Characterization of the Stereochemical Structure of Poly(*tert*-butyl acrylate) by One- and Two-Dimensional NMR Spectroscopy

Miloš Suchopárek and Jiří Spěváček*

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

Received June 9, 1992; Revised Manuscript Received September 25, 1992

ABSTRACT: Two samples of poly(*tert*-butyl acrylate) (PtBuA) prepared by group-transfer and anionic polymerization were studied by a combination of one- and two-dimensional NMR methods. Lines in ^{1}H and ^{13}C NMR spectra of PtBuA solutions could be assigned to the configurational triads (CH range) and tetrads (CH_2 range). For analysis of the CH_2 range, the application of the inverse HETCOR (HMQC) technique was essential. The results obtained by the analysis of line intensities at tetrad level confirm that both PtBuA samples obey Bernoullian statistics.

Introduction

It is well-known that NMR spectroscopy is probably the most effective method for characterizing the configurational structure of polymers, because the chemical shift is sensitive to configurational sequences.[1,2] In the last 10 years this capability has been further enhanced by the development of spectrometers working at high magnetic fields. For configurational analysis, however, the resolved lines in the NMR spectrum have to be assigned to various stereochemical sequences in the polymer. Traditional techniques were not always suitable for unequivocal line assignment; to this end, two-dimensional NMR is very useful, especially the homonuclear (COSY) and heteronuclear (HETCOR) correlation spectroscopies;[3] these methods have been applied in studies of the stereochemical structure of a number of polymer systems.[4-9] The usefulness of the f_1-decoupled version of the COSY experiment in a study of poly(vinyl alcohol) was demonstrated by Gippert and Brown.[10] Kotyk et al.[11] demonstrated the advantage of proton-detected heteronuclear multiple-bond correlation (HMBC) NMR spectroscopy in a study of the microstructure of poly(methyl methacrylate) (PMMA). The heteronuclear spin-lock relay experiment was used to assign configurational tetrads and pentads to lines in ^{13}C NMR spectra of poly(vinyl chloride).[12] Of the acrylate polymers, the configurational structure has so far been studied in poly(methyl acrylate) (PMA), poly(isopropyl acrylate) (PiPA), and poly(1-naphthyl acrylate) but only by classical one-dimensional NMR spectroscopy.[13-15] Matsuzaki et al.[14] observed indications of resolution into three components for CH and CH_2 resonances in 25-MHz ^{13}C NMR spectra of PMA and PiPA; they assigned these components to various triads (CH) and groups of two or three tetrads (CH_2), presuming that the system obeys Bernoullian statistics.

As part of a broader study of *tert*-butyl acrylate (tBuA) oligomers and polymers, the aim of this work was the assignment of NMR bands and subsequent characterization of the configurational structure of poly(*tert*-butyl acrylate). The stereochemical structure of PtBuA has not been studied so far. A combination of one-dimensional (^{1}H and ^{13}C) and two-dimensional NMR methods was applied to the study of two samples of PtBuA prepared by different methods (group-transfer and anionic polymerization). In this study the inverse HETCOR experiment (HMQC) played an essential role; we point out its importance in studies of poorly soluble polymers.

Experimental Section

Samples. Two samples of PtBuA were prepared under different conditions. PtBuA I was prepared by group-transfer polymerization of tBuA in tetrahydrofuran at −11 °C. The polymerization time was 75 min; 1-methoxy-1-[(trimethylsilyl)oxy]-2-methylpropene was used as the initiator. PtBuA II was prepared by anionic polymerization of tBuA in toluene at −60 °C. The polymerization time was 5 min; butyllithium was used as the initiator. In analogy to the preparation of PMMA, it could be assumed that polymer I should be atactic, while polymer II should be predominantly isotactic.

NMR Measurements. Solutions of PtBuA in C_6D_6 or in $CDCl_3$ were measured in 5-mm tubes. The internal standard was hexamethyldisiloxane (HMDS), with a signal at 0.05 ppm from TMS in ^{1}H spectra and at 2 ppm in ^{13}C spectra. All cited chemical shifts (including all figures) are referred to HMDS. NMR spectra were measured at 70 °C (C_6D_6) or 60 °C ($CDCl_3$) using a Varian Unity-500 spectrometer operating at 499.8 MHz for ^{1}H NMR and 125.7 MHz for ^{13}C NMR and using a Bruker AC-300 spectrometer operating at 300.1 MHz for ^{1}H NMR and 75.5 MHz for ^{13}C NMR.

F_1-Decoupled COSY spectra were obtained with 2% (all concentrations are presented as weight percent) PtBuA solutions in C_6D_6 using the pulse sequence RD–90°–$t_1/2$–180°–(Δ–$t_1/2$)–45°–FID.[16] The operating frequency was 499.8 MHz. The fixed interval Δ was set at 0.175 s. A total of 32 scans with 640 increments was accumulated with a relaxation delay of 1.25 s. A sine-bell apodization function without phase shift was applied in both dimensions before Fourier transformation. The total acquisition time was 15 h.

