Characterization of the stereochemical structure of poly(acrylic acid) by one- and two-dimensional $^{13}C-^1H$ nuclear magnetic resonance spectra

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The stereochemical structure of two samples of poly(acrylic acid) (PAA) of different tacticities was studied by a combination of one- and two-dimensional (2D) $^{13}C-^1H$ nuclear magnetic resonance (n.m.r.) spectra. Lines in ^{13}C n.m.r. spectra of PAA solutions in D_2O could be assigned to configurational triads (CH region) and hexads or hexad pairs (CH_2 region). For analysis of the CH_2 region, the application of the inverse HETCOR (heteronuclear correlation) (i.e. heteronuclear multiple-quantum coherence, HMQC) 2D $^{13}C-^1H$ n.m.r method was essential. Both for CH and for CH_2 carbon resonances our assignment differs from those previously published in the literature. The studied PAA samples prepared by radical polymerization or by hydrolysis of poly(t-butyl acrylate) obtained by anionic polymerization obey Bernoullian statistics.

(Keywords: poly(acrylic acid); stereochemical structure; nuclear magnetic resonance)

INTRODUCTION

Nuclear magnetic resonance (n.m.r.) spectroscopy is a very sensitive method for characterizing the stereochemical structure of polymers, because the chemical shift is sensitive to configurational sequences[1-3]. The existence of spectrometers working at higher magnetic field has made it possible to observe resolved lines from longer configurational sequences in the spectra of a number of systems, including vinyl polymers. However, only a few studies have been published on the stereochemical structure of poly(acrylic acid) (PAA), all based on classic one-dimensional ^{13}C n.m.r. spectra[4-7]. In these studies no effect of the tacticity on the carbonyl resonance was detected. In 22.6 MHz ^{13}C n.m.r. spectra of PAA, Schaefer[4] observed three components for both methine and methylene resonances; in both cases he assigned the upfield component to the isotactic (meso, *m*) sequences (triads for CH resonances) and the downfield component to the syndiotactic (racemic, *r*) sequences. While the same assignment has been published for the methine region in further studies of PAA[5,6] (extended to pentad analysis in 75 MHz ^{13}C n.m.r. spectra by Chang *et al.*[6]), several controversial interpretations exist for the methylene region. Watts[5] ascribed the downfield CH_2 component to the *m* sequences and the upfield component to a mixture of *m* and *r* sequences, but his assignment was based only on the similarity of the

methylene region in ^1H and ^{13}C n.m.r. spectra and as such lacks any substantiation. Pham *et al.*[7] assigned the CH_2 resonances at lowest and highest field to *rrr* and *mmm* tetrads, respectively. On the other hand, Chang *et al.*[6] assume that, in the CH_2 region, the resonance at lowest field corresponds to *mmr* or *mrr* tetrads.

Traditional techniques based on one-dimensional n.m.r. spectra are not always sufficient for unequivocal line assignment; to this end, two-dimensional (2D) n.m.r. is very useful, in particular the homonuclear (COSY) and heteronuclear (HETCOR) correlation spectroscopies[3]. Recently we have studied the stereochemical structure of some polyacrylates by a combination of one- and two-dimensional n.m.r. methods[8,9]. For a reliable assignment of methylene resonances in ^1H and ^{13}C n.m.r. spectra to configurational tetrads, we found the application of the inverse HETCOR (i.e. HMQC, heteronuclear multiple-quantum coherence) $^{13}C-^1H$ n.m.r. method to be essential, as it enabled us to define the resonances of methylene carbons with equivalent and non-equivalent protons. In this paper this 2D n.m.r. technique combined with one-dimensional ^{13}C and ^1H n.m.r. spectra was applied to the study of two samples of PAA of different tacticities prepared by different methods.

