Macromolecules **1994,** *27,* 6301-6306

High-Resolution NMR Analysis of the Tacticity of Poly(*n*-butyl methacrylate)

Gregory R. Quinting and Rubing Cai*

Sherwin-Williams Company, 10909 South Cottage Grove Avenue, Chicago, Illinois 60628

Received February 15, 1994; Revised Manuscript Received July 11, 1994[●]

ABSTRACT: High-resolution ^{13}C and ^{1}H NMR measurements were carried out to determine the tacticity of poly(*n*-butyl methacrylate) with particular focus on the peak assignments for the *n*-alkyl side chain. Both free radical and anionic poly(*n*-butyl methacrylate) were examined, with the former being predominantly syndiotactic and the latter isotactic. The ^{1}H NMR resonances for the *n*-alkyl chain of these polyacrylics show a combination of effects from configurational sensitivity and homonuclear scalar interactions. A combination of *J*-resolved ^{1}H NMR and ^{1}H–^{13}C heteronuclear correlated 2D NMR spectra was used to characterize the previously unobserved, long-range chemical shift effects due to tacticity.

Introduction

High-resolution nuclear magnetic resonances spectroscopy (NMR) has been widely used to determine polymer conformation and configuration in solution since the late 1960s.[1] Before the invention of Fourier transform NMR and the consequent capability to easily do signal averaging, however, ^{1}H NMR was the only means available for polymer chemists to determine tacticity in the 1960s.[2] During the 1970s, the advances in Fourier transform NMR led to the use of ^{13}C NMR to measure tacticity and sequence distribution in vinyl polymers.[3] In the last decade, various advanced 2D NMR methods have been developed to make comprehensive spectral assignments of vinyl polymers.[4-6] Although both high-resolution ^{13}C and ^{1}H NMR have been used in the tacticity measurements of polymers, ^{13}C NMR is advantageous because of its large chemical shift range and the spectral simplification afforded by proton-decoupling. This thereby allows long configurational sequences to be observed and analyzed. On the other hand, high-resolution ^{1}H NMR has higher sensitivity than ^{13}C NMR. Though ^{1}H NMR spectra of polymers contain as much or more information as the corresponding ^{13}C NMR spectra, a large portion of information is often obscured because of broad, overlapping multiplet peaks; despite this, a combination of ^{13}C and ^{1}H NMR measurements can often help to determine polymer tacticity completely.

Previous ^{1}H NMR work involved extensive studies of two representative vinyl polymers: poly(methyl methacrylate) (PMMA) and poly(vinyl chloride).[7-12] These studies led to substantial understanding of polymer microstructure for the simplest methacrylate polymer: PMMA. To avoid problems from peak overlap and *J*-couplings, earlier ^{1}H NMR work for poly(alkyl methacrylate)s entailed their conversion to PMMA and subsequent tacticity analysis of the converted PMMAs.[13-15] Ivin et al. reported the ^{13}C NMR spectrum of poly(*n*-butyl methacrylate) but did not observe any configurational sensitivity for the resonances of the *n*-butyl side chain.[16]

Poly(methyl methacrylate) is widely used in coatings; however, it exhibits a glass transition temperature (T_g) at 105 °C and consequently forms a very brittle film at room temperature. Therefore, copolymerization of methyl methacrylate with low-T_g comonomers must often be done to prepare lower T_g polymers. Replacing the methyl group in methyl methacrylate with a long alkyl side chain imparts steric hindrance in molecular packing. This lowers the glass transition temperature as a result of the increased free volume within which the polymer chains can move. For example, poly(*n*-butyl methacrylate) (PBMA) has a T_g of 20 °C, while poly(*n*-butyl acrylate) shows a T_g of −54 °C. As a result, *n*-butyl methacrylate and *n*-butyl acrylate are commonly used as comonomers to achieve low-T_g copolymers.

Herein, we report results of both ^{13}C and ^{1}H NMR measurements to study the tacticity of PBMA with particular focus on peak assignments for the *n*-butyl side chain. In the high-resolution (400 MHz) ^{1}H NMR spectrum for PBMA at high temperature, the peaks of the *n*-butyl chain exhibit not only the expected *J*-couplings from adjacent protons but also heretofore unreported chemical shift differences from monomer configurational effects. To make the complete ^{1}H and ^{13}C peak assignments and thereby elucidate the tacticity of PBMA, we also obtained the *J*-resolved 2D ^{1}H NMR and heteronuclear ^{1}H–^{13}C correlated 2D NMR spectra of PBMA at high temperature.