A classical ^{13}C–^{1}H HETCOR spectrum with proton decoupling in the F_1 domain[17-19] was obtained with a 60% solution of PtBuA I in C_6D_6 (with PtBuA II, solutions of concentration higher than 5% could not be prepared). The operating frequency for ^{13}C was 125.7 MHz. The delay times Δ_1 and Δ_2 were set at 3.7 and 1.8 ms, respectively; the number of increments was 64. A sine-bell apodization function with phase shift was applied in both dimensions prior to Fourier transformation. The total acquisition times were 15 and 19.5 h, respectively.

HMQC (inverse HETCOR) spectra[20,21] were obtained with 5% solutions of both polymers in C_6D_6. In order to enhance the effectiveness of suppressing the signals of protons bound to ^{12}C, the sequence BIRD[22] was inserted before the beginning of the basic sequence. The operating frequency for ^{1}H was 499.8 MHz. The delay separating the BIRD sequence from the basic HMQC sequence was set at 0.5 s. A total of 48 scans was accumulated over 280t_1 increments with a relaxation delay of 1 s. A sine-bell apodization function with phase shift was applied in both dimensions prior to Fourier transformation. The total acquisition time was 12 h for every experiment.

The heteronuclear H–H–C relay spectra were obtained with a 60% solution of PtBuA I in C_6D_6 both by the classical[23] and

© 1993 American Chemical Society

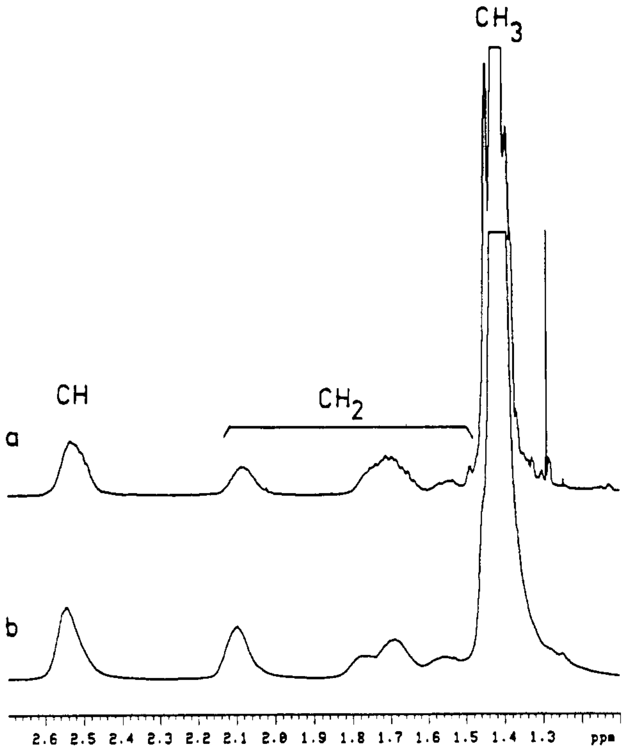

Figure 1. 500-MHz ^{1}H NMR spectra of solutions of PtBuA I (a) and PtBuA II (b) in C_6D_6; concentrations 5% (a) and 2% (b).

by the improved method, the heteronuclear spin-lock relay experiment;[24] in the latter case, due to the unacceptably large base-line distortion[25] caused by the strong *tert*-butyl signal, the INEPT part of the sequence was replaced by the original INEPT sequence with refocusing pulses. The operating frequency for ^{13}C was 75.5 MHz. With the heteronuclear spin-lock relay spectrum, a total spin lock time of 15 ms was used, consisting of five 3-ms periods in which the transmitter phase was alternated by 180° to compensate for off-resonance effects.[26] The delay times Δ_1 and Δ_2 were set at 3.7 and 2.2 ms, respectively. A total of 1344 scans was accumulated over $64t_1$ increments with a relaxation delay of 1.5 s. A simple exponential function (lb = 2) was applied in the f_2 dimension and a sine-bell function with a phase shift in the f_1 dimension, prior to Fourier transformation. The total acquisition time was 62 h.