EXPERIMENTAL

Samples
Two samples of PAA were prepared under different

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conditions. Atactic (a) PAA was prepared by radical polymerization of purified acrylic acid at 60°C in aqueous medium using potassium peroxysulfate as initiator. Predominantly isotactic (i) PAA was prepared by hydrolysis of the crystalline, predominantly isotactic poly(t-butyl acrylate) (i-PtBuA); the latter polymer was prepared by anionic polymerization of tBuA in hexane at −70°C, using butyllithium as the initiator. Details of the preparation both of the i-PtBuA and of i-PAA (by hydrolysis of the i-PtBuA) are given elsewhere[10].

N.m.r. measurements

Solutions of PAA in D_2O were measured in 5 mm n.m.r. tubes. The concentration of the solution was 10% (w/v) for a-PAA and 2% (w/v) for i-PAA (this was the maximum attainable concentration for this polymer). Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), in ^{13}C n.m.r. spectra with a signal at −1.6 ppm from tetramethylsilane (TMS), was used as the internal standard. All cited chemical shifts are referred to DSS. N.m.r. spectra were measured at 85°C using a Varian Unity-500 spectrometer operating at 499.8 MHz for ^1H n.m.r. and 125.7 MHz for ^{13}C n.m.r. In 1D ^{13}C and ^1H n.m.r. measurements, 30° pulses with pulse interval 5.3 s and 5.9 s were used. Under these conditions we could measure the correct intensities for all lines of main-chain carbons and protons.

HMQC (inverse HETCOR) spectra[11,12], which enable us to achieve a much higher sensitivity compared to classic HETCOR, were also obtained with 10% (a-PAA) and 2% (i-PAA) solutions in D_2O at 85°C. In order to enhance the effectiveness of suppressing the signals of protons bound to ^{12}C, the sequence BIRD[13] (bilinear rotation decoupling) was inserted before the beginning of the basic sequence. The delay separating the BIRD sequence from the basic HMQC sequence was set at 0.3 s. A total of 48 scans were accumulated over 512 t_1 increments with a relaxation delay of 0.6 s for the a-PAA solution. For the i-PAA solution, a total of 128 scans were accumulated over 256 t_1 increments with a relaxation delay of 0.5 s. A sine-bell apodization function with phase shift was applied in both dimensions prior to Fourier transformation. The total acquisition time was 17 h and 19 h for a- and i-PAA, respectively.

RESULTS AND DISCUSSION

The ^1H n.m.r. spectra of a-PAA and i-PAA solutions in D_2O, measured at 85°C, are shown in *Figure 1*. In the methylene region, the low-field and high-field bands centred at 1.98 ppm and 1.65 ppm, respectively, correspond to non-equivalent protons in *m* diads; the central band at 1.79 ppm corresponds to *r* diads[7]. From their intensities the populations of *m* and *r* diads in both studied samples could be easily obtained: in a-PAA (*m*) = 0.5, in i-PAA (*m*) = 0.74.

The ^{13}C n.m.r. spectra of 10% and 2% solutions of a-PAA and i-PAA, respectively, in D_2O, measured again at 85°C, are shown in *Figure 2*. For all carbon types the chemical shifts of corresponding lines in the spectra of a- and i-PAA are slightly different, being larger for i-PAA. For the lines of methine and methylene carbons, this difference amounts to 0.15 ppm and 0.1 ppm, respectively. The difference of chemical shifts for a-PAA and i-PAA is evidently a consequence of the fact

that ^{13}C chemical shifts of PAA depend on pH[4,6]; in the pH range 2–8, all lines are similarly shifted to lower field (larger chemical shift) with increasing pH. Owing to different concentration of the solution and the presence of DSS, the pH values of the studied a- and i-PAA solutions (measured directly in n.m.r. tubes, no D_2O correction) were pH = 2.3 and 3.0 for a-PAA and i-PAA solutions, respectively.