Experimental Section

Materials. Three PBMA samples were used in this report: one obtained from a commercial source, a second prepared by free radical polymerization, and the third prepared by anionic polymerization. Sample A ($M_n = 6.7 \times 10^4$, $M_w = 2.2 \times 10^5$) was obtained from Scientific Polymer Products (catalog no. 111C, lot no. 25G). Sample B ($M_n = 5.2 \times 10^4$, $M_w = 1.6 \times 10^5$) was prepared by free radical polymerization initiated by 2,2′-azobis(isobutyronitrile) (AIBN). *n*-Butyl methacrylate was purified by washing three times with 5% NaOH solution and then several times with distilled water. After being dried over sodium sulfate, the monomer was filtered and distilled under vacuum. The polymer was prepared by solution polymerization with 5×10^{-3} mol/L AIBN initiator in 50 wt % 2-butanone at 60.0 °C. After polymerization for 30 min, the polymer was precipitated in methanol and dried at 80 °C under vacuum. Sample C ($M_n = 3.1 \times 10^4$, $M_w = 2.7 \times 10^5$) was prepared by anionic polymerization initiated by *n*-butyllithium (2.5 M in hexane (Aldrich)). The monomer/solvent (hexane) weight ratio was 1/2.5, and the initiator/monomer molar ratio was 2/100. The anionic polymerization was carried out at −80 °C for 5 h. The polymer was then precipitated from methanol and vacuum dried at 80 °C for 4 h. The molecular weight measurements were carried out using a Waters 510 gel permeation chromatograph using polystyrene as the calibration standard.

NMR Measurements. The PBMA samples were dissolved in 1,2,4-trichlorobenzene (Aldrich) along with a small quantity of benzene-d_6 (Aldrich) for internal lock. All NMR spectra were obtained on a Bruker (formerly G.E. NMR Instruments) Omega

---

[●] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

0024-9297/94/2227-6301$04.50/0

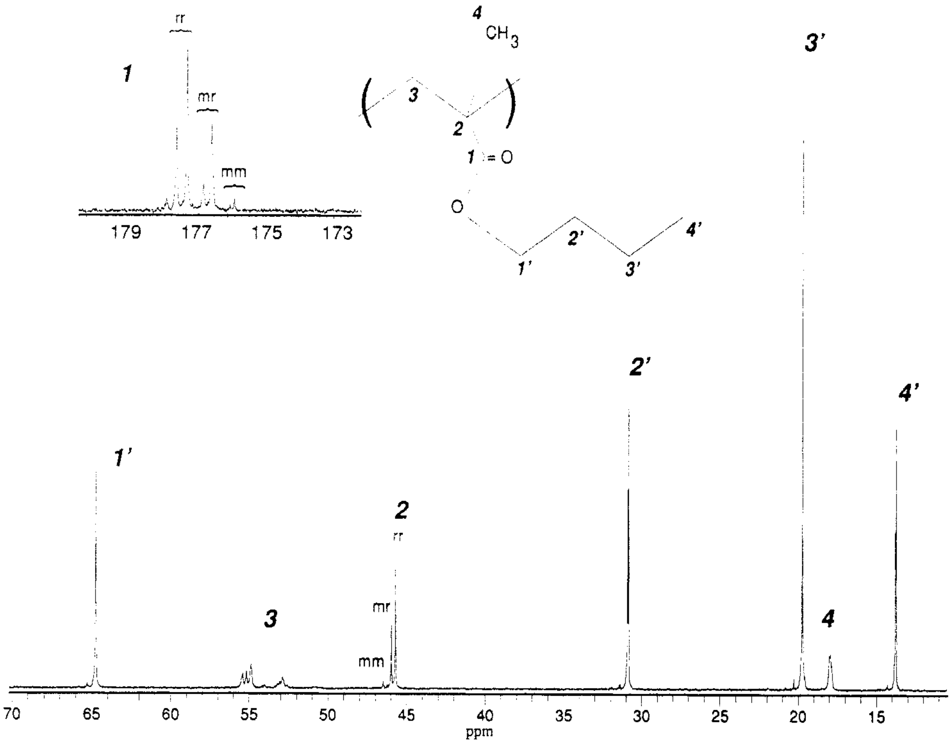

Figure 1. ^{13}C NMR spectrum of syndiotactic PBMA (sample A) in 1,2,4-trichlorobenzene at 100 °C.