Results and Discussion

In Figure 1 are shown the ^{1}H NMR spectra of 5% and 2% solutions of PtBuA I and II, respectively, in C_6D_6, measured at 70 °C. In Figure 2 are shown the ^{13}C NMR spectra of 10% and 5% solutions of polymers I and II, respectively, in C_6D_6, measured again at 70 °C. A comparison of the spectra of the two polymers reveals that in ^{13}C spectra (mainly in the resonance range of methylene carbons at 33–37 ppm) band splitting occurs, reflecting various populations of stereoisomeric sequences (n-ads) in the polymer chain. ^{1}H NMR spectra are much less informative in this respect. On the basis of a comparison of the methine resonances in ^{13}C NMR spectra of the two polymers, in view of the expected configurational structure (assuming that PtBuA I should be atactic, whereas PtBuA II should be more isotactic), and in accord with the assignment of methine resonances in ^{13}C NMR spectra of PiPA to triad sequences proposed by Matsuzaki et al.,[14] we can state that in ^{13}C NMR spectra the methine resonances of mm-centered sequences appear at higher field and those of rr-centered sequences at lower field with respect to mr-centered sequences. In C_6D_6 solutions the resonances of rr- and mr-centered sequences partly overlap, thus preventing quantitative determination of triad populations in the polymer chain by direct integration of ^{13}C methine resonances. However, we have found that this information can much better be obtained by integration of methine bands in ^{13}C spectra of $CDCl_3$ solutions of PtBuA (see Figure 3) where bands of rr and mr triads do not overlap. On the other hand, in ^{1}H NMR spectra of $CDCl_3$ solutions, methylene resonances are seriously overlapped by the strong band of *tert*-butyl groups, so that they cannot be quantitatively analyzed in this solvent. By analysis of the methine range in ^{13}C NMR spectra of PtBuA in $CDCl_3$, the following triad populations were determined.

PtBuA I: (rr) = 0.26; (mr) = 0.49; (mm) = 0.25

PtBuA II: (rr) = 0.08; (mr) = 0.42; (mm) = 0.50

Projections of homonuclear 2D J-resolved spectra of C_6D_6 solutions of both polymers have shown that the broad

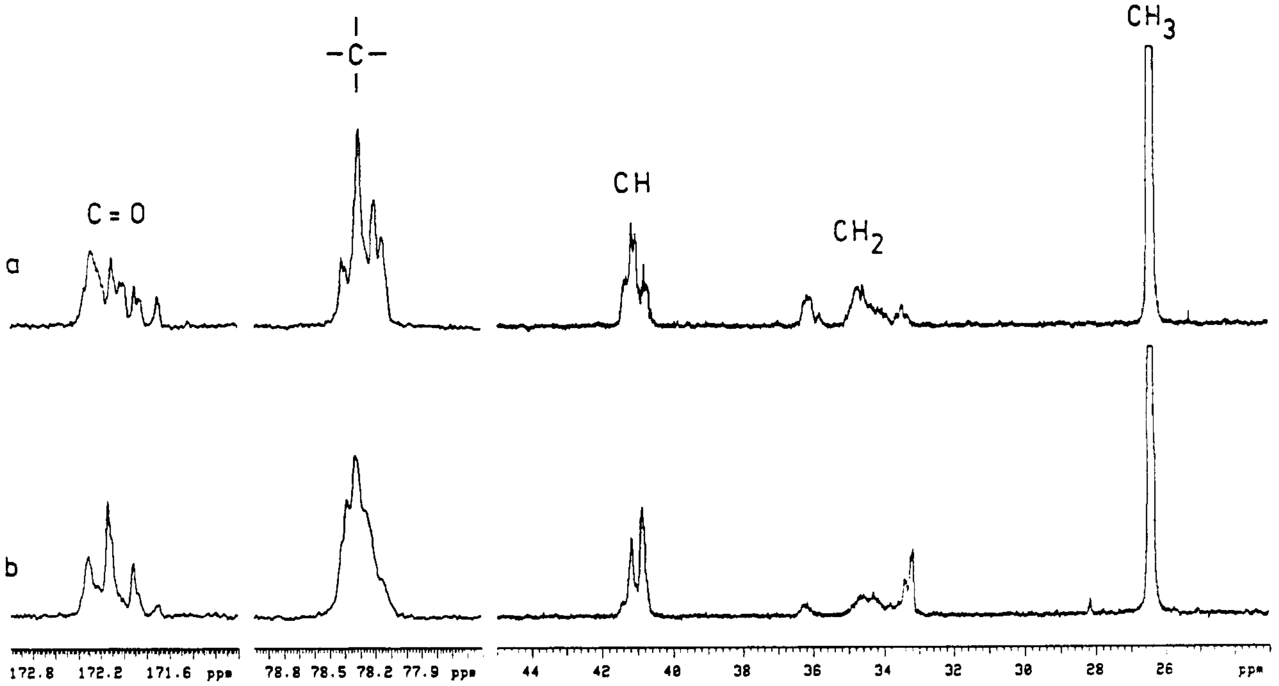

Figure 2. 125-MHz ^{13}C NMR spectra of solutions of PtBuA I (a) and PtBuA II (b) in C_6D_6; concentrations 10% (a) and 5% (b).

