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Microstructure Study of Methyl Methacrylate/ *n*-Butyl Acrylate Copolymer by ^{13}C NMR Spectroscopy

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Abstract: Detailed analysis of carbonyl signal in the 100 MHz ^{13}C NMR spectrum of methyl methacrylate/*n*-butyl acrylate copolymer samples, PMMA/*n*BA, of different compositions, prepared by free radical polymerization, provided information on distribution of configurational-compositional triads and pentads. Incremental calculation of chemical shifts of individual sequences permitted spectral simulation and verification of the signal attribution.

Keywords: ^{13}C NMR spectroscopy; Acrylic copolymers; Methyl methacrylate; Microstructure; *n*-Butyl acrylate

INTRODUCTION

Acrylic copolymers exhibit a large variety of physical and chemical properties, leading to their great industrial importance. Their standard applications are as coatings and adhesives, and many recent engineering, optical, and medical materials are composed of acrylic

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(co)polymers. This imposes the necessity of their detailed characterization since it is generally recognized that it is their microstructure, i.e., distribution of the comonomers along the macromolecular chain and their stereochemical arrangement (tacticity), that fundamentally influences their physical and chemical properties. For example, Kitayama et al.^[1] have shown that glass-transition temperature, T_g , being the crucial parameter for all the mechanical applications of polymers, can be varied between -60 and $+120^\circ$ for methyl methacrylate/lauryl methacrylate copolymer by simply changing its composition and tacticity.

It has been shown that really deep insight into the chain microstructure can be achieved for acrylate–methacrylate copolymers,^[2] since in this case the carbonyl signal in the ^{13}C nuclear magnetic resonance (NMR) spectra is spread over a relatively large zone of about 4 ppm, offering splitting up to configurational–compositional pentads. Analysis of such a system has been performed in detail for the copolymer of methyl methacrylate and ethyl acrylate, PMMA/EA.^[3,4] It required development of a method of spectrum simulation based on incremental calculation of chemical shifts of individual sequences. The method seems to be quite general and applicable to other copolymer systems. Usually for acrylate–methacrylate copolymers the configurational effect of an acrylate comonomer is not very profound. In the case of PMMA/EA^[4] only traces of configurational splitting were observed in the carbonyl signal of the 100 MHz ^{13}C NMR spectrum for the pure acrylate sequences, thus for this copolymer practically only one comonomer introduced configurational effects, and the number of configurational–compositional sequences taken into account was considerably reduced.

The analogous copolymer of methyl methacrylate and *n*-butyl acrylate, PMMA/*n*BA, has so far been considered identical from this point of view, since Brar and Kaur^[5] have reported no configurational effect from the acrylate units in the carbonyl signal of the 75 MHz ^{13}C NMR spectrum recorded in CDCl_3 , and their microstructural analysis neglected configurational effects introduced by *n*-butyl acrylate units. However, we have observed that resolution of carbonyl signals in the 100 MHz ^{13}C NMR spectrum of PMMA/*n*BA copolymer recorded in deuterated acetone exhibits lines of sequences up to configurational–compositional pentads. Moreover, it has been already shown in our previous study^[6] that in the 100 MHz ^{13}C NMR spectra of poly(*n*-butyl acrylate), P*n*BA, it was possible to assign individual configurational sequences up to the pentad level.

Therefore, in this work we would like to perform the microstructural analysis of PMMA/*n*BA copolymer based on carbonyl signal and taking into account configurational effects of both comonomers.

EXPERIMENTAL SECTION

A series of methyl methacrylate/*n*-butyl acrylate copolymer samples, PMMA-*n*BA, 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 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, the reaction mixtures were diluted with acetone and poured into a large volume of a water-methanol mixture to precipitate the copolymers. They were washed with methanol and vacuum dried to constant weight.^[3] Respective homopolymers, i.e., poly(methyl methacrylate), PMMA, and poly(*n*-butyl acrylate), PnBA, were obtained in an analogous manner.

The NMR spectra were recorded with a Bruker AM 400 spectrometer at 40°C, using 10 wt% solutions in acetone- d_6 . The 400 MHz ^1H NMR spectra were obtained for sample concentration of 10% (w/v), applying pulse delay of 5 s and 240 scans.^[7] To record the 100 MHz ^{13}C spectra a gated decoupling sequence was applied to avoid the nuclear Overhauser effect, 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.).