Table 1. Triad and Pentad Distribution of PBMA from ^{13}C NMR (Gaussian Fit)

Sample A

		carbonyl	carbonyl	quaternary	Bu-methylene	Bu-CH$_3$	P_m = 0.210 (Bernoullian)	
pentad	triad	C-1	C-1	C-2	C-2′	C-4′	pentad	triad
mmmm							0.002	
mmmr	mm	0.005	0.024	0.029		0.058	0.015	0.044
rmmr		0.019					0.028	
mmrm							0.015	
mmrr	mr	0.068	0.347	0.348	0.367	0.346	0.055	0.332
rmrm							0.055	
rmrr		0.278					0.207	
mrrm		0.021					0.028	
rrrm	rr	0.201	0.629	0.623	0.634	0.596	0.207	0.624
rrrr		0.408					0.390	

Sample B

		carbonyl	carbonyl	quaternary	Bu-methylene	Bu-CH$_3$	P_m = 0.190 (Bernoullian)	
pentad	triad	C-1	C-1	C-2	C-2′	C-4′	pentad	triad
mmmm							0.001	
mmmr	mm		0.020	0.022	0.008		0.011	0.036
rmmr		0.020					0.024	
mmrm							0.011	
mmrr	mr	0.066	0.323	0.336	0.292		0.047	0.308
rmrm							0.047	
rmrr		0.258					0.202	
mrrm		0.022					0.024	
rrrm	rr	0.210	0.657	0.643	0.701		0.202	0.656
rrrr		0.425					0.430	

Sample C

		carbonyl	carbonyl	quaternary	Bu-methylene	Bu-CH$_3$	P_m = 0.950 (Bernoullian)	
pentad	triad	C-1	C-1	C-2	C-2′	C-4′	pentad	triad
mmmm							0.815	
mmmr	mm			0.902			0.086	0.903
rmmr							0.002	
mmrm							0.086	
mmrr	mr			0.098			0.005	0.095
rmrm							0.005	
rmrr							0.000	
mrrm							0.002	
rrrm	rr			0.000			0.000	0.003
rrrr							0.000	

Table 2. Triad and Pentad Distribution of PBMA from ^{13}C NMR (Lorentzian Fit)

Sample A

pentad	triad	carbonyl C-1	carbonyl C-1	quaternary C-2	Bu-methylene C-2′	Bu-CH_3 C-4′	P_m = 0.210 (Bernoullian)	
							pentad	triad
mmmm							0.002	
mmmr	mm	0.010	0.032	0.051		0.038	0.015	0.044
rmmr		0.022					0.028	
mmrm							0.015	
mmrr	mr	0.079	0.351	0.358	0.338	0.314	0.055	0.332
rmrm							0.055	
rmrr		0.272					0.207	
mrrm		0.034					0.028	
rrrm	rr	0.199	0.617	0.590	0.663	0.648	0.207	0.624
rrrr		0.383					0.390	

Sample B

pentad	triad	carbonyl C-1	carbonyl C-1	quaternary C-2	Bu-methylene C-2′	Bu-CH_3 C-4′	P_m = 0.190 (Bernoullian)	
							pentad	triad
mmmm							0.001	
mmmr	mm		0.020	0.040	0.030		0.011	0.036
rmmr		0.020					0.024	
mmrm							0.011	
mmrr	mr	0.091	0.341	0.338	0.246		0.047	0.308
rmrm							0.047	
rmrr		0.250					0.202	
mrrm		0.061					0.024	
rrrm	rr	0.200	0.641	0.622	0.724		0.202	0.656
rrrr		0.380					0.430	

Sample C

pentad	triad	carbonyl C-1	carbonyl C-1	quaternary C-2	Bu-methylene C-2′	Bu-CH_3 C-4′	P_m = 0.950 (Bernoullian)	
							pentad	triad
mmmm							0.815	
mmmr	mm			0.890			0.086	0.903
rmmr							0.002	
mmrm							0.086	
mmrr	mr			0.110			0.005	0.095
rmrm							0.005	
rmrr							0.000	
mrrm							0.002	
rrrm	rr			0.000			0.000	0.003
rrrr							0.000	