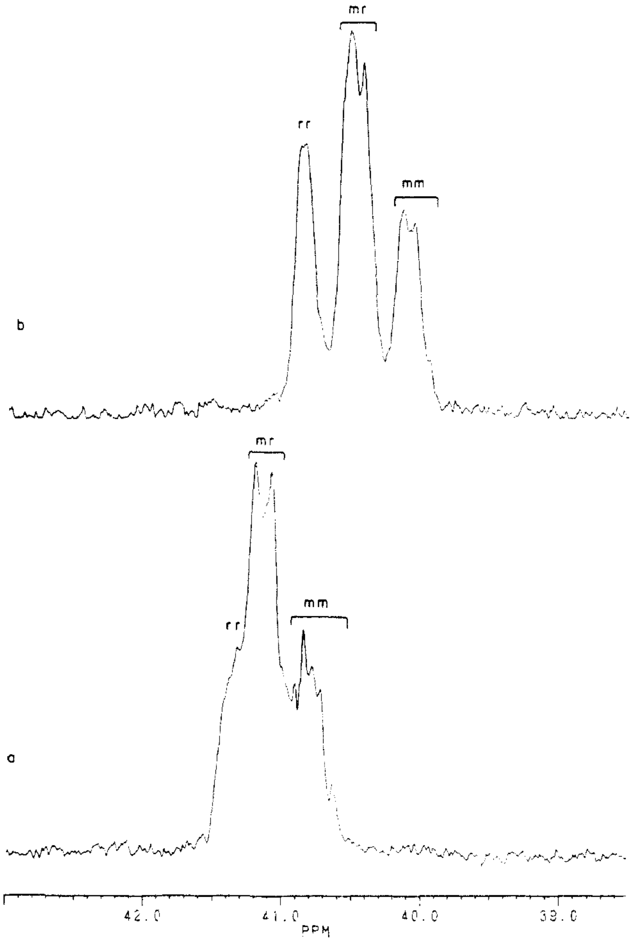

Figure 3. Range of methine resonances in 75-MHz ^{13}C NMR spectra of PtBuA I in C_6D_6 (a) and $CDCl_3$ (b); concentration 10%.

multiplets in ^{1}H spectra consist of a surprisingly large number of signals differing by chemical shifts, indicating a large sensitivity of proton chemical shifts to the structure of the PtBuA chain. This was also confirmed by F_1-decoupled COSY spectra; an F_1-decoupled COSY spectrum of PtBuA I in C_6D_6 is shown in Figure 4. In this spectrum, the cross peaks of the methine multiplet (2.4–2.6 ppm) indicate that the chemical shifts of methine protons reflect even pentad structure. The cross peaks of methylene protons then reflect hexad structure of the polymer chain. This spectrum enables us to obtain an idea about the position of the resonances of magnetically equivalent and nonequivalent methylene protons in the ^{1}H NMR spectrum (some of them even reach into the strong peak of *tert*-butyl protons). A comparison of F_1-decoupled COSY spectra of both polymers further shows that the methine proton band of the heterotactic (mr) triad (or better the bands of mr-centered pentads) rather surprisingly occurs at a higher field than the mm and rr methine resonances. Our conclusion is also confirmed by a section of the HETCOR spectrum (280 increments) (Figure 5) of the 60% solution of PtBuA I in C_6D_6, showing cross peaks of methine carbon resonances with the resonances of their own methine protons. From the spectrum it is evident that the signals corresponding to mr-centered sequences and resonating in the ^{13}C spectrum between the mm- and rr-centered sequences, as expected, exhibit cross peaks with methine protons at higher field and that, in the range of methine protons, resonances of mm- and rr-centered sequences overlap.

