Configurational Assignments for Poly(methacrylonitrile) Using Double-Quantum-Filtered Phase-Sensitive COSY and Proton-Detected $^{1}H-^{13}C$ Shift-Correlated NMR Spectroscopies

Limin Dong,[†] David J. T. Hill,[*,†] James H. O'Donnell,[†] and Andrew K. Whittaker[‡]

Polymer Materials & Radiation Group, Department of Chemistry, and Centre for Magnetic Resonance, The University of Queensland, Brisbane, Australia 4072

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ABSTRACT: The configurational assignments of poly(methacrylonitrile) are derived from double-quantum-filtered phase-sensitive ^{1}H homonuclear shift-correlation and proton-detected $^{1}H-^{13}C$ heteronuclear shift-correlation NMR spectroscopies. The overlapping peaks for different tacticities in the 1D spectrum have been separated and assigned by 2D methods. Assignments to the methylene region of the ^{1}H and ^{13}C spectra have been made to hexad and tetrad levels, respectively. The results indicate that the previous assignments for this system are invalid.

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 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.[2] These labor-intensive methods have largely been replaced in recent years by two-dimensional homonuclear and heteronuclear correlation NMR spectroscopies. However, one of the problems often encountered with homonuclear correlation NMR spectroscopy is lack of resolution. Overlap between different tacticities in higher order configurational sequences becomes a serious problem that can be exacerbated by the absolute intensity calculation frequently made in the final stages of processing the 2D spectral data. The application of phase-sensitive methods may alleviate the overlap in the off-diagonal responses which are not coupled to one another and significantly improve the resolution.[3] In addition, if proton-carbon correlations are required, until recently the less abundant and less receptive ^{13}C nucleus had to be detected, necessitating a concentrated solution and long measurement time.[4] However, the development of proton-detected heteronuclear shift-correlated NMR technology allows the use of less concentrated samples and shorter measurement times to obtain satisfactory $^{13}C-^{1}H$ heteronuclear coupling information.[5]

In this work, double-quantum-filtered phase-sensitive proton shift-correlated (DQF-PS COSY) and proton-detected heteronuclear shift-correlated NMR spectroscopies have been used to investigate the tacticity of atactic poly(methacrylonitrile). The tacticities of monosubstituted and disubstituted vinyl polymers have been widely investigated.[6] The extensive work of Tonelli on monosubstituted vinyl polymers has shown that the γ-gauche effect on chemical shifts can be exploited to obtain tacticity information.[1] However, Tonelli has further recently shown that the γ-gauche approach is not applicable to disubstituted vinyl polymers[7] and suggests that in disubstituted vinyl polymers conformationally sensitive backbone bond valence angles may lead to failure of the γ-gauche rule. In this work, we selected poly(methacrylonitrile) in order to try to establish a method which can be used to analyze disubstituted vinyl polymers more easily.

Poly(methacrylonitrile) has previously been studied by 1D NMR; tacticity assignments for the ^{1}H and ^{13}C nuclei have been reported.[8-12] However, in these papers, empirical arguments were used to assign the peaks to the different configurational sequences and no account was given to the possibility of overlapping peaks and subsequent distortion of the peak intensities. In the present study, we find that in the 1D ^{1}H spectrum there is considerable overlap between the peaks for different tacticities. Two-dimensional homonuclear COSY spectra can separate the overlapping peaks and reveal additional fine structure. Hexad level tacticities in the methylene proton region have been assigned. Meanwhile, by use of the assignments in the ^{1}H spectra, the tacticities of the methylene carbons have been reassigned in the heteronuclear 2D spectra. We show that the previous tacticity assignments for ^{1}H and ^{13}C spectra reported in the literature are invalid.

Experimental Section

Materials. Poly(methacrylonitrile) was prepared by free-radical polymerization in the bulk at 60 °C initiated by benzoyl peroxide. The conversion was limited to 15%. A determination of the molecular weight by gel permeation chromatography in DMF at 80 °C indicated the M_n to be 2.5×10^4 and the M_w/M_n to be 2.2.

NMR Spectroscopy. The NMR spectra were recorded on a Bruker AMX-500 spectrometer using 7% (w/v) solutions in DMSO-d_6 at room temperature. The DQF-PS COSY experiment employed a recycle time of 2.7 s, with 32 transients being collected for each t_1 value. A total of 512 spectra, each containing 2048 data points, were accumulated.

