopy*, ed. D. O. Hummel. Weinheim: Verlag Chemie, p. 192.