The composition F_M (mole fraction of methyl methacrylate) of the copolymers was calculated from the ^1H NMR spectra.^[7] The average copolymer composition (F_M) can be readily obtained by using the equation:

$$F_M = \frac{2 \times A_1}{2 \times A_1 + 3 \times A_2}$$

where A_1 and A_2 represent the total peak areas of the proton resonances $-\text{OCH}_3$ of the MMA unit and of the $-\text{OCH}_2-$ of the *n*BA unit, respectively. This is shown in Figure 1, where a 400 MHz ^1H NMR spectrum of PMMA/*n*BA copolymer ($F_M = 0.58$) is shown. The composition of copolymers as determined by ^1H NMR is given in Table I.

RESULTS AND DISCUSSION

Three samples of the copolymer of methyl methacrylate and *n*-butyl acrylate, PMMA/*n*BA, of various compositions, as well as the samples of respective homopolymers, i.e., poly(methyl methacrylate), PMMA, and poly(*n*-butyl acrylate), PnBA, were obtained by means of radical polymerization. ^1H NMR spectra of the copolymers were used to

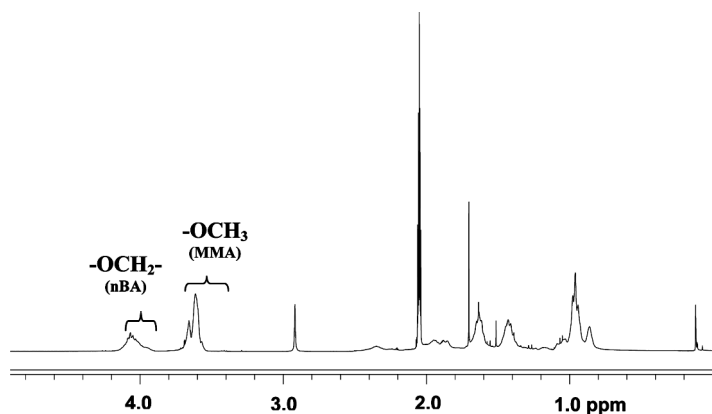


Figure 1. 400 MHz ^1H NMR spectrum of PMMA/nBA with $F_M = 0.58$ in acetone- d_6 .

determine the composition of the samples according to the method given in Aerdts et al.^[7] An example spectrum is given in Figure 1, and the results are presented in Table I. For all the samples 100 MHz ^{13}C NMR spectra were recorded in acetone- d_6 , and it was observed that the splitting of the carbonyl signal in the range from 174.5 to 179.0 ppm reveals compositional–configurational triads and also several pentads (Figure 2). This splitting is much more profound than that observed in CDCl_3 , usually applied to polyacrylics. Figure 2 shows the carbonyl signals of the copolymers of different compositions (Figures 2(b)–(d)) as well as the signals of both homopolymers (Figures 2(a), (e)). Based on the data on sequence distribution of stereosequences of PMMA,^[8] $P(mm) = 0.02$, $P(\overline{m}\overline{r}) = 0.34$, and $P(rr) = 0.64$, and PnBA,^[6] $P(mm) = 0.08$, $P(\overline{m}\overline{r}) = 0.38$, and $P(rr) = 0.54$, and composition of copolymer samples from ^1H NMR data, it was possible to calculate the distribution of compositional–configurational triads applying Bernoullian distribution (Table II). Chemical shifts of individual triads were calculated incrementally.^[4] For example, the position of the M_rBrB

Table I. Composition of methyl methacrylate/*n*-butyl acrylate copolymer samples

Methyl methacrylate (mol%)	
Monomer mixture	Copolymer
50.0	35.0
75.0	58.0
90.0	75.0

