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Absolute Configuration Assignments for Poly(methyl methacrylate) and Poly(α-methylstyrene) Using Proton-Detected Heteronuclear Shift-Correlated NMR Spectroscopy

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ABSTRACT: Absolute configuration assignments of poly(methyl methacrylate) (PMMA) and poly(α-methylstyrene) (PAMS) are derived from proton-detected heteronuclear shift-correlated NMR spectra. When recorded with high digital resolution, spectra display characteristic skewed coupling patterns caused by passive geminal methylene coupling in tetrads that lack a center of symmetry. It is shown how this information can be used for interpreting NMR spectra of vinyl polymers. A partial hexad interpretation of the methylene ^{13}C spectrum of PMMA is given. Many new and corrected configuration assignments are derived for ^{13}C and ^{1}H peaks in PAMS.

Introduction

The contribution of two-dimensional nuclear magnetic resonance spectroscopy (2D NMR) to the study of homopolymer microstructure has been universally recognized.[1] The traditional approach for establishing configurational sequences in terms of tacticities[2] with the help of NMR relied heavily on the use of labeled isotopes, model compounds, polymers of different tacticities, and modified polymers as well as on the application of empirical rules and theoretical calculations and, particularly, on the assumption of specific polymerization statistics. Two-dimensional homonuclear correlation NMR spectroscopy (mainly COSY and NOESY) made interpretation less dependent on the initial assumption about the polymerization process. Long-range interactions between protons representing different tacticity were directly revealed through long-range J-coupling interactions in the case of COSY and dipolar coupling interactions in the case of NOESY. The correlation spectrum was interpreted in terms of allowed correlations between tactic sequences of order n and $n + 1$. An independent or absolute method of configuration assignment was thereby established.[3]

The corresponding long-range heteronuclear correlation experiment (HETCOR) provided equivalent structural information between ^{13}C and ^{1}H nucleus. Furthermore, it extended the application of the technique to nonprotonated carbons as carbonyls and quaternary carbons, the chemical shifts of which are rich in long-range information. Except in rare situations,[4] the sensitivity of the conventional ^{13}C-detected version of the experiment proved inadequate for synthetic polymers that were not enriched with ^{13}C. In some cases, spin-lock RELAY[5] or COLOC[6] experiments were more successful. More recently, proton-detected heteronuclear shift-correlated NMR spectroscopy[7] has been developed as an alternative for studying long-range interactions in synthetic polymers without resorting to isotopic ^{13}C enrichment.[8,9]

In this study we report results of one-bond and multiple-bond versions of proton-detected heteronuclear shift-correlated NMR, which is referred to as heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple-bond coherence (HMBC) NMR, respectively. Two homologous disubstituted vinyl polymers (Figure 1), poly(methyl methacrylate) (PMMA) and poly(α-methylstyrene) (PAMS), were chosen on the basis of corresponding tacticity assignments of their ^{13}C NMR spectra[10] as well as on the basis of different levels of interpretation, particularly of the ^{1}H spectrum. The observation of corresponding shift behavior was particularly intriguing in view of extensive work by Tonelli[1] on the γ-gauche effect in monosubstituted vinyl polymers. His work showed that ^{13}C chemical shifts in vinyl polymers can be predicted from and are sensitive to side-chain-dependent γ-gauche shielding contributions. However, in a recent paper Tonelli[11] reported a breakdown of the γ-gauche approach in disubstituted vinyl polymers.

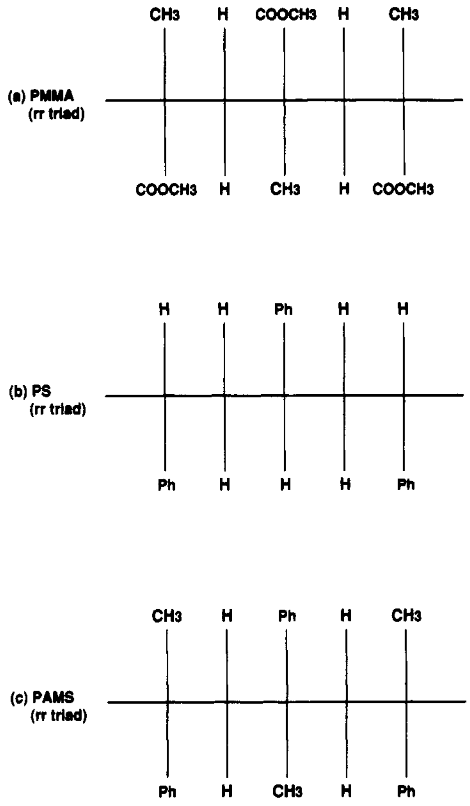

Figure 1. Structures of (a) poly(methyl methacrylate) (PMMA), (b) polystyrene (PS), and (c) poly(α-methylstyrene) (PAMS).

PMMA was studied by both 1D and 2D NMR;[10,12-14] the ^{1}H and ^{13}C assignments are well supported. We have previously used PMMA as a model for testing the effectiveness of HMBC.[8] PAMS, on the other hand, was

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Table I
Possible Tetrad–Pentad Correlations in PMMA and PAMS between CH_2 Protons (Tetrads) and Carbon-13 Nucleus (Pentad) Two or Three Bonds Removed[a]

	rrrr	rrrm	rrmr	rrmm	mrrm	rmrm	rmmr	rmmm	mrmm	mmmm
rrr	s	s								
rrm		d	d	d	d					
rmr			d			d				
rmm				d			d	d	d	
mrm						s			s	
mmm								d		d

[a] s = singlet crosspeak, d = pair of skewed doublets.

studied exclusively by 1D NMR; the ^1H and ^{13}C assignments relied on isotopic substitution studies and simulations of polymerization statistics.[15-19] Neither the ^{13}C nor the ^1H NMR spectra were fully interpreted.