The 1D ^{13}C NMR spectra were recorded by using a 90° pulse and 12-s repetition delay with inverse-gated decoupling during acquisition. The proton-detected $^{1}H-^{13}C$ heteronuclear chemical-shift correlation spectrum was recorded by using the standard Bruker pulse program INVBTP.[5] The 48 scans were accumulated with a recycle delay of 2 s for each of the 512 experiments, resulting in a 512 × 2048 data matrix (after Fourier transformation), covering 800 Hz in the *F*2 dimension and 5000 Hz in the *F*1 dimension.

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[*] To whom correspondence should be addressed.

[†] Polymer Materials & Radiation Group, Department of Chemistry.

[‡] Centre for Magnetic Resonance.

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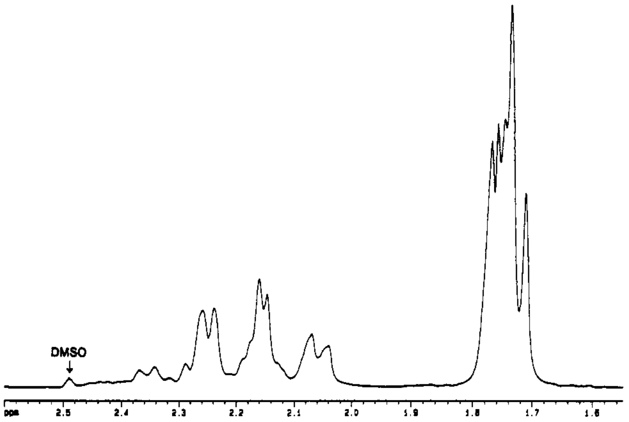

Figure 1. 1D ^1H NMR spectrum of poly(methacrylonitrile).

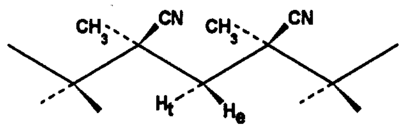

Figure 2. Configuration of poly(methacrylonitrile) for meso symmetry between two adjacent monomeric units. The e and t notations for the methylene protons refer to erythro and threo protons, respectively, which are syn and anti to the nitrile group in the trans–trans conformation.

Results and Discussion

The ^1H NMR spectrum of poly(methacrylonitrile) (Figure 1) shows peaks in two regions due to the α-methyl protons (1.65–1.85 ppm) and the methylene protons (2.0–2.5 ppm), respectively. Unlike the ^1H spectrum of poly(methyl methacrylate),[13] the α-methyl protons of poly(methacrylonitrile) are not very sensitive to the stereochemical configuration, with signals due to the different tactic sequences lying in the narrow range of 1.68–1.82 ppm. However, the methylene group gives signals in the broad interval 2.0–2.5 ppm and therefore may be used to assign the different configurational sequences.

The methylene protons may be divided into two groups for the following reasons. The first group consists of equivalent protons connected to the same carbon, such as methylene protons in a symmetrical racemic diad, for which a single peak is observed. The second group is methylene protons connected to the same carbon but which are inequivalent, such as methylene protons in a meso diad. In the latter case, the protons will be coupled to each other (geminal coupling), and the resonance will be observed as AX doublets. Figure 2 shows the molecular stereochemical structure for meso symmetry between two quaternary carbons. The two methylene protons connected to the same carbon have different chemical surroundings. The e and t notations for the methylene protons refer to erythro and threo protons, which are syn and anti to the nitrile group in the trans–trans conformation, respectively. From previous work on methacrylate and acrylate polymers,[13-15] we should observe that H_e and H_t have different chemical shifts.

The 500-MHz DQF-PS COSY spectrum for poly(methacrylonitrile) obtained under the same conditions as in the 1D experiment is shown in Figure 3. The principal correlating influence is the geminal coupling, J_{gem}, of the inequivalent methylene protons connected to the same carbon. The W-shaped four-bond coupling between the α-methyl proton and the methylene proton observed for poly(methyl methacrylate) cannot be seen here,[13] and therefore, the peaks at lower chemical shift due to the α-methyl proton have not been plotted.