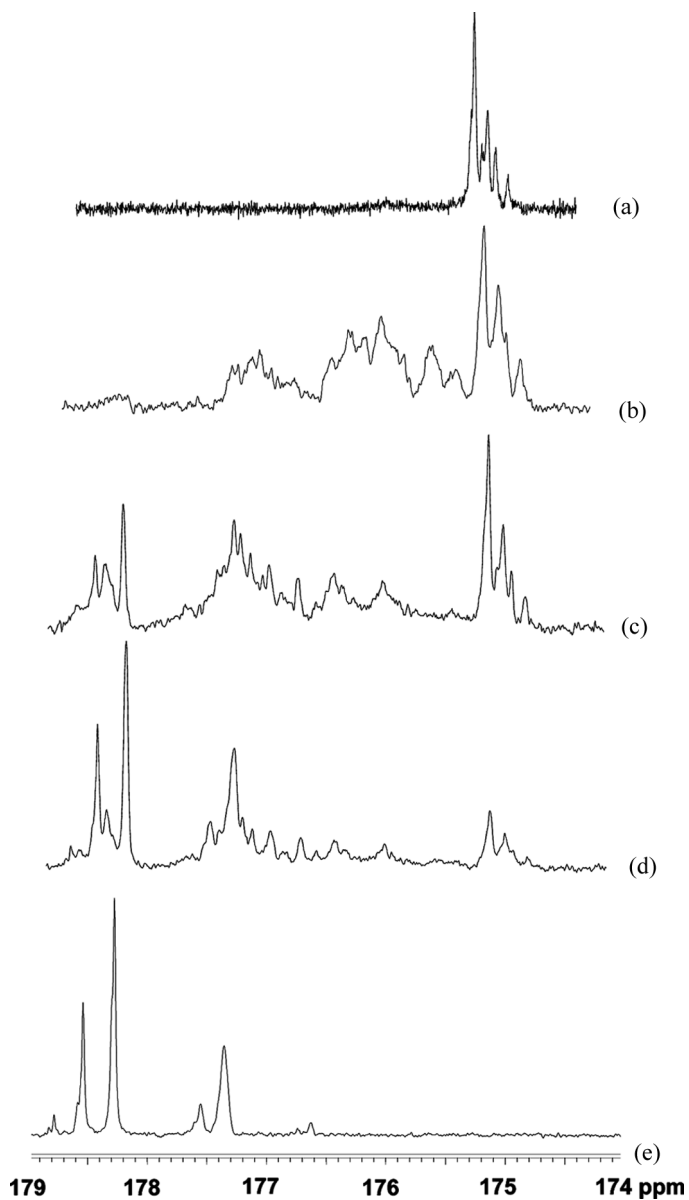


Figure 2. 100 MHz ^{13}C NMR spectrum of carbonyl signal of PnBA (a) and PMMA (e) homopolymers and PMMA/nBA copolymer in acetone- d_6 with F_M : 0.35 (b), 0.58 (c), and 0.75 (d).

Table II. Probabilities of configurational–compositional triads of PMMA/nBA calculated according to Bernoulli statistics and chemical shifts calculated incrementally

Probability	F_M			δ [ppm]
	0.35	0.58	0.75	
P(\overline{BmBmB})	0.0200	0.0054	0.0011	174.75
P(\overline{BmBrB})	0.1082	0.0292	0.0062	174.92
P(\overline{BrBrB})	0.1463	0.0394	0.0083	174.09
P(\overline{BmMmB})	0.0224	0.0155	0.0071	174.93
P(\overline{BmMrB})	0.0703	0.0486	0.0223	175.51
P(\overline{BrMrB})	0.0550	0.0380	0.0174	176.08
P(\overline{MmBmB})	0.0311	0.0215	0.0098	176.25
P(\overline{MmBrB})	0.0842	0.0582	0.0266	176.42
P(\overline{MrBmB})	0.0487	0.0337	0.0154	175.82
P(\overline{MrBrB})	0.1316	0.0911	0.0417	175.99
P(\overline{MmMmB})	0.0118	0.0209	0.0208	175.29
P(\overline{MmMrB})	0.0184	0.0327	0.0325	175.86
P(\overline{MrMmB})	0.0503	0.0892	0.0888	176.73
P(\overline{MrMrB})	0.0786	0.1396	0.1389	177.30
P(\overline{MmBmM})	0.0121	0.0214	0.0213	177.74
P(\overline{MmBrM})	0.0378	0.0672	0.0669	177.31
P(\overline{MrBrM})	0.0296	0.0525	0.0523	176.88
P(\overline{MmMmM})	0.0015	0.0070	0.0152	175.65
P(\overline{MmMrM})	0.0131	0.0600	0.1298	177.09
P(\overline{MrMrM})	0.0281	0.1280	0.2767	178.52