From *Figure 2* we can see that, in 125 MHz ^{13}C n.m.r. spectra, a fine splitting also occurs for the carbonyl band, reflecting various pentad structures. Even more interesting is the range of the methine carbons. On the basis of a comparison of the intensities of methine resonances in ^{13}C n.m.r. spectra of a- and i-PAA, we can assume that resonances of *mm* triads appear at lower field and those of *rr* triads (or *rr*-centred pentads) at higher field with respect to *mr* triads. By analysis of the methine range in ^{13}C n.m.r. spectra, the triad populations were determined for a- and i-PAA; the results are given in *Table 1*. The experimental contents in *Table 1* are based on integrals taken in local minima of the resonance curve by using the spectrometer's integration software; they agreed well with values obtained by deconvolution of partly overlapping lines and curve fitting. For both polymers, the triad populations agree with the diad data obtained from ^1H n.m.r. spectra, fulfilling well the necessary relationship between diads and triads: $(m) = (mm) + (mr)/2$, $(r) = (rr) + (mr)/2$; thus supporting the correctness of our assignment at the triad level. The spectra presented in *Figure 2* contradict the previously published assignments of CH resonances[4-6] with the downfield and upfield components assigned to *rr* and *mm* triads, respectively.

By means of the established triad populations, we can test whether the propagation of the polymer chain obeys Bernoullian statistics. The probability $P_{r/m}$ that the monomeric unit added to a polymer chain terminated by a racemic diad will generate a meso diad is given by the relation[1]:

$$P_{r/m} = \frac{(mr)}{2(rr) + (mr)} \qquad (1)$$

and similarly for $P_{m/r}$:

$$P_{m/r} = \frac{(mr)}{2(mm) + (mr)} \qquad (2)$$

When $P_{r/m} + P_{m/r} = 1$, then chain propagation obeys random Bernoullian statistics and $P_{r/m}$ is equal to P_m, the population of *m* diads in the polymer chain. For a-PAA, relations (1) and (2) yield $P_{r/m} = 0.5$ and $P_{m/r} = 0.5$; and for i-PAA, $P_{r/m} = 0.74$ and $P_{m/r} = 0.27$. As for both polymers the sum of the placement probabilities is equal to 1 within experimental error (1.00 for a-PAA and 1.01 for i-PAA), we can state that both a-PAA and i-PAA obey Bernoullian statistics (i.e. that possible deviations from the Bernoullian model are not significant). This finding is not surprising because a-PAA was prepared by radical polymerization, for which Bernoullian statistics is very common[1,2]; i-PAA was obtained by hydrolysis of the anionically prepared PtBuA and the validity of the Bernoullian model for PtBuA prepared by anionic polymerization was shown in our earlier paper[8]. The finding that both studied polymers obey Bernoullian statistics enabled us to obtain also a partial assignment at
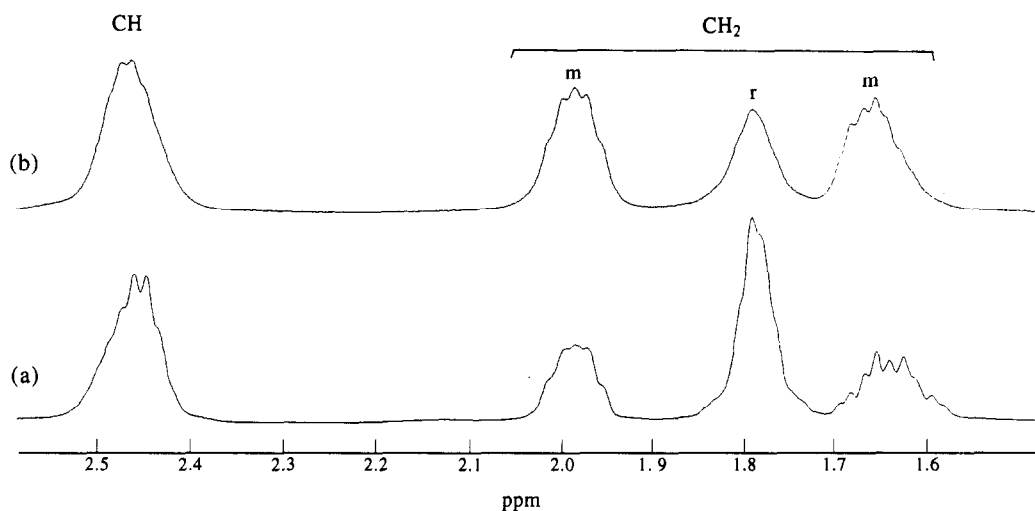
Figure 1 The 500 MHz ^{1}H n.m.r. spectra of solutions of a-PAA (a) and i-PAA (b) in D_2O; concentrations 10% (a) and 2% (b), temperature 85°C