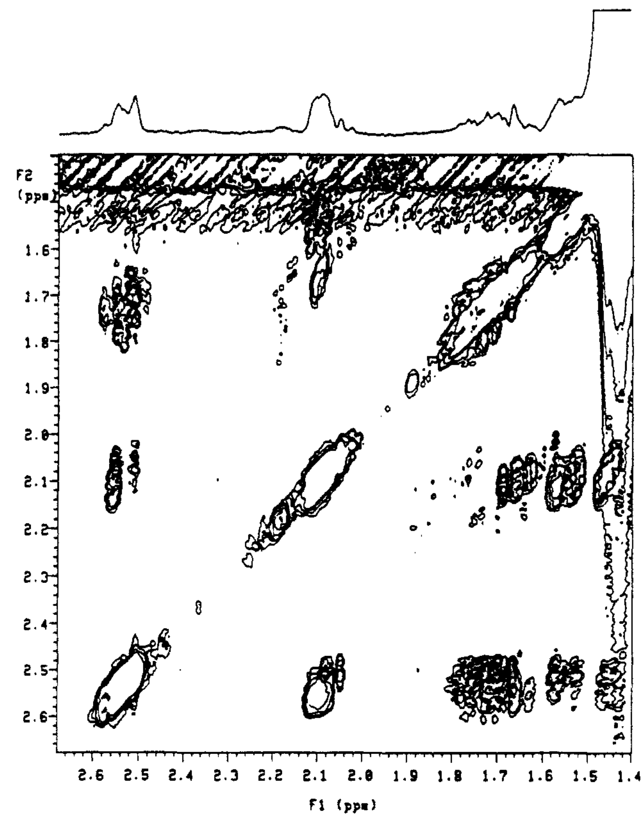

Figure 4. Section of a 500-MHz 2D F_1-decoupled COSY spectrum of a 2% solution of PtBuA I in C_6D_6.

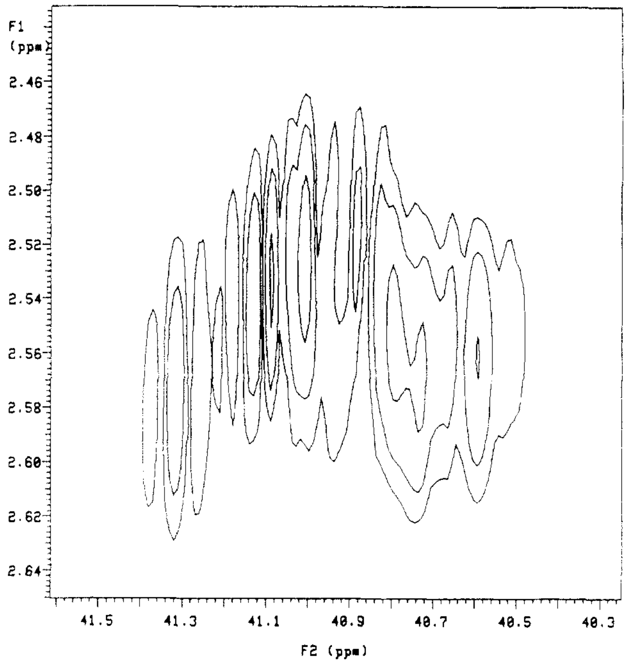

Figure 5. Region of correlations of 125-MHz ^{13}C methine resonances with their directly bound protons in a 2D HETCOR spectrum of a 60% solution of PtBuA in C_6D_6.

In spite of lower resolution in the ^{1}H domain (64 increments), the region of methylene carbon cross peaks with the resonances of their own directly bound protons, in a classically measured HETCOR spectrum of a 60% solution of PtBuA I in C_6D_6, indicated that the ^{13}C methylene resonances reflect at least a hexad configurational structure of the polymer chain. In order to also obtain a HETCOR spectrum of polymer II (where the maximum attainable concentration in C_6D_6 was 5%), we have applied the inverse HETCOR method (sequence HMQC), enabling us to achieve a much higher sensitivity, to 5% solutions of both polymers I and II in C_6D_6. The spectra of the solutions of the two polymers are shown in Figure 6. From the inverse HETCOR spectra of PtBuA it can easily be seen that, of the six NMR-resolvable tetrad sequences (mmm, mmr, mrm, mrr, rmr, and rrr), three tetrads contain magnetically nonequivalent CH_2 protons