triad can be calculated as:

$$\delta_{MrBrB} = \delta_{0B} + \alpha_{rB}^B + \alpha_{rM}^B$$

where δ_{0B} is the chemical shift of the center of the carbonyl signal for the PnBA homopolymer (position of the carbonyl signal of the *n*-butyl acrylate unit without any influence of its neighbors), and α_{rB}^B and α_{rM}^B represent the incremental change of the chemical shift of this signal introduced by their neighboring units, B (*n*-butyl acrylate) and M (methyl methacrylate, respectively, both in configuration *r*.

To calculate the chemical shifts of all possible compositional–configurational triads it is necessary to know eight α increments and two origin shifts, δ_{0M} and δ_{0B} , being the centers of carbonyl signals of PMMA and PnBA, respectively. From the previous studies on homopolymers the data on the homosequences of M unit, i.e., the values of α_{rM}^M and α_{mM}^M , can be taken from PMMA^[8] while α_{rB}^B and α_{mB}^B can be taken from PnBA^[6] (Table III). The remaining mixed α increments were derived

Table III. Values of α and β increments (in ppm) used to calculate the chemical shifts of triads and pentads

$\delta_{0M} = 177.45$	$\delta_{0B} = 174.91$
$\alpha_{rM}^M = 0.538$	$\alpha_{rB}^B = 0.091$
$\alpha_{mM}^M = -0.898$	$\alpha_{mB}^B = -0.071$
$\alpha_{rB}^M = -0.684$	$\alpha_{rM}^B = 0.989$
$\alpha_{mB}^M = -1.255$	$\alpha_{mM}^B = 1.417$
$\beta_{rMrM}^M = -0.126$	$\beta_{rBrB}^B = -0.014$
$\beta_{mMrM}^M = -0.003$	$\beta_{mBrB}^B = 0.031$
$\beta_{rMmM}^M = 0.126$	$\beta_{rBmB}^B = 0.014$
$\beta_{mMmM}^M = -0.076$	$\beta_{mBmB}^B = -0.051$
$\beta_{rBrM}^M = 0.114$	$\beta_{rMrM}^B = -0.197$
$\beta_{mBrm}^M = 0.162$	$\beta_{mMrM}^B = -0.091$
$\beta_{rBmM}^M = -0.272$	$\beta_{rBrM}^B = -0.004$
$\beta_{mBmM}^M = -0.385$	$\beta_{mBrM}^B = 0.007$
$\beta_{rMrB}^M = -0.010$	$\beta_{rMmM}^B = 0.470$
$\beta_{mMrB}^M = -0.011$	$\beta_{mMmM}^B = 0.217$
$\beta_{rBrB}^M = -0.015$	$\beta_{rBmM}^B = 0.009$
$\beta_{mBrB}^M = -0.021$	$\beta_{mBmM}^B = -0.017$
$\beta_{rMmB}^M = 0.100$	$\beta_{rMrB}^B = 0.026$
$\beta_{mMmB}^M = -0.108$	$\beta_{mMrB}^B = 0.012$
$\beta_{rBmB}^M = -0.152$	$\beta_{rMmB}^B = 0.263$
$\beta_{mBmB}^M = -0.216$	$\beta_{mMmB}^B = 0.120$

from the copolymer spectra utilizing the triad distribution, for example:

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

and

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

The attribution of respective lines in the carbonyl signal of the copolymer can be verified by spectrum simulation. Having on one hand the intensities of individual lines calculated from sequence distribution and on the other hand the positions of lines from incremental calculations, it is possible to simulate the spectrum for assumed line width. If we use relatively small line width (say 2 Hz) (Figure 3) it is possible to clearly show the position of each line and verify the correctness of chemical shift