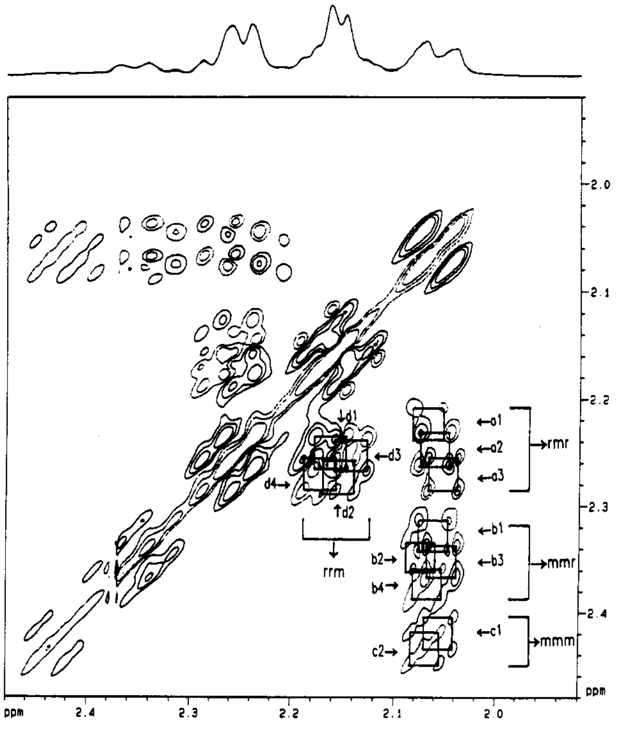

Figure 3. Methylene region of the DQF-PS COSY spectrum of poly(methacrylonitrile). The tacticity assignments have been marked on the figure: (a1) mrmrm, (a2) mrmrr, (a3) rrmrr; (b1) rmmrr, (b2) mmmrm, (b3) mmmrr or rmmrm, (b4) rmmrm or mmmrr; (c1) mmmmr or mmmmm + rmmmr, (c2) mmmmm + rmmmr or mmmmr, (d1) rrrmr, (d2) mrrmm, (d3) rrrmm or mrrmr, (d4) mrrmr or rrrmm.

In Figure 3, the positive contours are shown as the dashed lines and negative as solid lines. For the geminal coupling, the cross-peaks have been adjusted into the pure absorption phase. Each coupling consists of four peaks in the anti phase arranged in a square pattern with frequency spacings parallel to the axes equal to J_{gem}. From the spectrum, we find that cross-peaks occur in the regions 2.00–2.11 and 2.20–2.48 ppm. The cross-peaks may be identified as geminal couplings between H_t and H_e in meso diads. As with poly(methylmethacrylate), the H_t proton in poly(methacrylonitrile) is syn to the α-methyl group in the trans–trans conformation so that these protons should have lower chemical shifts than the H_e protons and the shifts should not be as sensitive to higher tacticity levels. Therefore, the peaks in the region 2.00–2.11 ppm may be assigned to the H_t proton and the peaks at 2.20–2.48 ppm may be assigned to the H_e proton in meso diads. Meanwhile, integrating the area of the peaks due to the H_t proton at 2.00–2.11 ppm in the 1D spectrum with respect to the total area for the methylene protons, we can obtained the meso diad fraction in the poly(methacrylonitrile), $P_m = 0.406$.

By carefully examining the 2D cross-peak region between 2.00–2.11 and 2.20–2.48 ppm, we may find that higher tacticity levels may be identified. The three cross-peak regions for the H_e protons of 2.20–2.29, 2.31–2.39, and 2.40–2.48 ppm may be assigned to the rmr, mmr, and mmm tetrads, respectively, since across this series the erythro protons will be increasingly deshielded by the proximity of the nitrile groups. Furthermore, additional fine structure may be found in each region. We have calculated the tacticity fractions for different orders assuming that the free-radical polymerization of methacrylonitrile is controlled by Bernoullian statistics.[16] These intensities for different tacticity sequences calculated from the Bernoullian distribution will allow the assignment of the peaks to the hexad level in each tetrad group. In the mrmrm

Table 1. Tacticity Assignments for the Methylene Proton Resonance Peaks

tactic sequence[a]	H_t, ppm	H_e, ppm
mrmrm (0.024)	2.052, 2.081	2.205, 2.234
mrmrr (0.069)	2.045, 2.074	2.229, 2.261
rrmrr (0.051)	2.036, 2.065	2.253, 2.284
rmmrr (0.069)	2.045, 2.076	2.312, 2.341
mmmrm (0.032)	2.059,[b] 2.089	2.332, 2.362[b]
mmmrr (0.047) or rmmrm	2.038, 2.067	2.336, 2.366
rmmrm (0.047) or mmmrr	2.052, 2.081	2.358, 2.387
mmmmr (0.032) or mmmmm + rmmmr	2.040, 2.069	2.403, 2.434
mmmmm + rmmmr (0.035) or mmmmr	2.054, 2.083	2.419, 2.448
rrrmr (0.101)	2.146, 2.177	2.233, 2.264
mrrmm (0.047)	2.140, 2.169	2.255, 2.287
rrrmm (0.069) or mrrmr	2.127, 2.158	2.236, 2.266
mrrmr (0.069) or rrrmm	2.157, 2.189	2.257, 2.285
rrr (0.210)	2.11–2.20	
mrm (0.098)	2.20–2.31	