400WB spectrometer with a 9.4 T 89 mm bore magnet. A 5 mm proton-dedicated probe was used for the proton spectra, while a 10 mm tunable proble was used for the carbon spectra. All spectra were obtained with a sample temperature of 100 ± 0.2 °C. Typical parameters for the proton spectra were 5 μs pulse width (~45°), pulse delay 2 s, 16384 acquisition points, 6000 Hz spectral width, and 32 scans. The parameters for the carbon spectra were 12 μs pulse width (~45°), pulse delay 1 s, 16384 acquisition points, 22500 Hz spectral width, and 256 scans. Decoupling was gated on only during acquisition to suppress any nuclear Overhauser enhancement. The parameters for the 2D JRES spectrum were 16 scans/evolution block, 128 blocks, evolution dwell time 10 ms, acquisition dwell time 314 ms, and *4096* points per block. Processing parameters for the 2D JRES spectrum were sinebell weighting and magnitude calculation in both dimensions. The parameters for the HETCOR spectrum were 16 scans/evolution block, 512 blocks, evolution dwell time 332.5 μs, acquisition dwell time 166.5 μs, and *2048* points per block. Processing parameters for the HETCOR spectrum were phase-sensitive hypercomplex, one zero fill in t_1, and double exponential weighting (parameter value: 3) in t_1 and t_2.

Results and Discussion

Carbon-13 NMR. ^{13}C NMR Spectrum of Syndiotactic PBMA at 100 °C. Figure 1 shows the ^{13}C NMR spectrum of syndiotactic PBMA (sample A) obtained at 100 °C in 1,2,4-trichlorobenzene. The resolution in the ^{13}C spectrum is high enough to reveal unexpected splittings of the side-chain methylene C-2′ and methyl C-4′ peaks. Especially striking is that the relative areas of the three peaks assigned to C-4′ seemed to match the relative peak areas for the quaternary carbon: C-2. This observation leads to the suspicion that the splitting is perhaps due to previously unobserved long-range tacticity effects on chemical shift, seen not only in the carbon spectrum but also in the proton spectrum (vide infra). The side-chain C-1′ and C-3′ peaks do not show analogous fine splittings. The carbonyl carbon C-1 region of the spectrum reveals detailed pentad chemical shift sensitivity, while the backbone quaternary carbon C-2 peaks show the relative areas characteristic for a triad distribution. The peaks between 52 and 56 ppm show the diad and tetrad distributions for the β-methylene, C-3. One of the peaks for the methyl carbon (C-4) overlaps with the side-chain methylene C-3′ peak, and hence no information could be extracted.

We determined tacticity through analysis of the carbonyl (C-1), quaternary (C-2), side-chain methylene (C-2′), and methylene (C-4′) resonances. First, curve fitting was used to determine the relative peak areas which were then compared to peak areas calculated based on Bernoullian statistics. The reported P_m value was established when a best fit between the calculated and observed peak areas was obtained. Both Lorentzian and Gaussian curve fits