pentad level for the upfield region of the CH resonances (*rr*-triads) in ^{13}C n.m.r. spectra, based on a comparison of the experimental intensities with those predicted for the Bernoullian model. Although for i-PAA the exact experimental intensities of individual lines at the pentad level could not be determined, the shape of the respective region in the ^{13}C n.m.r. spectrum as shown in *Figure 2* is in agreement with the assignment as presented in *Table 1*.

From *Figure 2* it is evident that the range of the methylene resonances is the most informative from the point of view of the stereochemical structure of PAA samples and line resolution at hexad level is visible in 125 MHz ^{13}C n.m.r. spectra. First, a reliable assignment of the methylene carbon resonances to various tetrads was necessary. For this purpose the same approach was used as in our recent studies of several polyacrylates, based on the application of the inverse HETCOR 2D n.m.r. method[8,9]. HETCOR (^{13}C–^{1}H) n.m.r. spectra (methylene region only) of a-PAA and i-PAA in D_2O solutions, obtained by the inverse (HMQC) technique,
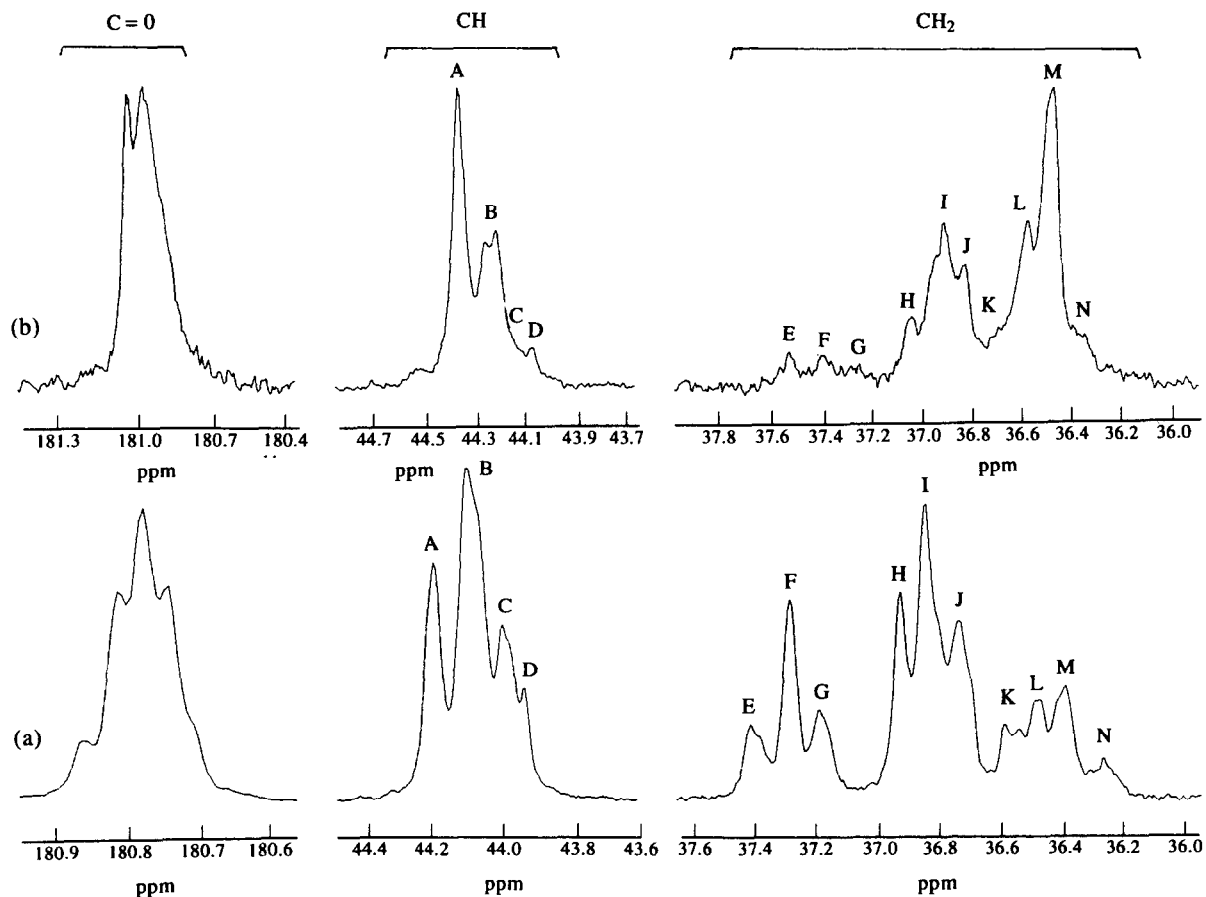