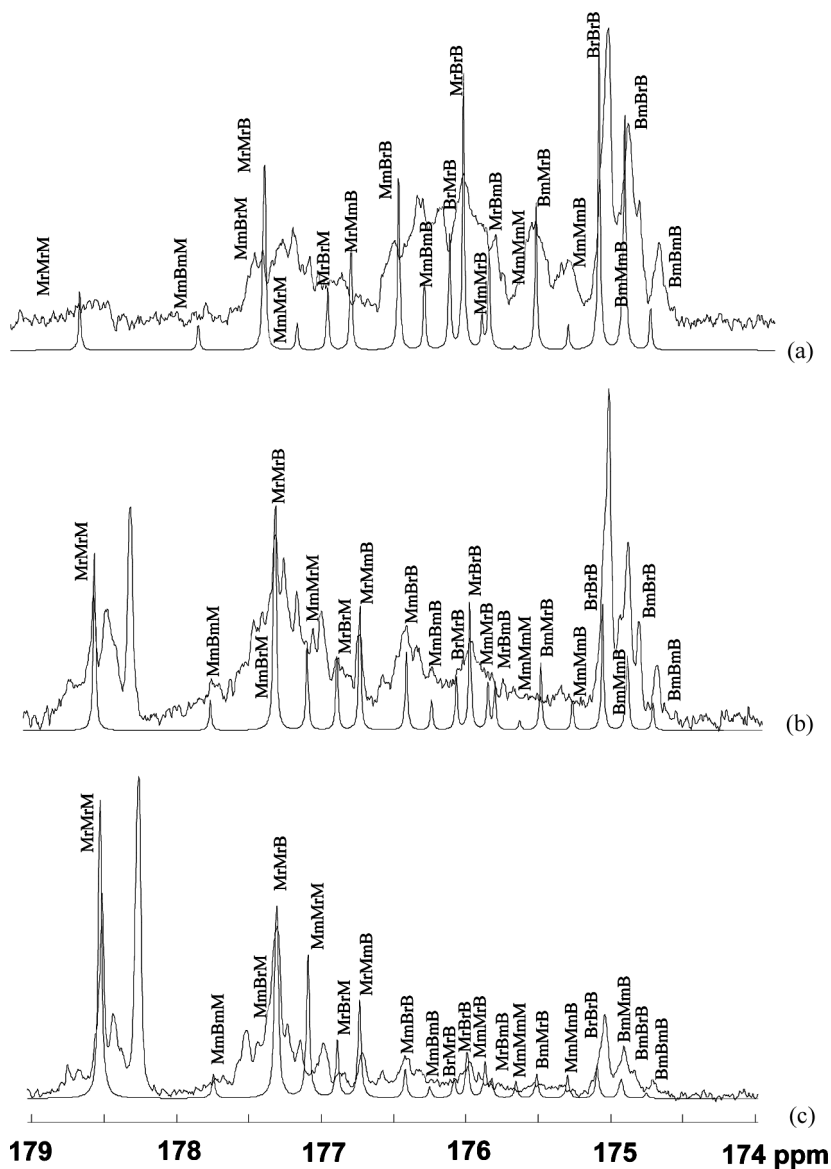


Figure 3. Simulation of the carbonyl signal of PMMA/nBA at the triad level using Bernoullian statistics and 2 Hz line width, F_M : 0.35 (a), 0.58 (b), and 0.75 (c).

calculation. To obtain better agreement between experimental and simulated spectra it is necessary to increase the line widths to about 8 Hz (Figure 4). Comparison of the experimental and simulated carbonyl