In the present work we describe the strategy of using HMQC and particularly HMBC for interpreting spectra of synthetic polymers with a minimum of initial assumptions. The approach is validated with PMMA and then applied to PAMS.

Experimental Section

Sample Preparation. Atactic PMMA and atactic PAMS were purchased from Pressure Chemical Co. and Scientific Polymer Products Co., respectively. The polymers were used without further purification. The PMMA sample was nearly monodisperse ($M_w/M_n = 1.12$) and had a GPC peak molecular weight (M_p) of 840 000 as quoted by the supplier. The atactic character of the sample was confirmed by ^1H NMR spectroscopy, which yielded $P_m = 0.25$. The PAMS sample had a supplier-quoted $M_p = 680\,000$ and $M_w/M_n = 1.10$. P_m measured by ^1H NMR was 0.25. All samples for NMR study were prepared as 7.5% (w/v) solutions in chlorobenzene-d_5 (MSD Isotopes).

Spectroscopy. NMR spectra were obtained with a Varian VXR-500 NMR spectrometer operating at 499.843 and 125.697 MHz ^1H and ^{13}C frequencies, respectively. HMQC and HMBC[7] spectra were acquired at either 30 or 70 °C. An important feature of the data acquisition of the HMBC experiment was the large number of data points acquired in both the t_1 and t_2 dimensions (at least 2K × 2K). Such high digital resolution in t_1 distinguished this experiment from what is typically reported for 2D NMR experiments.

Results and Discussion

Methodology. Long-range correlation spectra such as HMBC spectra can be interpreted with the help of a correlation matrix as shown in Table I. Each of the 16 matrix elements represents an allowed crosspeak between a stereosequence of length n and a sequence of length $n + 1$. The specific situation shown in Table I is applicable to PMMA and PAMS for a methylene proton in a tetrad configuration J-coupled to a carbon atom in a pentad configuration; in PMMA the carbon atom is carbonyl, and in PAMS, quaternary aromatic carbon atom (C_1). Once the chemical shift coordinates of a crosspeak have been labeled as pentad and tetrad, the identity of other crosspeaks lying along one of these coordinates is narrowed down to a few possibilities. This is at once apparent from Table I. For a given pentad each crosspeak determines at most two tetrads, and each tetrad determines at most four pentads, depending on site symmetry.

Symmetry considerations enable one to interpret the HMBC spectrum with a minimum of initial assumptions. In this respect, the 2D pattern resulting from the coupling of a ^{13}C nucleus with mutually J-coupled methylene protons H_A and H_B is of particular interest. The projection of this spectrum onto the ^1H axis is a familar AB pattern which is further split due to ^{13}C–^1H coupling (Figure 2).[20,21] In the present situation, the ^{13}C–^1H coupling (J_{C-HA}, J_{C-HB}) is not resolved, and the pattern reduces to a pair of skewed doublets. On the other hand, J coupling does not manifest itself when methylene protons are equivalent because of site symmetry, and a single crosspeak results. This happens only for rrr and mrm methylene tetrad (Table I) and gives rise to four singlet crosspeaks. These are easy to pinpoint in the spectrum and provide a good starting point for interpretation.

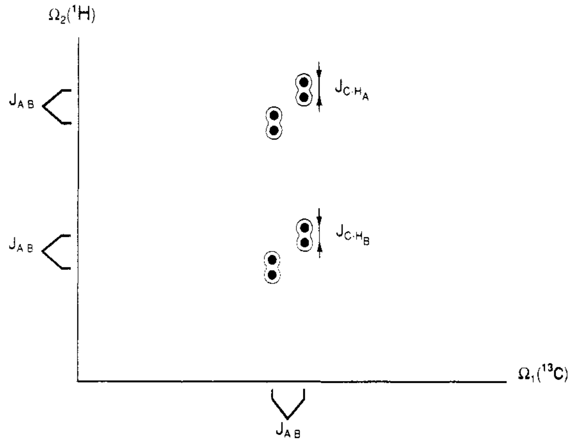

Figure 2. Graphical representation of passive J-coupling in HMBC spectra of PMMA and PAMS, where long-range J-coupling exists between a carbon and geminal methylene protons. In practice, the line width does not allow resolution of the heteronuclear coupling.[21]

When one crosspeak region has been interpreted, each peak frequency labeled as a stereosequence provides a coordinate for one or more crosspeaks outside that region. For instance, the methylene protons to carbonyl carbon crosspeaks provide coordinates for interpreting the methylene protons to methyl crosspeaks, etc. This provides internal checks for self-consistency of interpretation. A particularly simple situation arises among isosteric groups, for instance between methyl protons and carbonyl carbon in PMMA, where both coordinates are identical (or at least of the same parity).

Evidently, the HMQC spectrum is used in a complementary fashion to the HMBC spectrum and represents a further test of mutual consistency of the individually interpreted ^1H and ^{13}C spectra. It does not, however, provide independent confirmation of tacticity assignments.

The assignment procedure outlined above will be illustrated in detail in the interpretation of the methylene proton–carbonyl carbon HMBC spectrum of PMMA.