Figure 2 The 125 MHz ^{13}C n.m.r. spectra of solutions of a-PAA (a) and i-PAA (b) in D_2O; concentrations 10% (a) and 2% (b), temperature 85°C

Table 1 Methine ^{13}C n.m.r. chemical shifts and experimental and calculated triad and pentad contents for PAA obeying Bernoullian statistics

| | | | Sequence content | | | |
| | | | a-PAA | | i-PAA | |
Signal[a]	Chemical shift[b] (ppm from DSS)	Sequence	Calc. $(P_m = 0.5)$	Exp.	Calc. $(P_m = 0.74)$	Exp.
A	44.19	mmm	0.25	0.25	0.54_8	0.53
B	44.05–44.10	mr	0.50	0.50	0.38_5	0.40
C + D	43.92–43.99	rr	0.25	0.25	0.06_8	0.07
C	43.96–43.99	$\left.\begin{array}{l}rrrr \\ rrrm\end{array}\right.$	$\left.\begin{array}{l}0.06_3 \\ 0.12_5\end{array}\right\}0.18_8$	0.19	$\left.\begin{array}{l}0.00_5 \\ 0.02_6\end{array}\right\}0.03_1$	—[c]
D	43.92	$mrrm$	0.06_3	0.06	0.03_7	—[c]

[a] Cf. *Figure 2*
[b] Chemical shifts for 10% solution of a-PAA in D_2O
[c] Not determined

are shown in *Figure 3*. While in both the ^{1}H and ^{13}C domains the chemical shifts for PAA samples are somewhat different from those for various polyacrylates, and in particular the total region of CH_2 resonance in the ^{13}C domain is much narrower for PAA (only 1.2 ppm for PAA in comparison to 2–3 ppm for polyacrylates), the shape of the HETCOR spectra is very similar for both polymer types. Similarly as for polyacrylates, also here these spectra enabled us to define the resonances of methylene carbons with equivalent and non-equivalent protons. In *Figure 3*, always nine cross-peaks can be seen corresponding to three tetrads containing magnetically non-equivalent CH_2 protons (*mmm, rmr, mmr*) and three tetrads containing magnetically equivalent CH_2 protons (*rrr, mrm, mrr*). At the same time in the ^{13}C n.m.r. spectrum, always one of the tetrads with non-equivalent protons and one of the tetrads with equivalent protons overlap. Comparison of the intensities of various resonances for a-PAA and i-PAA samples, with the