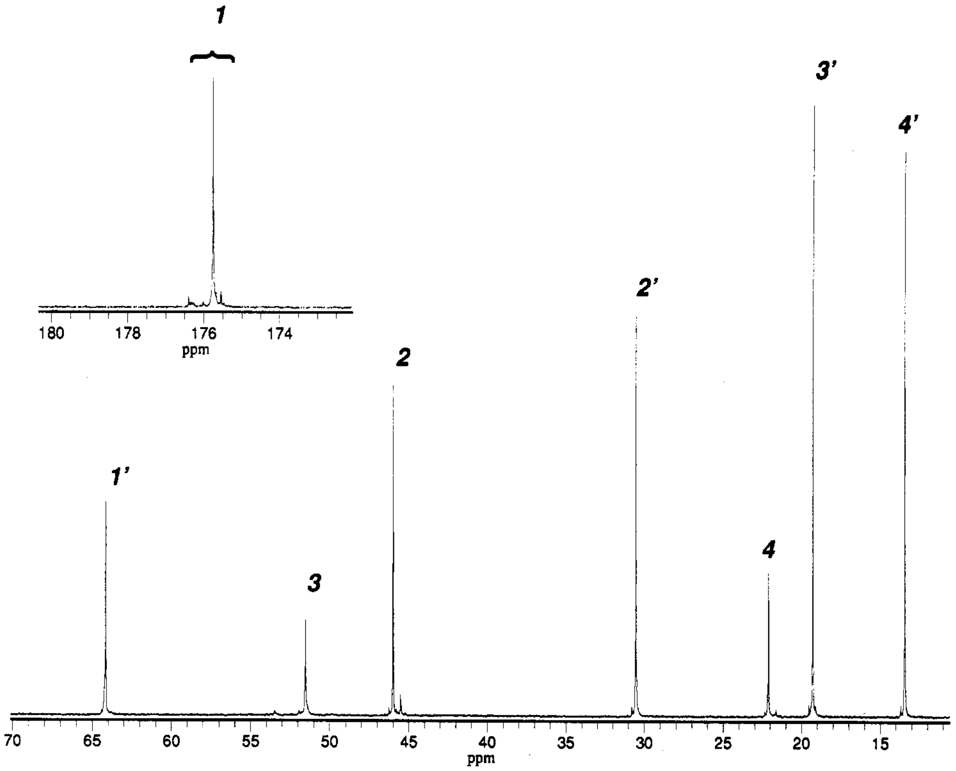

Figure 2. ^{13}C NMR spectrum of isotactic PBMA (sample C) in 1,2,4-trichlorobenzene at 100 °C.

were used to extract the peak areas. For some groups of peaks, the Gaussian fit had the least amount of error. Tables 1 and 2 show the experimental vs calculated best-fit relative peak intensities for each resonance region and the corresponding P_m values. The backbone methylene (C-3) resonance shows diad, tetrad, and even hexad sensitivity; however, the resonances did not have a sufficient signal-to-noise ratio to give accurate curve fit results. In comparison to the triad distribution results, those for the diad distribution gave less agreement between calculated and experimental peak areas. Table 3 shows the results of a similarly applied analysis of the backbone (C-3) resonances for syndiotactic PBMA. Overall, the best fit was obtained using a Bernoullian model with an average P_m value of 0.21 and 0.19 for the syndiotactic samples A and B, respectively. Hence, for sake of simplicity, the remaining discussion will focus on the syndiotactic sample A and the isotactic sample C, which will be subsequently referred to as syndiotactic and isotactic PBMA, respectively.

The curve fitting results did not show any significant dependence on the pulse delay for a set of three spectra where the pulse delay was varied. This led to the conclusion that enough time was given between scans for relaxation to occur such that the relative peak areas would not be dependent on any differences in relaxation times.

^{13}C NMR Spectrum of Isotactic PBMA (Sample C) at 100 °C. Figure 2 shows the ^{13}C spectrum of isotactic PBMA (sample C) obtained at 100 °C in 1,2,4-trichlorobenzene. The quaternary backbone carbon (C-2) resonances of isotactic PBMA were the only peaks intense enough for accurate curve fitting and tacticity determination. Analysis of the quaternary region gave a P_m value of 0.95. Though the methyl peak (C-4′) for the butyl group appeared at first to be a singlet, a close examination revealed shoulders, tentatively attributed to the same long-range effects of tacticity observed for the syndiotactic PBMA sample. The splitting pattern is again analogous to that for the quaternary peak. The farthest downfield and largest of the three peaks corresponds to the mm triad, with the smaller two upfield peaks being the mr and rr peaks, respectively. Deconvolution of the C-4′ methyl carbon peaks and subsequent analysis gave a P_m value of 0.95.