PMMA Spectra. The 1D ^1H and ^{13}C spectra of PMMA are shown in Figure 3. The overall HMBC spectrum is shown in Figure 4. Excluding the methoxy group, we recognize eight groups of crosspeaks, which account for all possible two- and three-bond heteronuclear J-coupling interactions of methylene proton (1.4–2.1 ppm) and methyl protons (1.0–1.35 ppm) with carbonyl, methylene, quaternary aliphatic, and methyl ^{13}C nuclei (in sections A, B, C, and D of Figure 4, respectively). Since the carbonyl ^{13}C's display the widest chemical shift dispersion of the spectrum, their long-range correlations with the methylene

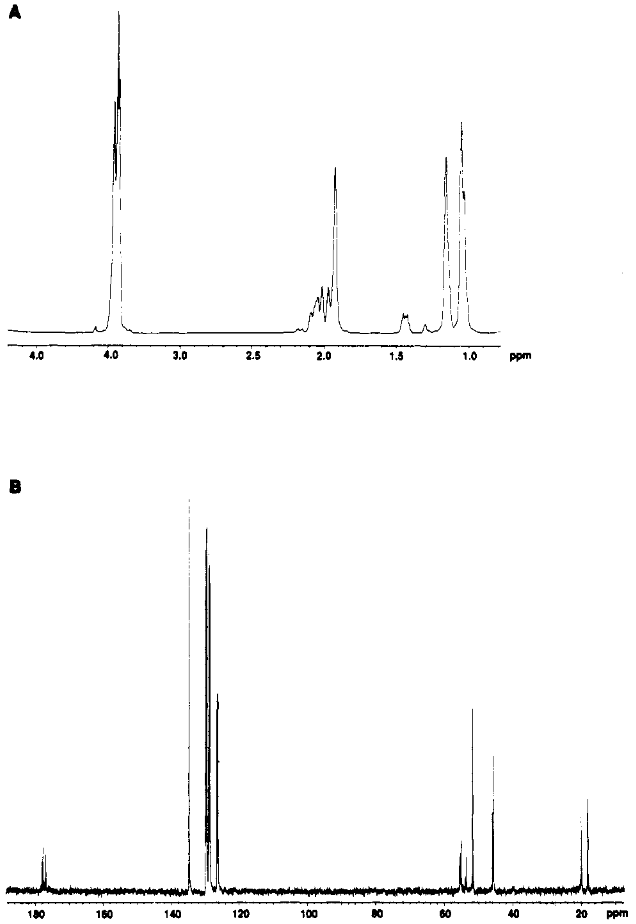

Figure 3. (A) 500-MHz ^1H NMR spectrum of PMMA; (B) 125-MHz ^{13}C NMR spectrum of PMMA in chlorobenzene-d_5 at 70 °C.

protons shall be discussed first with the help of Figure 5. As suggested in the preceding section we start by pinpointing the singlet crosspeaks. Three of the four are easily identified as rrrr,rrr; mrrr,rrr; mrmr,mrm and/or mmrm,-mrm, which are labeled 4, 2, and 5, respectively, in Figure 5. The assignment of rrrr,rrr is unambiguous; as is apparent from Table I, only rrrr yields a single crosspeak: rrrr,rrr. Alternatively, qualitative knowledge of the diad distribution (P_m) may suggest proper assignment based on peak intensities from the 1D spectrum. It is important to keep in mind that the intensities of the two-dimensional crosspeaks reflect J-coupling strength and relaxation rates in addition to species population. Assignment should therefore not be based on crosspeak intensities alone.

Crosspeak 2 is assigned to mrrr,rrr since it is the only other crosspeak with a rrr coordinate. Crosspeak 3B is assigned to mrrr,mrr(B). In Figure 5, mrr(H_A) is buried in the wings of the rrr crosspeaks. However, we detect it in spectra that were acquired with different values of the long-range coupling constant. This is a common observation. At the chemical shift of mrr(H_B) we observe only two of the three expected intersections, with pentads mmrr, mrrm, and rmrr. Pentad mrrm is unique in that it contains only one tetrad, mrr. We therefore assign crosspeak 1 to mrrm,mrr(H_B). The lost crosspeak, 6B, of the mrr(H_B) tetrad, must correspond to mmrr,mrr(H_B) and/or rmrr,-mrr(H_B). The self-consistent outcome of the interpretation justifies identification of 6B as rmrr,mrr(H_B). By continuing the process of labeling tetrads with the help of known pentads, and vice versa, we further derive the following assignments: 5 to rmrm,mrm, 6A to rmrr,mrr-(H_A), 7A to rmrr,rmr(H_A), 7B to rmrr,rmr(H_B), 8A to rmrm,rmr(H_B), and 9A to rmmr,rmm(H_A).