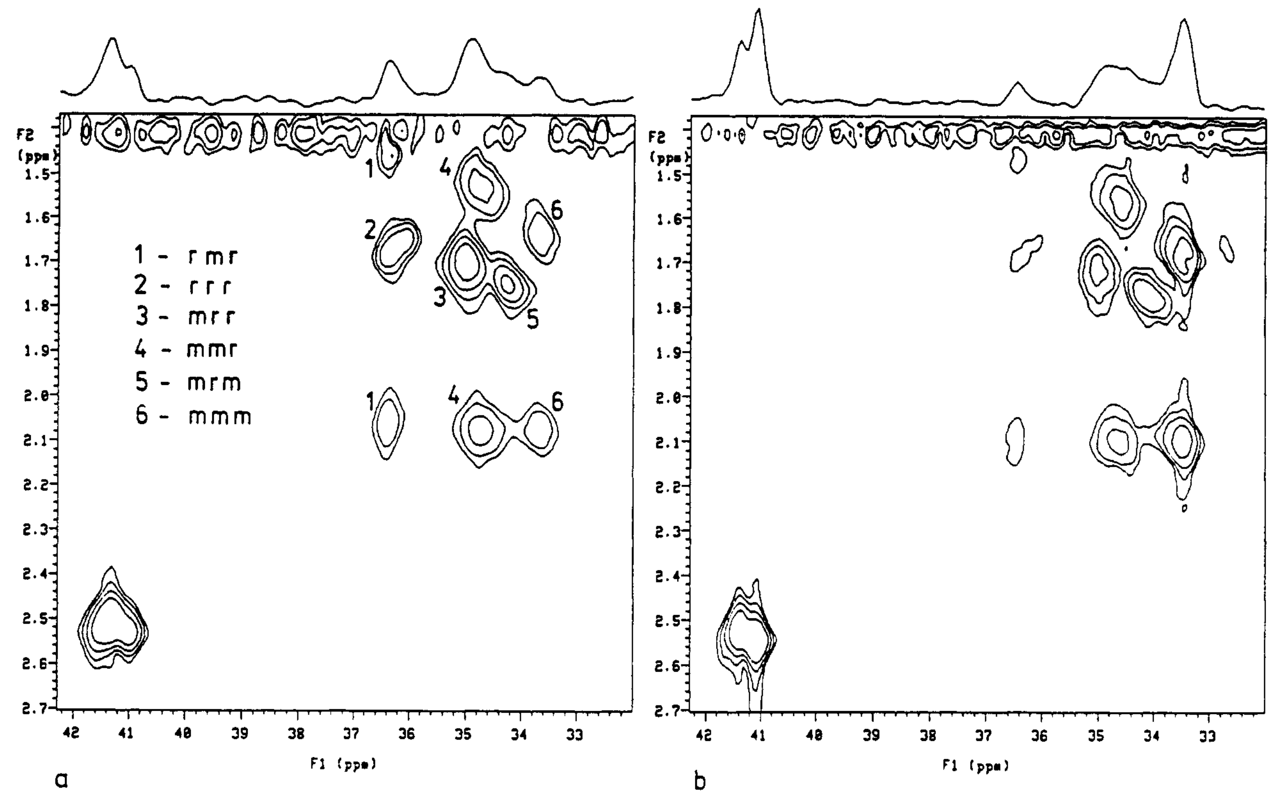

Figure 6. Section of 2D HETCOR (500 MHz for ^1H) spectra of 5% solutions of PtBuA I (a) and PtBuA II (b) in C_6D_6 obtained by the inverse HETCOR experiment (HMQC).

Table I
Calculated Configurational Tetrad Contents for PtBuA Obeying Bernoullian Placement Statistics and Chemical Shifts of Corresponding Methylene Resonances in C_6D_6 Solvent

	tetrad content		chemical shift (ppm from HMDS)	
tetrad	PtBuA I (P_m = 0.49)	PtBuA II (P_m = 0.72)	^{13}C	^1H
mmm	0.12	0.37	33.1–33.7	1.66, 2.10
mrm	0.12	0.15	33.7–34.3	1.78
mmr	0.24	0.29	34.2–34.9	1.55, 2.10
mrr	0.26	0.11	34.6–35.2	1.73
rrr	0.13	0.02	35.6–36.4	1.69
rmr	0.13	0.06	35.9–36.4	1.48, 2.10

and three contain magnetically equivalent CH_2 protons. As, in a general case, equivalent protons are only expected to occur in the mrm and rrr tetrads, it is evident that one of the tetrads mmr or mrr will have accidentally magnetically equivalent CH_2 protons (we assume that the tetrads mmm and rmr have magnetically nonequivalent CH_2 protons).

In assigning these methylene tetrad resonances, it is possible to start from their assumed intensities calculated from triad populations and the known statistics governing the propagation of the polymer chain. By means of the established triad populations, we can test whether the propagation reaction obeys the rules of Bernoullian statistics. The probability that the monomer unit added to a polymer chain terminated by a racemic diad will generate a meso diad ($P_r/_m$) is given by the relation[1]

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

and similarly for $P_{m/r}$

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

When $P_{r/m} + P_{m/r} = 1$, then chain propagation obeys Bernoullian statistics and $P_{r/m}$ is equal to P_m, the population of the m diad in the polymer chain. For PtBuA I relations (1) and (2) yield $P_{r/m} = 0.49$ and $P_{m/r} = 0.49$, and for PtBuA II $P_{r/m} = 0.72$ and $P_{m/r} = 0.30$. As for both polymers the sum of the above placement probabilities approximates to 1 within experimental error (0.98 for polymer I and 1.02 for polymer II), we can state that the polymerization reactions of both polymers obey Bernoullian statistics. Consequently, we can calculate the tetrad populations from the known value of P_m; the results are summarized in Table I.