Table 3. Diad and Tetrad Distribution of Syndiotactic PBMA from ^{13}C NMR

			backbone methylene C-3			P_m = 0.210 (Bernoullian)		
hexad	tetrad	diad	hexad	tetrad	diad	hexad	tetrad	diad
mmmmmm						0.000		
mmmmmr	mmm			0.000		0.003	0.009	
rmmmmr						0.006		
mmmmrm						0.003		
mmmmrr	mmr	m		0.076	0.262	0.012	0.070	0.210
rmmmrm			0.027			0.012		
rmmmrr			0.049			0.043		
mrmrm						0.006		
mrmrr	rmr		0.017	0.186		0.043	0.131	
rrmrr			0.169			0.082		
mmrmm						0.002		
mmrmr	mrm					0.012	0.035	
rmrmr						0.022		
mmrrm						0.012		
mmrrr						0.043		
rmrrm	mrr	r	0.083	0.173	0.706	0.043	0.262	0.790
rmrrr			0.090			0.164		
mrrrm						0.022		
mrrrr	rrr		0.157	0.533		0.164	0.493	
rrrrr			0.376			0.308		

Proton NMR. ^1H NMR Spectrum of Syndiotactic PBMA at 100 °C. Figure 3 shows the ^1H spectrum of syndiotactic PBMA at 100 °C. Note that the multiplicities for the butyl side chain resonances do not seem consistent with the rules for scalar couplings. For example, the methyl resonances are an apparent quartet instead of the triplet that one expects from scalar coupling to two adjacent and equivalent methylene protons. Further scrutiny reveals that the resonances for the adjacent

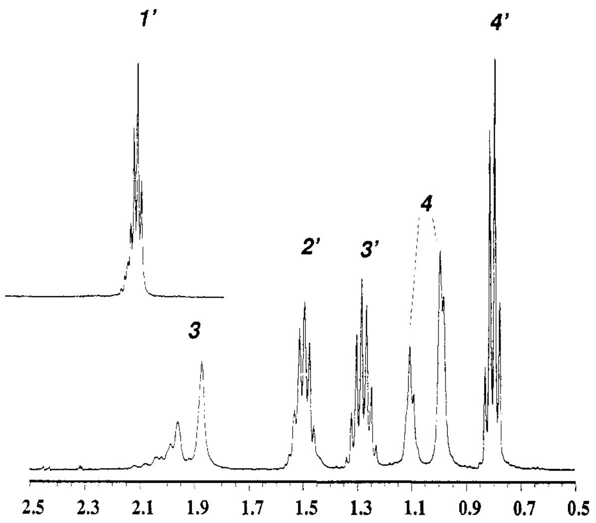

Figure 3. ^1H NMR spectrum of syndiotactic PBMA in 1,2,4-trichlorobenzene at 100 °C.

Table 4. Relative Peak Integrals of Syndiotactic PBMA from Proton NMR (Gaussian Fit)

P_m = 0.210							H-4′	
mm	mr	rr		mm	mr	rr	calcd[a]	obsd[a]
0.044	0.332	0.624		0.011			0.011	0.000
				0.022	0.083		0.105	0.096
				0.011	0.166	0.156	0.333	0.344
					0.083	0.312	0.395	0.404
						0.156	0.156	0.156
			sum	0.044	0.332	0.624	1.000	1.000
P_m = 0.210							H-1′	
mm	mr	rr		mm	mr	rr	calcd[a]	obsd[a]
0.044	0.332	0.624		0.011			0.011	0.007
				0.022			0.022	0.014
				0.011	0.083		0.094	0.070
					0.166		0.166	0.110
					0.083	0.156	0.239	0.257
						0.312	0.312	0.363
						0.156	0.156	0.179
			sum	0.044	0.332	0.624	1.000	1.000
P_m = 0.210							H-3′	
mm	mr	rr		mm	mr	rr	calcd[a]	obsd[a]
0.044	0.332	0.624		0.001			0.001	0.000
				0.007	0.010		0.017	0.010
				0.014	0.052	0.020	0.085	0.070
				0.014	0.104	0.098	0.215	0.204
				0.007	0.104	0.195	0.306	0.311
				0.001	0.052	0.195	0.248	0.265
					0.010	0.098	0.108	0.115
						0.020	0.020	0.024
			sum	0.044	0.332	0.624	1.000	1.000

[a] Calcd, calculated integral from a combination of triad distributions; obsd, observed integral from curve-fitting proton NMR spectrum.

methylene protons are an apparent heptet where one expects a hextet. The case is analogous, though less obvious for the two other butyl methylene groups. Curve fitting the butyl methyl "quartet" gave an area ratio for the two overlapping triplets which closely matches the rr:mr ratio as determined by analysis of the ^{13}C spectrum. We obtained similar ratios by analysis of the other butyl multiplets. (See Table 4.)