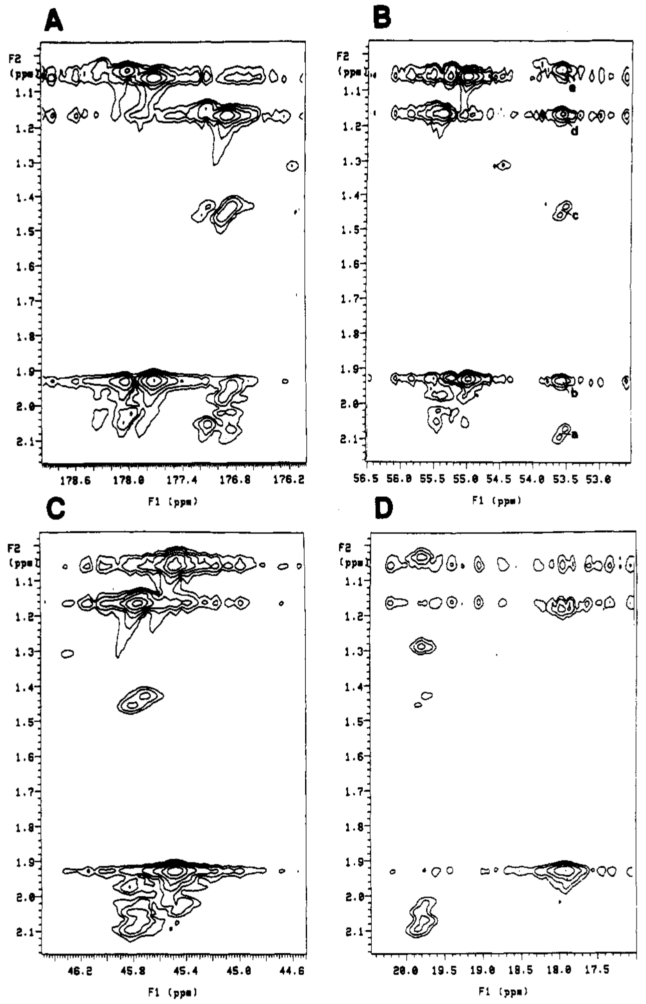

Figure 4. Low contour level plot of 500-MHz HMBC spectrum of PMMA in chlorobenzene-d_5 (7.5% w/v); crosspeaks of CH_2 and CH_3 ^1H's with (A) carbonyl ^{13}C, (B) methylene ^{13}C, (C) quaternary ^{13}C, and (D) methyl ^{13}C. The 2D spectrum was acquired as an array of 2K × 2K complex data points with sweep widths of 1721 and 22 831 Hz in the t_2 and t_1 dimensions, respectively. The t_2 dimension was processed with a combination sine-bell/Gaussian function.

The methylene proton and carbonyl assignments as tetrad and pentads, respectively, agree with the literature.[10,12,13,22,23] It is also clear from the literature[22] that the mmrm and mmrr carbonyl resonances are nearly coincident with the more abundant rmrm and rmrr peaks, respectively. In the HMBC spectrum one therefore expects mmrm,mrm and mmrr,mrr to overlap with rmrm,-mrm (5) and rmrr,mrr (6A, 6B) crosspeaks, respectively. On the other hand, mmrm,mmr and mmrr,mmr should be well separated from other crosspeaks, since the only other intersections of mmr are with upfield resonances rmmm and mrmm.[10,13,22,23] Unfortunately, crosspeaks expected for mmr(H_B) around 2.17 ppm[12] are very weak and obscured by t_1 noise. Crosspeaks for mmr(H_A) probably cannot be separated from rmrm,rmr(H_A) and rmrr,rmr-(H_A). Their weakness may be tentatively attributed to the all-trans arrangement prevalent in isotactic sections,[12] where carbonyl carbon and low-field erythro methylene proton form a 60° angle and therefore experience the smallest J coupling. Moreover, the peaks are weak intrinsically due to the low population of meso diads.

Assignments of the methyl proton peaks follow directly from the known identity of the carbonyl carbon peaks, since methyl protons and carbonyl carbons are labeled as identical n-ads. Syndiotactic and heterotactic methyl protons are shown to be resolved as pentads; isotactic

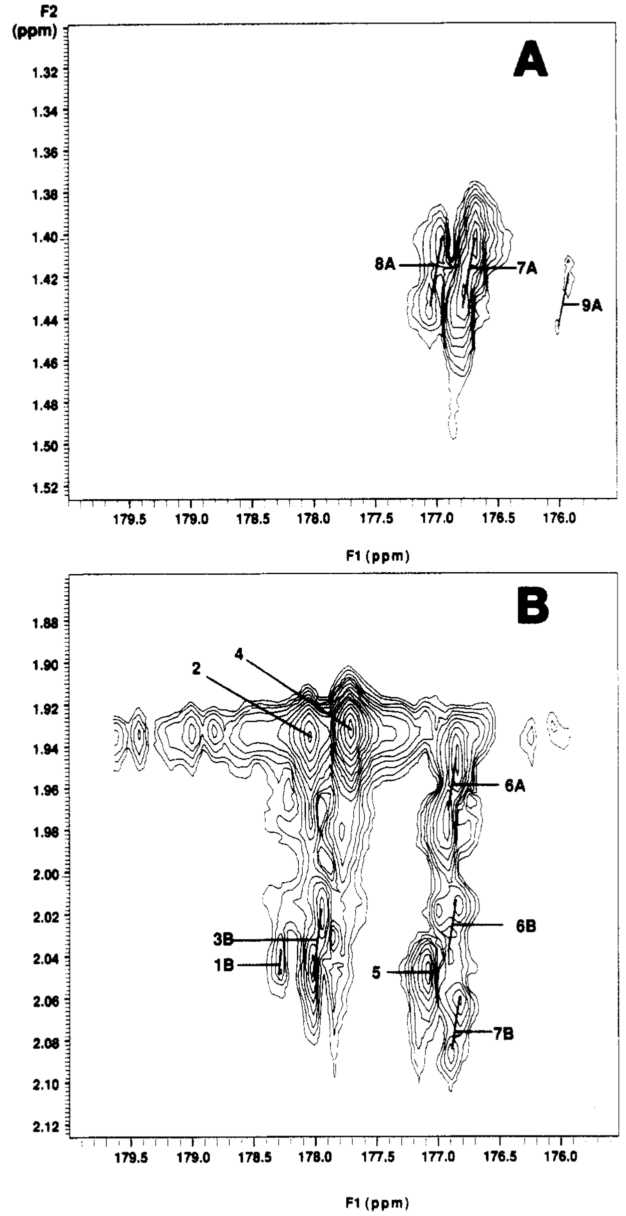

Figure 5. High-resolution HMBC spectrum of PMMA in chlorobenzene-d_5 at 70 °C; crosspeaks between methylene ^{1}H's and carbonyl ^{13}C's. Acquisitions and processing conditions are as in Figure 4, except that both dimensions were zero-filled to 8K data points prior to Fourier transformation.