Inspecting the expected tetrad populations in polymer II (Table I), we see that the populations of tetrad rmr (nonequivalent CH_2 protons) and of tetrad rrr (equivalent CH_2 protons) are very low. Therefore, in the HETCOR spectrum of polymer II (Figure 6b) we can assign the resonances marked 1 to the rmr tetrad and the resonance marked 2 to the rrr tetrad. On the basis of their intensities, the resonances marked 6 in HETCOR spectra of both polymers can safely be assigned to the mmm tetrad. For assigning the nonequivalent resonances 4 we can make use of the ^1H NMR spectrum. From the HETCOR spectrum it is evident that all three tetrads with nonequivalent CH_2 protons (the already assigned mmm and rmr, plus one of the pair mrr and mmr) contribute one proton to the methylene peak at 2.1 ppm in the ^1H spectrum. From the integrated area of this band, related to the area of the methine band, we can determine the sum of the populations of the three tetrads with nonequivalent CH_2 protons, amounting to 0.51 in PtBuA I and 0.73 in PtBuA II. From these values it follows that the third tetrad with nonequivalent CH_2 protons (resonances marked 4) is the tetrad mmr; i.e., the tetrad mrr has accidentally equivalent protons. On the basis of the expected intensities (Table I), the remaining resonances 3 and 5 were assigned to the tetrads mrr and mrm, respectively. In order to confirm the assignment of these methylene resonances, we have measured the heteronuclear H–H–C relay spectrum of a 60% solution of polymer I in C_6D_6 both classically and by a heteronuclear spin-lock relay experiment; the spectrum resulting from the latter

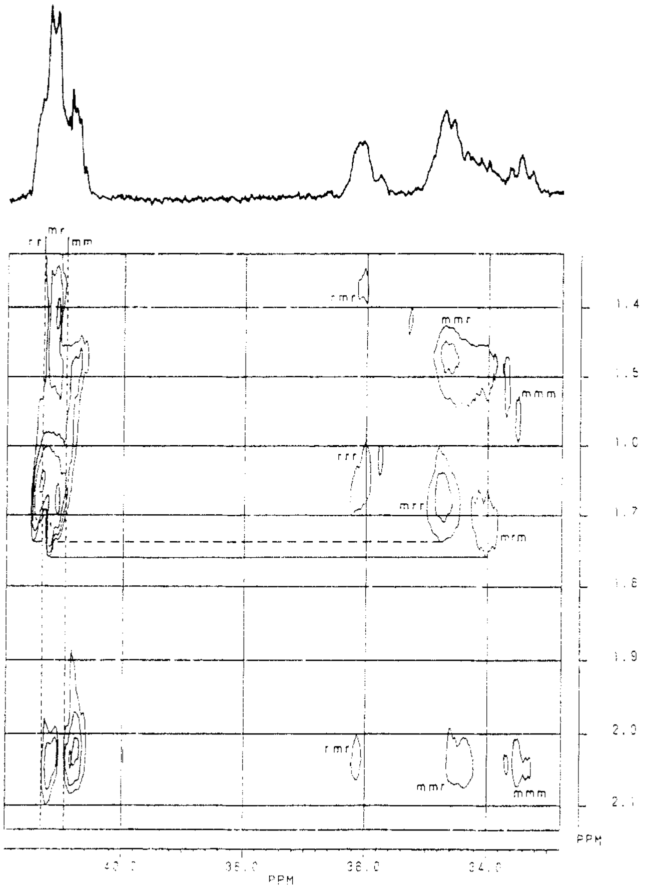

Figure 7. Section of a 2D heteronuclear spin-lock relay spectrum (75 MHz for ^{13}C) of a 60% solution of PtBuA I in C_6D_6.

is shown in Figure 7. The directly correlating methylene peaks (in the right part of this spectrum) are marked on the basis of the above assignment. The relay peak patterns (in the left part of the spectrum) arising from the magnetization transfer from CH_2 protons to the neighboring CH carbons via CH protons confirm the correctness of the methine triad assignment and support also the tetrad assignment of methylene resonances. For example, the two last assigned resonances of tetrads with equivalent CH_2 protons—mrr (accidentally equivalent protons) and mrm—can be unequivocally differentiated: the mrr tetrad exhibits relay peaks with the regions of rr and mr methine triads, whereas the mrm tetrad only gives a relay peak with the mr methine triad. The positions of tetrad methylene resonances of PtBuA in C_6D_6 in ^1H and ^{13}C spectra are summarized in Table I.

Thus from ^{13}C NMR spectra of PtBuA (in C_6D_6) it is possible to determine the population of the tetrad mmm by integration of the range 33.1–33.7 (region I), the sum of the populations of the tetrads mrm, mmr, and mrr by integration of the range 33.7–35.2 (region II), and the sum of the populations of the tetrads rmr and rrr by integration of the range 35.6–36.4 ppm (region III). By such integration we obtain for PtBuA I the values 0.13, 0.62, and 0.25 for the regions I–III, respectively, in excellent agreement with the values expected from Table I (0.12, 0.62, and 0.26). For PtBuA II the agreement between the expected and found values is poorer (the found values are 0.43, 0.48, and 0.09; the expected values are 0.37, 0.55, and 0.08). This is probably caused by the circumstance that in the spectrum of this polymer the regions I and II are not clearly separated, so that the integration limits are less well-defined. Nevertheless, it may be stated that, even at the tetrad level, the obtained results support the manifestation of Bernoullian statistics in both polymers.