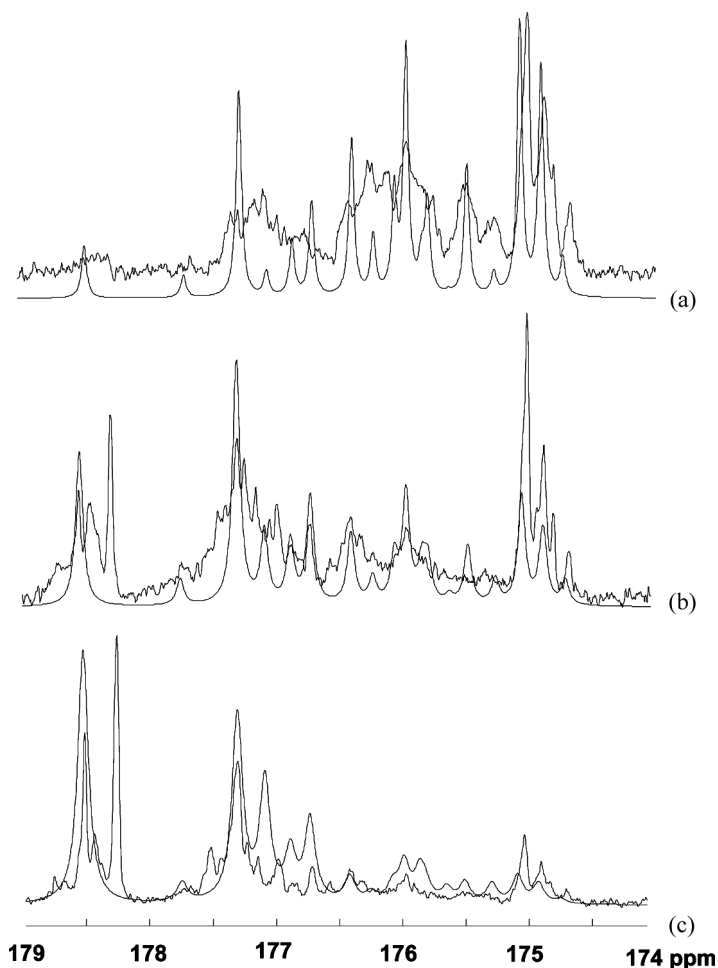


Figure 4. Simulation of the carbonyl signal of PMMA/nBA at the triad level using Bernoullian statistics and 8 Hz line width, F_M : 0.35 (a), 0.58 (b), and 0.75 (c).

signals of copolymers reveals significant discrepancy between some parts of the spectrum. Therefore, splitting into longer sequences, i.e., pentads, has to be taken into account for some triads, especially \overline{MrMrM} and \overline{MmMrM} triads. This observation can be supported by the analysis of the carbonyl signal in PMMA,^[8] where this region is split into configurational pentads and even heptads, which can be seen in Figure 2(e). Therefore, the carbonyl signal has to be resimulated taking into account splitting of the most differing triads, i.e., \overline{MrMrM} , \overline{MmMrM} , \overline{MrMrB} , and \overline{MrBrB} , into pentads. The pentad intensities were calculated from

Table IV. Probabilities of configurational–compositional pentads of PMMA/nBA calculated according to Bernoulli statistics and chemical shifts calculated incrementally

Sequence probability		F_M			δ [ppm]
		0.35	0.58	0.75	
$P(\overline{MrBrB})$	$P(\overline{BmMrBrBmB})$	0.0058	0.0017	0.0002	176.26
	$P(\overline{BmMrBrBrB})$	0.0158	0.0046	0.0007	176.24
	$P(\overline{BrMrBrBmB})$	0.0091	0.0026	0.0004	176.03
	$P(\overline{BrMrBrBrB})$	0.0247	0.0071	0.0011	176.00
	$P(\overline{BmMrBrBmM})$	0.0045	0.0033	0.0012	176.26
	$P(\overline{BmMrBrBrM})$	0.0071	0.0053	0.0019	176.25
	$P(\overline{BrMrBrBmM})$	0.0071	0.0053	0.0019	176.02
	$P(\overline{BrMrBrBrM})$	0.0111	0.0082	0.0029	176.01
	$P(\overline{MmMrBrBmB})$	0.0015	0.0011	0.0004	176.47
	$P(\overline{MmMrBrBrB})$	0.0041	0.0031	0.0011	176.45
	$P(\overline{MrMrBrBmB})$	0.0065	0.0048	0.0017	175.81
	$P(\overline{MmMrBrBrB})$	0.0177	0.0131	0.0046	175.78
	$P(\overline{MmMrBrBmM})$	0.0012	0.0022	0.0017	176.47
	$P(\overline{MmMrBrBrM})$	0.0019	0.0035	0.0027	176.46
	$P(\overline{MrMrBrBmM})$	0.0051	0.0096	0.0074	175.80
	$P(\overline{MrMrBrBrM})$	0.0080	0.0151	0.0116	175.79
$P(\overline{MrMrB})$	$P(\overline{BmMrMrBmB})$	0.0035	0.0026	0.0009	177.25
	$P(\overline{BmMrMrBrB})$	0.0094	0.0070	0.0024	177.39
	$P(\overline{BrMrMrBmB})$	0.0054	0.0040	0.0014	177.16
	$P(\overline{BrMrMrBrB})$	0.0148	0.0109	0.0039	177.30
	$P(\overline{BmMrMrBmM})$	0.0027	0.0052	0.0040	177.13
	$P(\overline{BmMrMrBrB})$	0.0042	0.0081	0.0062	177.52
	$P(\overline{BrMrMrBmM})$	0.0042	0.0081	0.0062	177.04
	$P(\overline{BrMrMrBrM})$	0.0066	0.0126	0.0097	177.43
	$P(\overline{MmMrMrBmB})$	0.0009	0.0017	0.0013	177.28
	$P(\overline{MmMrMrBrB})$	0.0024	0.0047	0.0036	177.41
	$P(\overline{MrMrMrBmB})$	0.0039	0.0074	0.0057	177.02
	$P(\overline{MrMrMrBrB})$	0.0105	0.0201	0.0154	177.16
	$P(\overline{MmMrMrBmM})$	0.0007	0.0034	0.0058	177.16
	$P(\overline{MmMrMrBrM})$	0.0011	0.0054	0.0090	177.54
	$P(\overline{MrMrMrBmM})$	0.0030	0.0148	0.0247	176.90
	$P(\overline{MrMrMrBrM})$	0.0047	0.0232	0.0386	177.29
$P(\overline{MmMrM})$	$P(\overline{BmMmMrMmB})$	0.0008	0.0016	0.0012	177.08
	$P(\overline{BmMmMrMrB})$	0.0013	0.0025	0.0019	176.99
	$P(\overline{BrMmMrMmB})$	0.0013	0.0025	0.0019	177.18
	$P(\overline{BrMmMrMmM})$	0.0021	0.0039	0.0030	177.09
	$P(\overline{BmMmMrMmM})$	0.0002	0.0011	0.0018	177.11
	$P(\overline{BmMmMrMrM})$	0.0009	0.0046	0.0077	176.85