methyl protons are resolved as an mm triad. From low to high field, the assigment follows the expected order:[12] mrrm, mrrr, rrrr, rmrm + mmrm, rmrr + mmrr, mm. The corresponding ^{13}C resonances can be read directly off the HMQC spectrum from the crosspeaks between methyl protons and carbons. They are resolved as triads and are in the order from low to high field mm, mr, rr. Quaternary ^{13}C assignments are derived from Figure 4C, by making use of crosspeaks with established ^{1}H methylene tetrads and ^{1}H methyl triads. Starting downfield, the order of resonances is, in terms of triads and pentads, mm, rmrr, mmrr, mrrr + mrrm + rrrr.[8]

A slightly different approach applies to ^{13}C–^{1}H long-range heteronuclear correlations among methylene and among methyl groups. These are evidently due to long-range coupling between identical groups in neighboring monomer units. Unfortunately, the methyl region is not amenable to detailed interpretation because of extensive t_1 ridges concentrated in this region. The methylene region, however, provides a number of interesting crosspeaks which can be understood in terms of hexad resolution. Consider, for instance, the five crosspeaks aligned at 53.6 ppm in Figure 4B. Peaks a and c are at the intersection of the rmr methylene ^{1}H tetrad, and b is at the intersection of the rrr methylene ^{1}H tetrad. Peaks d and e are at the intersection of the rr and rm methyl ^{1}H triad, respectively. Therefore, the only hexad that accounts for all crosspeaks is rmrrr. Using the same reasoning, hexads and tetrads mrmrr, rrmrr, mrrrr, mrmrr, rrrrr, mmm, and rmr are identified, from low to high field. In terms of ^{13}C methylene tetrads, the positions of all but rmm are therefore established.

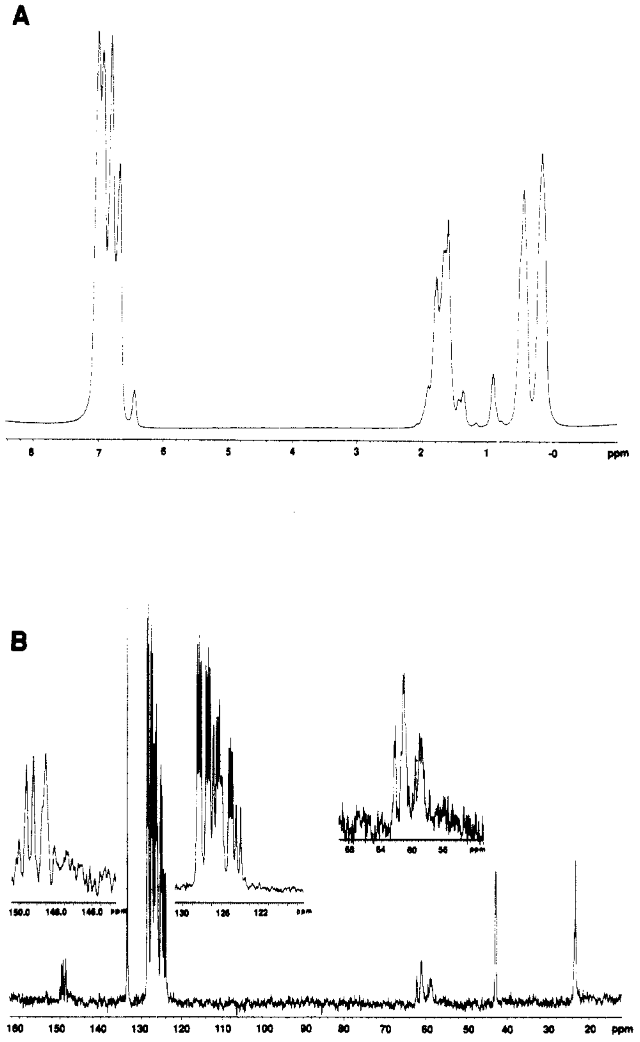

Figure 6. (A) 500-MHz ^{1}H NMR spectrum of PAMS; (B) 125-MHz ^{13}C NMR spectrum of PAMS in chlorobenzene-d_5 at 70 °C.

PAMS Spectra. The 1D ^{1}H and ^{13}C spectra are shown in Figure 6, and the overall HMBC spectrum is presented in Figure 7. Two expanded crosspeak regions are shown in Figure 8.

PAMS differs from PMMA by the replacement of the methacrylate group with a phenyl group. In both cases, the ^{13}C chemical shift of the quaternary carbon (carbonyl and quaternary aromatic carbon) is highly structure sensitive. Note, however, in PAMS the chemical shifts of the protonated aromatic carbons and of the aromatic protons are also microstructure sensitive. In PAMS as in PMMA the crosspeaks between methylene protons and side chain quaternary carbon are particularly well resolved (Figure 8A) and form the point of departure for the assignments (Table II). By analogy with PMMA, the identification of singlet crosspeaks provides rrr and mrm tetrad corrdinates for methylene protons as well as rrrr, rmrm, and mmrm pentad coordinates of C$_1$. The inter-