^1H NMR Spectrum of Isotactic PBMA at 100 °C. Figure 4 shows the ^1H NMR spectrum of isotactic PBMA at 100 °C. It does not show the "quartet" for the butyl methyl group (H-4′), which instead seems to be the expected triplet. However, further scrutiny reveals smaller peaks between the peaks of the triplet. The same long-range tacticity effect exists for isotactic PBMA; however, the larger triplet corresponds to the dominant mm triad sequence. The much smaller peaks correspond to the mr sequence.

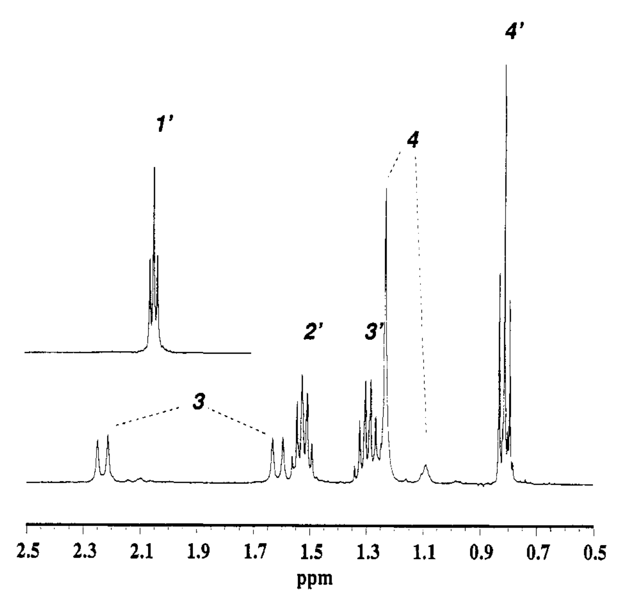

Figure 4. ^1H NMR spectrum of isotactic PBMA in 1,2,4-trichlorobenzene at 100 °C.

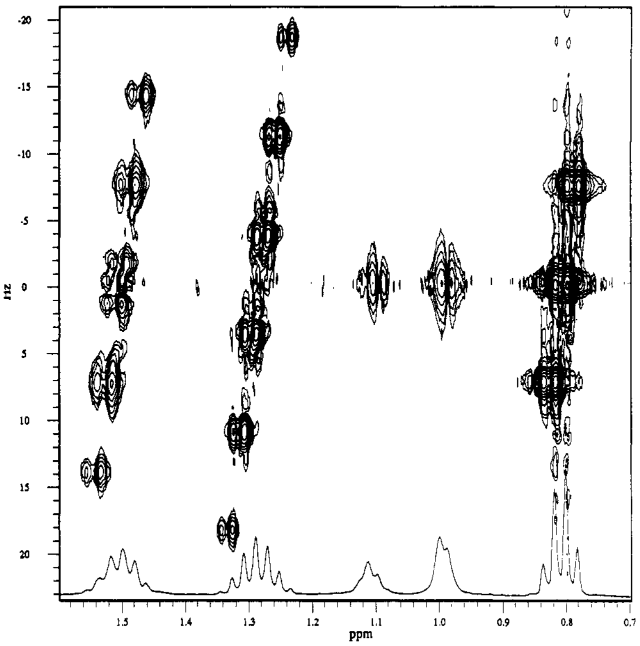

Figure 5. J-resolved 2D ^1H NMR spectrum of syndiotactic PBMA in 1,2,4-trichlorobenzene at 100 °C.

^1H 2D J-Resolved and HETCOR Spectra of Syndiotactic PBMA. The 2D J-resolved spectrum of PBMA shown in Figure 5 shows conclusively that the H-4′ resonances are two overlapping triplets. Furthermore, the adjacent CH_2 multiplet consists of two hextets overlapped to give an apparent heptet, and so on. Figure 6 shows the full HETCOR spectrum of PBMA, which reveals all the expected proton–carbon correlations. The proton and carbon peaks were narrow enough to make it possible to reveal the correlation between each of the three closely spaced butyl methyl carbon resonances and the overlapping triplet structure of the corresponding proton multiplet as shown in Figure 7. The evidence from the one-dimensional spectra discussed above already suggested quite strongly that the overlapping methyl triplets in the proton spectrum and the splitting for the butyl methyl