Also in the region of carbonyl ^{13}C resonance (Figure 2) the spectra exhibit resolution at the pentad level at least. In spite of relatively great efforts (selective INEPT experiments, COLOC experiments and the inverse long-range HETCOR experiment) we were unable to unequivocally assign these resonances, mainly because of the insufficient resolution of the methine triad and methylene tetrad resonances in ^1H NMR spectra (moreover, in 2D spectra the latter are often partly overlapped by a ridge of the strong *tert*-butyl band). Our spectra nevertheless indicate that the carbonyl bands of various pentads were not generated by fine splitting of triad resonances.

Conclusions

By means of 1D and 2D NMR techniques we were able to quantitatively characterize at the triad (methine resonances) and tetrad (methylene resonances) level the stereochemical structure of two samples of PtBuA (I and II) prepared by group-transfer and anionic polymerization. The values of the triad populations were obtained from the intensities of ^{13}C methine resonances in a $CDCl_3$ solution. The assignment of methylene resonances to tetrad structures and subsequent quantitative evaluation of ^{13}C spectra were made possible by the inverse HETCOR experiment (HMQC); this experiment is superior to any other in studies of poorly soluble polymers. Also the heteronuclear spin-lock relay experiment was found to be very helpful; in sensitivity and resolution (phase-sensitive presentation of spectra) it is preferable to the classical heteronuclear relay experiment. We have not succeeded in the assignment of the carbonyl ^{13}C resonances which appear very sensitive to the stereochemical structure of the PtBuA chain. From the intensities of the three regions of methylene signals in ^{13}C NMR spectra of PtBuA samples I and II in solution, it was established that both these polymers obey Bernoullian statistics.

Acknowledgment. The authors thank Dr. B. Masař and Dr. P. Vlček for preparing PtBuA I and II, respectively.

References and Notes

(1) Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic Press: New York, 1972.
(2) Randall, J. C. *Polymer Sequence Determination (Carbon-13 NMR Method)*; Academic Press: New York, 1977.
(3) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, U.K., 1987; Chapter 8–10.
(4) Cheng, H. N.; Lee, G. H. *Polym. Bull.* **1985**, *13*, 549.
(5) Chang, C.; Muccio, D. D.; Pierre, T. St. *Macromolecules* **1985**, *18*, 2334.
(6) Bruch, M. D.; Bonesteel, J. K. *Macromolecules* **1986**, *19*, 1622.
(7) Hatada, K.; Ute, K.; Tanaka, K. *Polym. J.* **1987**, *19*, 425.
(8) Hikichi, K.; Yasuda, M. *Polym. J.* **1987**, *19*, 1003.
(9) Hikichi, K.; Ikura, M.; Yasuda, M. *Polym. J.* **1988**, *20*, 851.
(10) Gippert, G. P.; Brown, L. R. *Polym. Bull.* **1984**, *11*, 585.
(11) Kotyk, J. J.; Berger, P. A.; Remsen, E. E. *Macromolecules* **1990**, *23*, 5167.
(12) Crowther, M. W.; Szeverenyi, N. M.; Levy, G. C. *Macromolecules* **1986**, *19*, 1333.
(13) Matsuzaki, K.; Okada, M.; Hosonuma, K. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 1179.
(14) Matsuzaki, K.; Kanai, T.; Kawamura, T.; Matsumoto, S.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 961.
(15) Spyros, A.; Dais, P. *Macromolecules* **1992**, *25*, 1062.
(16) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542.
(17) Bax, A. *J. Magn. Reson.* **1983**, *53*, 517.
(18) Rutar, V. *J. Magn. Reson.* **1984**, *58*, 306.
(19) Wilde, J. A.; Bolton, P. H. *J. Magn. Reson.* **1984**, *59*, 343.
(20) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.
(21) Bax, A.; Subramanian, S. *J. Magn. Reson.* **1986**, *67*, 565.
(22) Garbow, J. R.; Weitekamp, D. P.; Pines, A. *Chem. Phys. Lett.* **1982**, *93*, 504.
(23) Bax, A. *J. Magn. Reson.* **1983**, *53*, 149.
(24) Bax, A.; Davis, D. G.; Sarkar, S. K. *J. Magn. Reson.* **1985**, *63*, 230.
(25) Bax, A.; Sarkar, S. K. *J. Magn. Reson.* **1984**, *60*, 170.
(26) Davis, D. G.; Bax, A. *J. Am. Chem. Soc.* **1985**, *107*, 2820.