(Continued)

Table IV. Continued

Sequence probability	F_M				
	0.35	0.58	0.75	δ [ppm]	
$P(\overline{\text{BrMmMrMmM}})$	0.0003	0.0017	0.0028	177.20	
$P(\overline{\text{BrMmMrMrM}})$	0.0014	0.0072	0.0120	176.95	
$P(\overline{\text{MmMmMrMmB}})$	0.0002	0.0011	0.0018	177.26	
$P(\overline{\text{MmMmMrMrB}})$	0.0003	0.0017	0.0028	177.17	
$P(\overline{\text{MrMmMrMmB}})$	0.0009	0.0046	0.0077	177.18	
$P(\overline{\text{MrMmMrMrB}})$	0.0015	0.0072	0.0120	177.09	
$P(\overline{\text{MmMmMrMmM}})$	0.0001	0.0007	0.0026	177.29	
$P(\overline{\text{MmMmMrMrM}})$	0.0002	0.0031	0.0112	177.04	
$P(\overline{\text{MrMmMrMmM}})$	0.0002	0.0031	0.0112	177.21	
$P(\overline{\text{MrMmMrMrM}})$	0.0010	0.0132	0.0479	176.96	
$P(\text{MrMrM})$	$P(\overline{\text{BmMrMrMmB}})$	0.0018	0.0034	0.0026	178.72
	$P(\overline{\text{BrMrMrMmB}})$	0.0056	0.0107	0.0082	178.63
	$P(\overline{\text{BrMrMrMrB}})$	0.0044	0.0084	0.0064	178.54
	$P(\overline{\text{MmMrMrMmB}})$	0.0009	0.0046	0.0077	178.75
	$P(\overline{\text{MmMrMrMrB}})$	0.0014	0.0072	0.0120	178.66
	$P(\overline{\text{MrMrMrMmB}})$	0.0040	0.0197	0.0327	178.50
	$P(\overline{\text{MrMrMrMrB}})$	0.0063	0.0308	0.0512	178.41
	$P(\overline{\text{MmMrMrMmM}})$	0.0001	0.0015	0.0056	178.78
	$P(\overline{\text{MrMrMrMmM}})$	0.0010	0.0132	0.0479	178.52
	$P(\overline{\text{MrMrMrMrM}})$	0.0022	0.0282	0.1021	178.27