values predicted by the Bernoullian model (in a similar way as described in more detail in ref. 8), made it possible to assign the particular resonances in HETCOR spectra of PAA as shown in *Figure 3* and in *Table 2*. Both for a-PAA and for i-PAA, a very good agreement between the expected tetrad contents assuming the Bernoullian statistics and the experimental ones follows from *Table 2*. The HETCOR spectra presented in *Figure 3* show unambiguously that, for the methylene region in ^{13}C n.m.r. spectra of PAA solutions, the assignments as published in previous studies[5–7] were wrong. Moreover, from *Figure 3* one can also see that ^{1}H n.m.r. chemical shifts of the high-field proton are somewhat different in various *m*-centred tetrads; this fact is also reflected in the splitting of the corresponding resonance at 1.6–1.7 ppm in *Figure 1*.

Once we had the resonances of the methylene carbons reliably assigned at the tetrad level, we could extend this assignment (at least tentatively) to the hexad level. Based
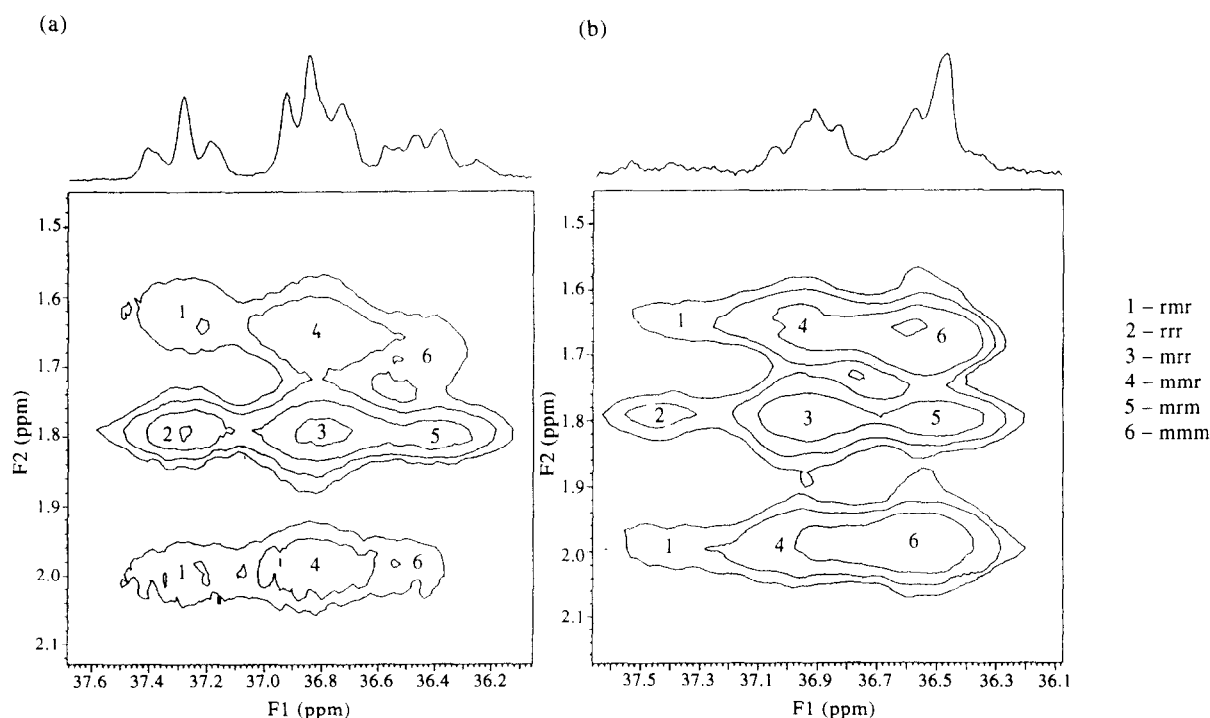

Figure 3 Section of 2D ^{13}C–^{1}H HETCOR n.m.r. spectra of solutions of a-PAA (a) and i-PAA (b) in D_2O obtained by the inverse HETCOR experiment (HMQC); concentrations 10% (a) and 2% (b), temperatures 85°C