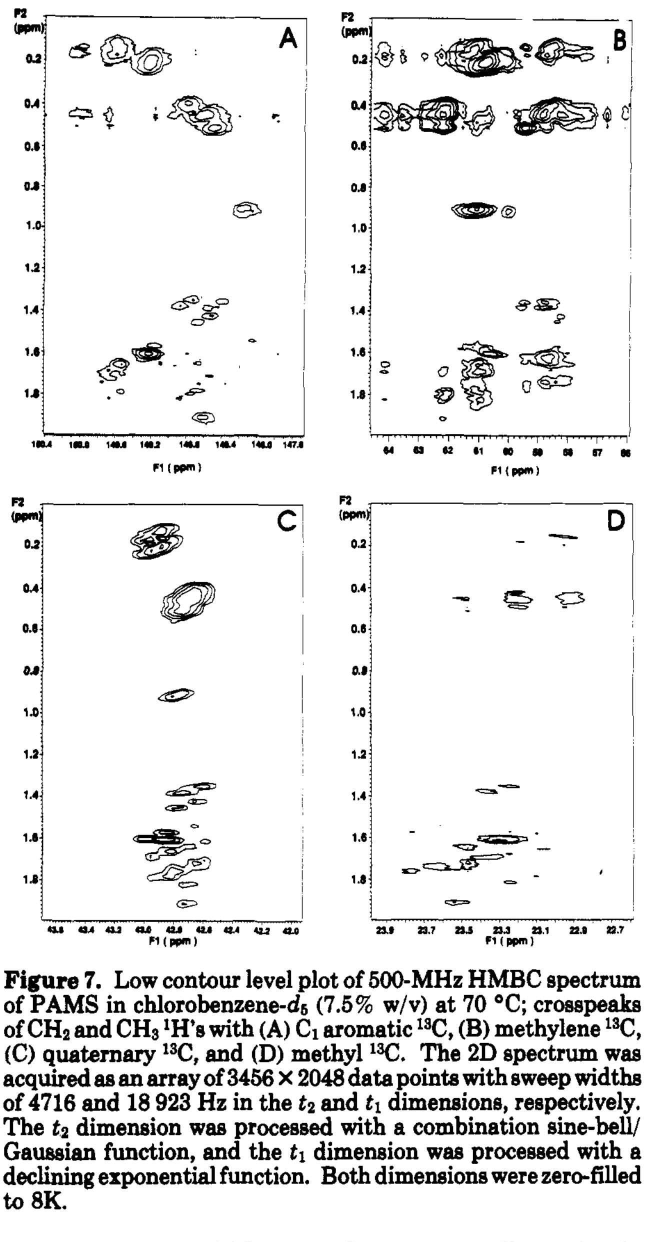

Figure 7. Low contour level plot of 500-MHz HMBC spectrum of PAMS in chlorobenzene-d_5 (7.5% w/v) at 70 °C; crosspeaks of CH_2 and CH_3 ^1H's with (A) C_1 aromatic ^{13}C, (B) methylene ^{13}C, (C) quaternary ^{13}C, and (D) methyl ^{13}C. The 2D spectrum was acquired as an array of 3456 × 2048 data points with sweep widths of 4716 and 18 923 Hz in the t_2 and t_1 dimensions, respectively. The t_2 dimension was processed with a combination sine-bell/Gaussian function, and the t_1 dimension was processed with a declining exponential function. Both dimensions were zero-filled to 8K.

pretation of the PAMS HMBC spectrum follows closely along the lines shown for PMMA, with two minor complications. First, the syndiotactic region of PAMS shows resolution as higher order *n*-ads. This is evidenced by additional crosspeaks in the proximity of rrrr,rrr (crosspeaks in Figure 8A). Second, the intensity difference between the crosspeaks of the two methylene protons of the same tetrad observed in PMMA is more pronounced and more general in PAMS. This is very evident from the absence of several crosspeaks in Figure 8A and Table II.

The methyl ^{13}C frequencies extend over a narrow range of only 0.8 ppm. However, some crosspeaks with the methylene ^1H resonances are well resolved in the high-resolution HMBC spectrum (Figure 8B) and allow a partial interpretation to be made in terms of ^{13}C pentads and ^1H tetrads (Tables III and IV).

Even closer are the ^{13}C frequencies of the quaternary aliphatic carbons (Figure 7C) which extend over only 0.4 ppm. Again, several ^{13}C pentad assignments are made from a high-resolution version of Figure 7C (Table V).

The methylene ^{13}C region (Figure 7B) is very well resolved in the 1D spectrum.[17] Direct assignments follow from the HMQC spectrum (not shown) and particularly from resolved peaks in the HMBC spectrum (Table V).

The self-consistent and simultaneous interpretation of the ^1H and ^{13}C spectra of PAMS presented here add considerably to existing knowledge and may provide a basis for further testing of theoretical models, as shall be explained in the conclusion to this section.

Like its parent compound polystyrene (PS), PAMS has eluded purely spectroscopic interpretation of its proton and ^{13}C NMR spectra in terms of stereosequences. PS has received considerably more attention than PAMS. In particular, epimerized polymers[24] as well as model oligomers[25,26] have been studied. The assignment of the quaternary aromatic C_1 carbon, the aromatic C_4 carbon, and the methylene carbons have been confirmed on a theoretical basis.[1] The assignement of the resolved portions of the ^{13}C spectrum in particular is therefore well supported.

With the help of selective ^{13}C labeling ^{13}C spectra of the aromatic carbons were studied successfully before the advent of 2D NMR. Line shapes were simulated by using a Bernouilli distribution of peak intensities. The pentad assignments resulting from these detailed studies[17,19] are in agreement with those obtained by the direct method used in this work (Table II). However, considerable discrepancies exist in the tacticity assignments of the methyl, methylene, and quaternary aliphatic ^{13}C peaks (Tables II, III, and V). Given the poor resolution of the 1D methyl and quaternary carbon ^{13}C spectra and the complex hexad resolution of the methylene spectra, the statistical approach leaves much room for ambiguities.