sequence distribution and their chemical shifts by the incremental method (Table IV). It is not necessary to take into account the splitting of all the triads into pentads since the carbonyl signal of the homopolymer of *n*-butyl acrylate exhibits configurational sensitivity only at the triad level.^[6] The respective values of β increments were derived from the data for the homopolymers in a manner analogous to α increments (Table III). Based on these data, the simulation was performed for line width of 8 Hz (Figure 5), yielding very good agreement between the experimental and simulated spectra. The sequence attribution at the triad and pentad level is presented in Figure 6 for the PMMA/nBA copolymer of $F_M = 0.58$ and for line width of 1 Hz, showing the positions of individual lines.

CONCLUSION

It was shown in this work that microstructural analysis of the copolymer of methyl methacrylate and *n*-butyl acrylate, PMMA/nBA, utilizing the carbonyl signal in the 100 MHz ^{13}C NMR spectrum recorded in acetone- d_6 has to be performed taking into account the configurational effects of

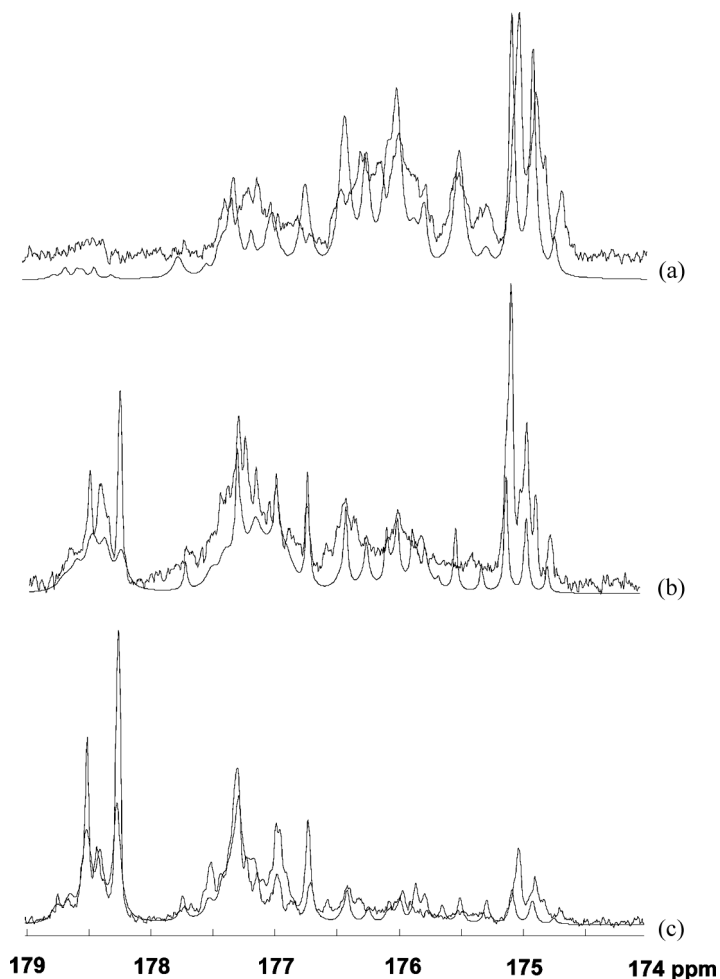


Figure 5. Simulation of the carbonyl signal of PMMA/nBA with the account of the pentad splitting and 8 Hz line width, F_M : 0.35 (a), 0.58 (b), and 0.75 (c).

both comonomers. The spectral data obtained from respective homopolymers, i.e., poly(methyl methacrylate), PMMA, and poly(*n*-butyl acrylate), PnBA, can be safely utilized in the analysis of the copolymer. Therefore, the increments used to calculate the position of respective configurational triads and pentads of homopolymers can be positively used to calculate the chemical shifts of configurational-compositional sequences in the copolymer. The configurational effect introduced by the methyl methacrylate unit can be observed at the pentad level while that of *n*-butyl acrylate is only at the triad level. Therefore, in the analysis

of the PMMA/nBA copolymer, only a part of the lines can be characterized in terms of pentads. The sequences of pure M composition can be observed at the pentad level, and those composed solely of B units can be observed at the triad level. The sequences of mixed composition exhibit partial pentad splitting.

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