Table 2 Methylene ^{13}C n.m.r. chemical shifts and experimental and calculated tetrad contents for PAA obeying Bernoullian statistics

		Tetrad content			
		a-PAA		i-PAA	
Chemical shift[a] (ppm from DSS)	Tetrad	Calc. ($P_m = 0.5$)	Exp.	Calc. ($P_m = 0.74$)	Exp.
37.15–37.41	$\begin{cases} rrr \\ rmr \end{cases}$	$\left.\begin{matrix} 0.12_5 \\ 0.12_5 \end{matrix}\right\} 0.25$	0.26	$\left.\begin{matrix} 0.01_8 \\ 0.05 \end{matrix}\right\} 0.06_8$	0.08
36.62–37.00	$\begin{cases} mrr \\ mmr \end{cases}$	$\left.\begin{matrix} 0.25 \\ 0.25 \end{matrix}\right\} 0.50$	0.49	$\left.\begin{matrix} 0.10 \\ 0.28_4 \end{matrix}\right\} 0.38_4$	0.36
36.20–36.60	$\begin{cases} mrm \\ mmm \end{cases}$	$\left.\begin{matrix} 0.12_5 \\ 0.12_5 \end{matrix}\right\} 0.25$	0.25	$\left.\begin{matrix} 0.14_2 \\ 0.40_5 \end{matrix}\right\} 0.54_7$	0.56

[a] Chemical shifts for 10% solution of a-PAA in D_2O

on the shape of the HETCOR spectra in *Figure 3* we assumed that both *r*- and *m*-centred hexads will cover practically the whole range of the carbon resonances of the given tetrad pair. For both PAA samples experimental intensities (determined in the same way as described for the analysis of CH range) were again compared with calculated hexad populations taking into account the validity of the Bernoullian model. In such a way a complete hexad assignment, summarized in *Table 3*, could be made. Under assumptions given above, no other combination of hexads satisfactorily fits the experimental intensities, with one exception only. For i-PAA, the intensities of the bands of the *rrr*- and *rmr*-centred hexads could not be exactly

determined; however, the shape of the ^{13}C n.m.r. spectrum in this region and the proportions of band intensities agree well with the calculated values. Nevertheless, the possibility that signals of *mrrrm* and *rrrr* hexads in *Table 3* are interchanged cannot be excluded. It is interesting that for *rrr*- and *rmr*-centred hexads, the order of methylene carbon resonances for PAA as shown in *Table 3*, from lower to higher field, is the same as that observed for poly(ethyl acrylate) and poly(butyl acrylate)[9].

CONCLUSIONS

Our analysis of the 1D and 2D ^{13}C–^{1}H n.m.r. spectra has

Table 3 Methylene ^{13}C n.m.r. chemical shifts and experimental and calculated contents of various hexads for PAA obeying Bernoullian statistics