The situation is even more serious in 1D ^1H spectra. The spectrum of the aromatic protons was interpreted with the help of deuterium labeling;[15] however, configurational assignments of ^{13}C and ^1H peaks from separate 1D NMR spectra[15,17] are not fully consistent with the assignment of ^{13}C–^1H pairs from the HMQC spectrum (results in Table VI). The direct method applied here provides the first unambiguous though still partial interpretation of methylene protons as tetrads and of methyl protons as pentads. Note that over time several interpretations were offered for the three triad components of the methyl protons: in order of increasing field, they were given[19] as syn, het, iso; het, iso, syn; and iso, het, syn, which seems to be the presently accepted interpretation. Our interpretation concurs with the latter order (Table III), which is, incidently, the same as in PMMA.

The steric constraints introduced by the methyl side chain in PAMS turn out to be severe enough to cause significantly different ^{13}C shieldings than in PS. It is apparent from Table I that stereosequences of PAMS bear little resemblance to those of PS; they are more similar to those of PMMA, as was pointed out by Randall.[10] The first observation is not surprising, since magnetic shielding has been correctly predicted by the rotational isomeric state model (RIS) and the mutual shielding of carbons in γ-position to each other.[1] However, this model seems to be contradicted by the second observation, since replacement of phenyl by carboxymethyl can be expected to result in a different distribution of rotational states as well as in different magnitudes of γ-effect shielding. This may therefore be another instance of breakdown of the γ-effect method in disubstituted vinyl polymers.[11]

As was pointed out by Tonelli,[27] the largest chemical shift dispersion in the ^{13}C spectrum of PS was observed for the methylene (4.2 ppm) and aromatic quaternary carbon, C_1 (1.2 ppm). Both carbons experience a large γ-effect, compared to which ring current contributions are minor; these are the primary effects on the shifts of the other carbons. In PAMS, the dispersion of methylene and C_1 ^{13}C shifts is even wider (5 and 2 ppm, respectively);

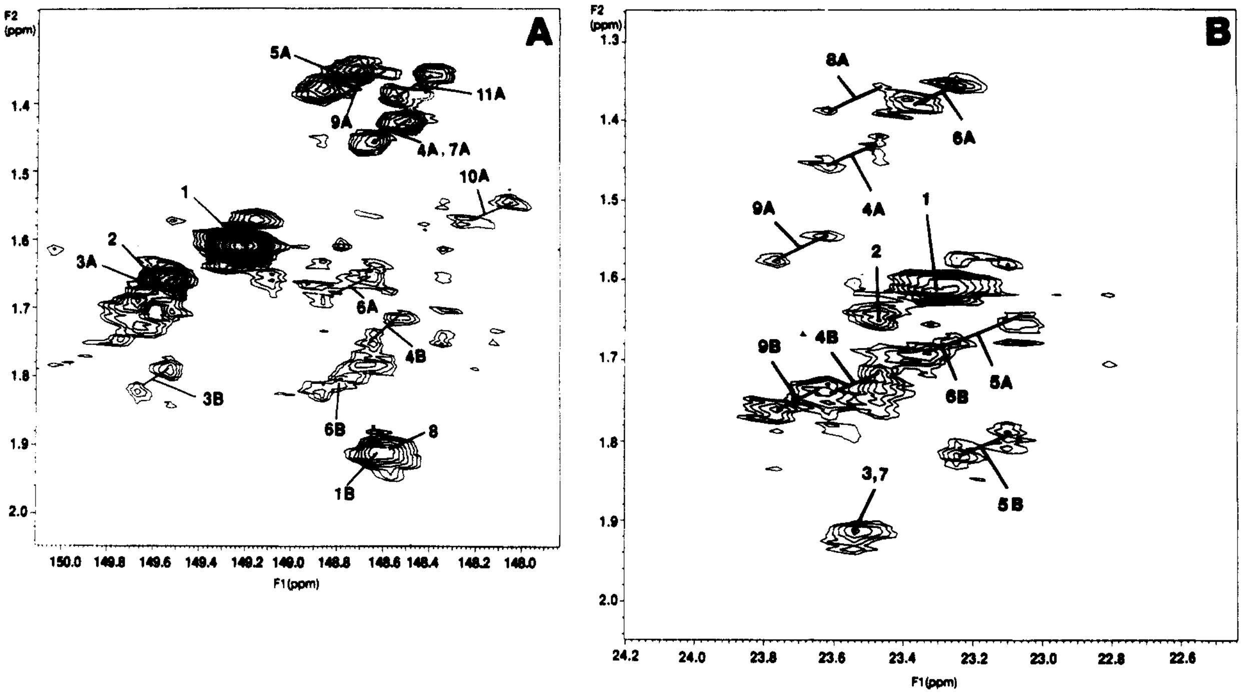

Figure 8. High-resolution HMBC spectra of PAMS in chlorobenzene-d_5 at 70 °C; (A) crosspeaks between quaternary aromatic (C_1) ^{13}C and methylene ^1H's. Acquisition and processing conditions are as for Figure 7, except that both dimensions were zero-filled to 8K data points prior to Fourier transformation. (B) Crosspeaks between methyl ^{13}C and methylene ^1H's.