[a] The values in the parentheses are the relative resonance intensities calculated for a Bernoullian distribution. [b] The chemical shift of the unresolved peak was calculated assuming a coupling constant of −15.0 Hz.

and mmmrm sequences, some cross-peaks in the four-peak square pattern cannot be observed because there is some overlap with other sequence resonances. However, we can assign them according to symmetry principles. In the mmm sequence region, there are only two four-peak squares which have similar resonance intensities. Therefore, according to the Bernoullian statistics, the two squares may be assigned to mmmmr and mmmmm + rmmmr hexads, respectively. Meanwhile, the coupling constants for each geminal coupling at the hexad tacticity level were also determined. The J_{gem} values for different tacticity sequences are all close to −15 Hz, which is the same as the corresponding value obtained for the poly(methyl methacrylate) system.[13]

In Figure 3, we find that there are no cross-peaks between the peaks from 2.00 to 2.11 ppm and those from 2.11 to 2.20 ppm. Therefore, the peaks from 2.11 to 2.20 ppm in the 1D spectrum may be assigned to the methylene protons in racemic diads. However, there are cross-peaks between the peaks from 2.11 to 2.10 ppm and those from 2.20 to 2.31 ppm. This coupling occurs since the higher order asymmetric configuration (tetrad tacticity rrm) causes inequivalence of the methylene protons in the central racemic diad, and therefore, the protons can also be divided into H_e and H_t types. In the manner discussed above, the coupling region of the rrm tetrad can be further assigned to the four hexad sequences. The coupling constants for every hexad level geminal coupling of the racemic diads have been calculated, and a single value of −15 Hz has been obtained, which is in agreement with the result obtained for the meso diads. Meanwhile, from a comparison of the resonance intensities in the 1D spectrum, the equivalent methylene protons for the tetrads rrr and mrm can be assigned to single peaks in the regions of 2.11–2.20 and 2.20–2.31 ppm, respectively. The results of the peak assignments in the methylene region are shown in Table 1.

In previous reports, the 1D ^1H spectrum of poly(methacrylonitrile) was assigned to the diad level by assuming that each tacticity group had a different chemical shift.[9] However, in the present work, we have clearly shown that overlap exists between the racemic and meso tacticity peaks in the 1D spectrum and, therefore, that the assignments given in the literature are incorrect. Using the 2D technique, we may separate the spectral overlap and assign the peaks to higher tacticity levels. According to these assignments, we have calculated the resonance intensities in the different intervals of the 1D spectrum using the Bernoullian distribution. The calculated results are in good agreement with the experimental values and are shown in Table 2.

Table 2. Resonance Intensities for the Different Tacticity Sequences Determined from the Methylene Region of the 1D ^1H Spectrum

chem shift, ppm	tacticity assignment	observn	calculn[a]
2.00–2.11	m (H_t)	0.203	0.203
2.11–2.20	rrr; rrm (H_t)	0.339	0.351
2.20–2.31	mrm; rmr (H_e); rrm (H_e)	0.323	0.313
2.31–2.48	mmr (H_e); mmm (H_e)	0.142	0.131

[a] Calculated for a Bernoullian distribution with a single statistical parameter P_m = 0.406.

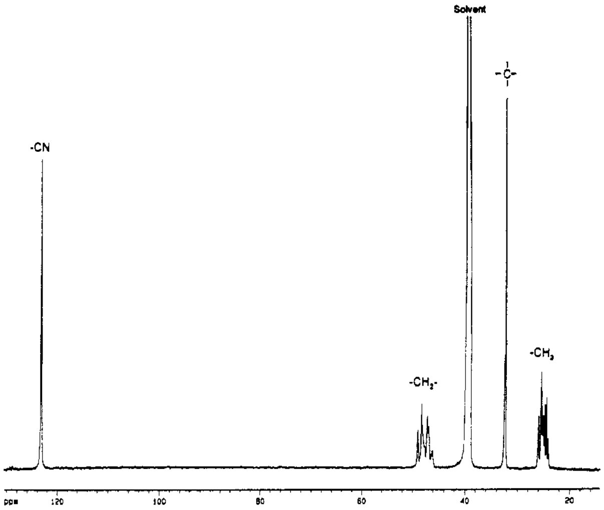

Figure 4. 1D ^{13}C NMR spectrum of poly(methacrylonitrile).