			Hexad content			
			a-PAA		i-PAA	
Signal[a]	Chemical shift[b] (ppm from DSS)	Hexad	Calc. ($P_m = 0.5$)	Exp.	Calc. ($P_m = 0.74$)	Exp
E	37.37–37.42	$\begin{cases} mrrrm \\ mrmrm \end{cases}$	$\left.\begin{matrix} 0.03_1 \\ 0.03_1 \end{matrix}\right\} 0.06_2$	0.06	$\left.\begin{matrix} 0.01 \\ 0.02_7 \end{matrix}\right\} 0.03_7$	–[c]
F	37.27	$\begin{cases} mrrrr \\ mrmrr \end{cases}$	$\left.\begin{matrix} 0.06_2 \\ 0.06_2 \end{matrix}\right\} 0.12_4$	0.12	$\left.\begin{matrix} 0.00_7 \\ 0.02 \end{matrix}\right\} 0.02_7$	–[c]
G	37.14–37.18	$\begin{cases} rrrr \\ rrmrr \end{cases}$	$\left.\begin{matrix} 0.03_1 \\ 0.03_1 \end{matrix}\right\} 0.06_2$	0.06	$\left.\begin{matrix} 0.00_1 \\ 0.00_3 \end{matrix}\right\} 0.00_4$	–[c]
H	36.92	$\left\{\begin{matrix} rmrrr \\ mmmrr \\ \text{or} \\ rmmrm \end{matrix}\right.$	$\left.\begin{matrix} 0.06_2 \\ \\ 0.06_2 \end{matrix}\right\} 0.12_4$	0.13	$\left.\begin{matrix} 0.00_7 \\ \\ 0.05_5 \end{matrix}\right\} 0.06_2$	0.05_5
I	36.78–36.83	$\left\{\begin{matrix} rmrrm \\ mmrrr \\ rmmrr \\ mmmrm \end{matrix}\right.$	$\left.\begin{matrix} 0.06_2 \\ 0.06_2 \\ 0.06_2 \\ 0.06_2 \end{matrix}\right\} 0.24_8$	0.23_5	$\left.\begin{matrix} 0.01_9 \\ 0.01_9 \\ 0.01_9 \\ 0.15_6 \end{matrix}\right\} 0.21_3$	0.20_5
J	36.72	$\left\{\begin{matrix} mmrrm \\ mmmrr \\ \text{or} \\ rmmrm \end{matrix}\right.$	$\left.\begin{matrix} 0.06_2 \\ \\ 0.06_2 \end{matrix}\right\} 0.12_4$	0.13	$\left.\begin{matrix} 0.05_5 \\ \\ 0.05_5 \end{matrix}\right\} 0.11$	0.10
K	36.53–36.58	$\begin{cases} rmrmr \\ rmmmr \end{cases}$	$\left.\begin{matrix} 0.03_1 \\ 0.03_1 \end{matrix}\right\} 0.06_2$	0.06_5	$\left.\begin{matrix} 0.01 \\ 0.02_7 \end{matrix}\right\} 0.03_7$	0.03_5
L	36.46–36.48	$rmmmm$	0.06_2	0.06_5	0.15_6	0.17
M	36.36–36.40	$\begin{cases} rmrmm \\ mmmmm \end{cases}$	$\left.\begin{matrix} 0.06_2 \\ 0.03_1 \end{matrix}\right\} 0.09_3$	0.09_5	$\left.\begin{matrix} 0.05_4 \\ 0.22_2 \end{matrix}\right\} 0.27_6$	0.28
N	36.25	$mmrmm$	0.03_1	0.03	0.07_8	0.06

[a] Cf. *Figure 2*

[b] Chemical shifts for 10% solutions of PAA in D_2O

[c] Not determined

shown that the assignment of methylene resonances in [13]C n.m.r. spectra of PAA to various tetrads as published in former publications[5-7] was incorrect; in this paper the assignments were revised. Contrary to [13]C n.m.r. spectra of polyacrylates, where in the methine range the band of *mm* triads appears at highest field[8,9], for PAA (pH = 2.3–3.0) *mm* triads appear at lowest field in the methine range. Based on triad data we have confirmed that both a-PAA prepared by radical polymerization and i-PAA prepared by hydrolysis of the anionically polymerized PtBuA obey Bernoullian statistics. By means of the inverse [13]C–[1]H HETCOR (HMQC) n.m.r. spectra we have proved that the assignment of methylene resonances to tetrad structures found by us recently for several types of polyacrylates[8,9] holds also for PAA. Therefore from the comparison of experimental integrated intensities with those predicted by the Bernoullian model, a complete tentative assignment of the resolved lines in the methylene region of the 125 MHz [13]C n.m.r. spectra to various hexads or hexad pairs was possible. For the range of the *rrr*- and *rmr*-centred hexads, this assignment is similar to that found by us for poly(ethyl acrylate) and poly(butyl acrylate)[9].

ACKNOWLEDGEMENTS

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