Table II
PAMS: Observed Correlations between C_1 ^{13}C Shifts and Methylene ^1H Shifts

crosspeak[a]	C_1 ^{13}C pentad	CH_2 ^1H tetrad	^{13}C (ppm)	^1H (ppm)
1	rrrrrr[b]	rrrrr[c]	149.21	1.61
2	rrrm	rrr	149.56	1.66
3A	rrrm	rrm(A)	149.58	1.67
3B	rrrm	rrrm(B)	149.57	1.80
4A	rrmr	rmr(A)	148.54	1.44
4B	rrmr	rmr(B)	148.56	1.73
5A	rrmm	rmm(A)	148.76	1.36
6A	rrmm	rrm(A)	148.74	1.67
6B	rrmm	rrm(B)	148.76	1.81
7A	rmrm	rmr(A)	148.54	1.44
8	rmrm	mrm	148.59	1.91
9A	rmmr	rmm(A)	148.96	1.37
10A	rmmm	mmm(A)[d]	148.13	1.56
11A	mrmm	rmm(A)	148.65	1.37
12	mrmm	mrm	148.59	1.91

[a] Labeling used in Figure 8A. [b] Resolved at heptad level. [c] Resolved at hexad level. [d] mmm(B) is clearly resolved in the CH_2 ^{13}C to CH_2 ^1H and in the C_{quat} ^{13}C to CH_2 ^1H crosspeak maps at 1.55 ppm.

Table III
PAMS: Observed Correlations between C_1 ^{13}C Shifts and Methyl ^{13}C and ^1H Shifts

pentad	^{13}C C_1 (ppm)	^1H methyl (ppm)	^{13}C methyl (ppm)
rrrrrr[a]	149.21	0.20	23.3
rrrm	149.56	0.17	23.45
mrrm	149.61	0.16	23.17
rrmr	148.54	0.46	23.17
rrmm	148.77	0.40	23.31
rmrm	148.54	0.46	23.55
rmmr	148.46	0.47	?
rmmm	148.13	0.91	23.69
mrmm	148.65	0.51	23.55
mmmm	148.59	1.08	?

[a] Resolved at heptad level.

the dispersion of the protonated aromatic carbons is also large (4 ppm overall; 1.5 ppm for C_4 alone vs 0.5 ppm in PS).

Table IV
PAMS: Observed Correlations between Methyl ^{13}C Shifts and Methylene ^1H Shifts

crosspeak[a]	methyl ^{13}C pentad	CH_2 ^1H tetrad	^{13}C (ppm)	^1H (ppm)
1	rrrrrr[b]	rrrrr[c]	23.30	1.61
2	rrrr	rrr	23.47	1.64
3	rmrm	mrm	23.54	1.91
4A	rmrm	rmr(A)	23.54	1.44
4B	rmrm	rmr(B)	23.54	1.73
5A	mrrm	rrm(A)	23.17	1.67
5B	mrrm	rrm(B)	23.17	1.80
6A	rmmr	rmm(A)	23.30	1.36
6B	rmmr	rmm(B)	23.30	1.69
7	mrmm	mrm	23.54	1.91
8A	mrmm	rmm(A)	23.54	1.36
9A	mmmm	mmm(A)	23.70	1.56
9B	mmmm	mmm(B)	23.70	1.75

[a] Labeling used in Figure 8B. [b] Resolved at heptad level. [c] Resolved at hexad level.

Table V
PAMS: ^{13}C Shifts of Methylene and Quaternary Aliphatic Carbons

^{13}C methylene		^{13}C quaternary	
tacticity	ppm	tacticity	ppm
rrrrr	60.70	rrrr	42.89
rrmrr	62.10	rrr	42.99
rrrmm	58.50	rrrm	42.93
rmrmr	58.35	rrmr or rmrm	42.77
rrmmm	≈60	rrmm	42.70
rmrmm	58.85	rmrm or rrmr	42.75
mrmrm	62.25	rmmm	42.79
mmrmm	59.50		
mmm	60.1		

Conclusions

HMQC and HMBC NMR spectra provide absolute stereosequence assignments in two homopolymers, PMMA and PAMS. HMBC spectra were particularly helpful when acquired with high digital resolution in both dimensions and transformed with zero-filling in both dimensions. Under these conditions skewed patterns indicative of

Table VI
PAMS: Observed One-Bond Correlations between Protonated Aromatic ^{13}C and ^1H Shifts

triad	^{13}C (ppm)	^1H (ppm)
rr (2)[a]	126.7	6.93
rr (3)	127.3	7.00
rr (4)	124.9	6.92
mm (2)	126.2	6.43
mm (3)[a]	126.7	6.93
mm (4)	124.0	6.70
rm (2)	126.4	6.67
rm (3)	127.9	6.80
rm (4)	124.4	6.78

[a] These crosspeaks overlap in the HMQC spectrum.

passive coupling were observed for crosspeaks involving inequivalent methylene protons. These observations provided a diagnostic tool for distinguishing symmetric from asymmetric methylene proton tetrads and a basis of absolute and unbiased tacticity assignment. Theoretically, the combined HMQC and HMBC correlation maps contain all possible J-coupling interactions between protons and ^{13}C atoms with J larger than a few hertz. Their combined information content is redundant and provides many opportunities for crosschecks. In an experimental spectrum, missing crosspeaks may therefore be inferred from information derived from another region of the 2D map.

The assignment methodology discussed herein was tested in detail with PMMA. The present work completes the heteronuclear assignment by providing correlation maps between all carbons and all long-range coupled protons. Both the ^{13}C and the ^1H NMR spectra of PMMA have been interpreted in considerable detail in the literature.[10,12-14,22,23] To our knowledge no assignments of the methylene ^{13}C peaks have been published. These are provided by the present work. All our other assignments agree within the limits of resolution with published data. The same methodology was applied to PAMS in a practical manner and provided new and corrected tacticity assignments of the ^{13}C and ^1H spectra.

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Registry No. PMMA, 9011-14-7; (α-methylstyrene) (homopolymer), 25014-31-7.