In order to examine the information from the ^{13}C nucleus, the 1D ^{13}C NMR spectrum and the 2D proton-detected heteronuclear shift-correlated NMR spectrum have been measured. Figure 4 shows the 1D spectrum and the assignments for each resonance. The methyl and methylene regions show fine structure due to tacticity splitting. The methyl group region of the 2D heteronuclear spectrum is shown in Figure 5. It is evident that peaks at higher chemical shifts for ^{13}C correspond to lower chemical shifts for ^1H and vice versa.

As seen above, in the proton spectra the methylene group provides much information about the higher tactic sequences of poly(methacrylonitrile). This information can be used to assign the ^{13}C spectra. Figure 6 shows the 2D heteronuclear NMR spectrum in the methylene region. There are cross-peaks between 2.00–2.48 ppm for protons and 45.5–50.0 ppm for carbons. The carbon peaks at 45.8–46.7 ppm which are coupled to the proton peaks at 2.20–2.31 ppm may be assigned to the mrm sequence, in which the methylene protons connected to the same carbon are equivalent. In the proton spectrum, we also concluded that the methylene protons connected to the same carbon in the rrr sequence are equivalent and have a single peak at 2.20–2.31 ppm. From Figure 6, we find that there is a strong coupling of protons in this region to the carbons with resonances at 48.0–48.7 ppm. However, some degree of coupling in the ^1H projection direction is observed. This may be interpreted as arising from the coupling between the inequivalent germinal methylene protons in the tactic sequence rrrrm. In the rrm tetrad, the methylene protons, H_t and H_e, give rise to the resonances at 2.11–2.20 and

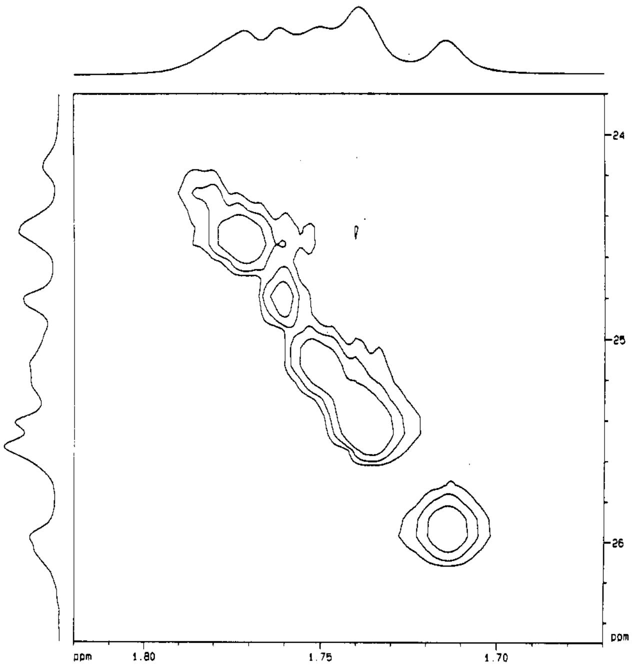

Figure 5. α-Methyl region of the 2D ^1H–^{13}C heteronuclear NMR spectrum of poly(methacrylonitrile).

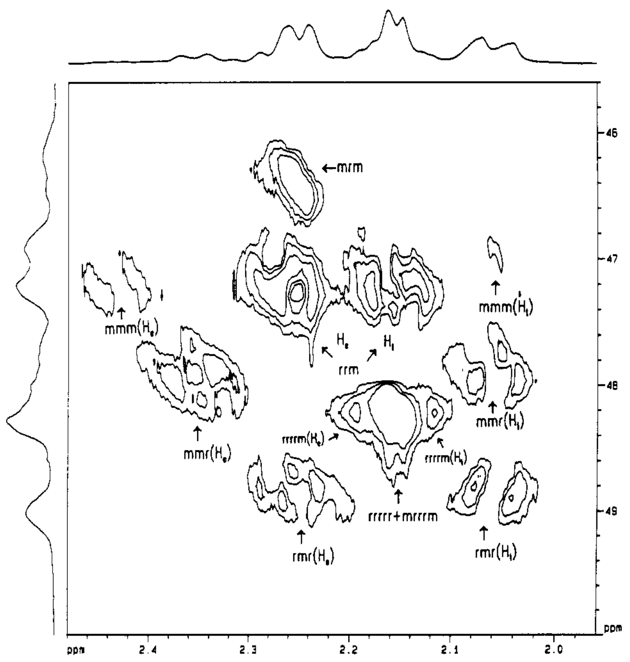

Figure 6. Methylene region of the 2D ^1H–^{13}C heteronuclear NMR spectrum of poly(methacrylonitrile). The tetrad tacticity assignments have been marked on the figure (H_e, erythro proton; H_t, threo proton).

2.20–2.31 ppm, respectively. Therefore, the peaks at 46.7–47.6 ppm in the carbon spectrum may also be assigned to the rrm tetrad. By correlating the assignments in the proton spectra, the carbon resonances in Figure 6 in the 48.7–49.6, 47.6–48.3, and 46.7–47.6 ppm regions may be assigned to rmr, mmr, and mmm sequences, respectively. These tactic assignments for the different cross-peaks in the methylene region of the heteronuclear 2D spectrum have been marked on Figure 6.

In this work, heteronuclear multiple quantum coherence (HMQC) was applied to the poly(methacrylonitrile) system. The bilinear (BIRD) pulse was used in order to presaturate all protons not directly attached to the ^{13}C nucleus. Previous research indicated that for larger molecules ($\omega\tau_c < 1$) the BIRD pulse would possibly attenuate signals arising from protons attached to ^{13}C because of the negative NOE effect, and therefore, the heteronuclear chemical shift correlation would not be observed.[5] However, in this study, we find that by selecting the experimental conditions properly, we also can obtain excellent heteronuclear correlation spectra for poly(methacrylonitrile). Only the cross-peaks for the mmm sequence between 2.11–2.20 ppm for the H_t proton and 46.7–47.6 ppm for the methylene carbon are attenuated, which may be caused by a differential negative NOE effect. There have been some previous reports[17] in which the intensities of the cross-peaks in the proton-detected ^1H–^{13}C shift-correlated spectrum for a polymer have been used directly for assigning peaks in the spectrum. But our work indicates that the negative NOE effects can distort the cross-peak intensities, which may then lead to incorrect assignments in some macromolecular systems if tacticity assignments are based solely on these cross-peak intensities.

Table 3. Tacticity Assignments for the Methylene Region of the 1D ^{13}C Spectrum

			resonance intensity		
chem shift,	assignment of carbon			calculation[a]	
ppm	this work	lit.	observn	this work	lit.
45.8–46.7	mrm	mmm	0.109	0.098	0.067
46.7–47.6	mmm + rrm	mrm + mmr	0.333	0.353	0.384
47.6–48.7	rrr + mmr	rrm + rmr	0.400	0.405	0.430
48.7–49.6	rmr	rrr	0.158	0.143	0.210

[a] Calculated for a Bernoullin distribution with a single statistical parameter P_m = 0.406.

Tacticity sequence assignments based on the 1D ^{13}C NMR spectra of poly(methacrylonitrile) have previously been made by other authors.[8,9] In the methylene region, the four peaks were assigned by these authors, from high to low field, to mrm, mmm + rrm, rrr + mmr, and rmr tetrads, respectively. Table 3 shows the assignments based on our work and those proposed by the previous workers. The resonance intensities of the four peaks have been calculated by using the Bernoullian distribution for our assignments of these peaks and for the assignments proposed by the previous authors. Table 3 also shows the calculated resonance intensities of the four peaks and those determined from our experimental measurements. It is evident that the experimental and calculated resonance intensities show close agreement for our assignments of these peaks and that the previous assignments of the peaks in the methylene region of the ^{13}C NMR spectra reported in the literature are invalid.

Conclusion

By means of DQF-PS COSY and proton-detected ^1H–^{13}C heteronuclear shift-correlation NMR, the tacticity of poly(methacrylonitrile) has been characterized to the hexad level for ^1H and to the tetrad level for ^{13}C. The overlap of the resonances for the different tacticities in the 1D spectra have been separated using 2D technqiues. The results indicate that the previous tacticity assignments reported in the literature for ^1H and ^{13}C resonances based upon 1D spectra are invalid.

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