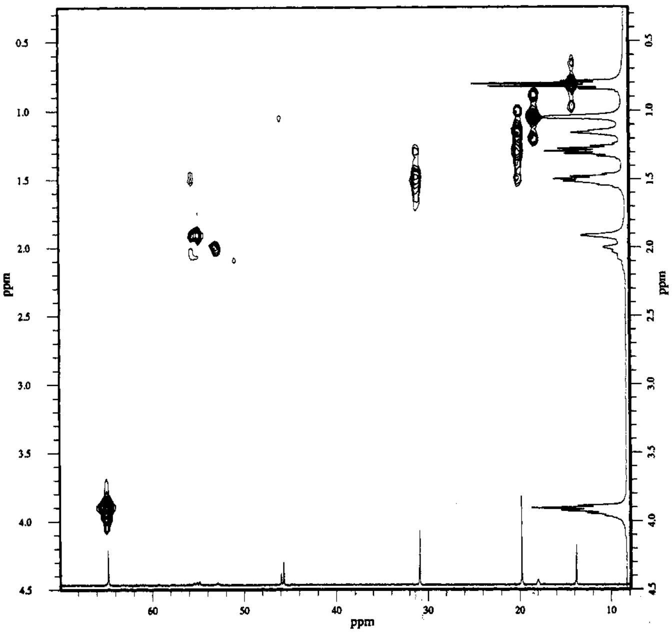

Figure 6. Magnitude-mode ^{1}H–^{13}C NMR HETCOR spectrum of syndiotactic PBMA in 1,2,4-trichlorobenzene at 100 °C.

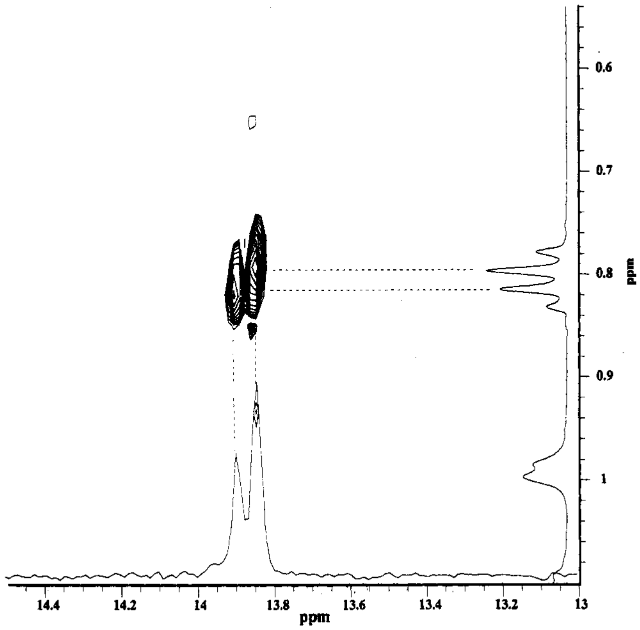

Figure 7. Subsection of high-resolution, phase-sensitive ^{1}H–^{13}C HETCOR spectrum of syndiotactic PBMA in 1,2,4-trichlorobenzene at 100 °C.

peak in the ^{13}C spectrum are the result of the chemical shift differences between monomer sequences with different tacticities. The HETCOR spectrum gives further support by showing a correlation between the ^{1}H triplet indicated as rr and the ^{13}C resonance also indicated earlier as rr. The interpretation is exactly parallel for the correlation of the mr carbon and proton resonances.

Conclusions

We used a combination of high-resolution ^{13}C and ^{1}H NMR measurements to determine the tacticity of poly(*n*-butyl methacrylate), with particular focus on the peak assignments for the *n*-butyl side chain. The *n*-butyl side chain resonances in the high-resolution ^{1}H NMR spectrum for PBMA at high temperature (100 °C) shows both the expected *J*-couplings from adjacent protons and the until now unreported chemical shift differences from monomer configurational effects. This long-range chemical shift effect due to tacticity was further confirmed by 2D *J*-resolved ^{1}H NMR and heteronuclear ^{1}H–^{13}C correlated NMR methods. Both free radical and anionic poly(*n*-butyl methacrylate)s showed the effect, with the former being predominantly syndiotactic and the latter isotactic. These results suggest that high-temperature and high-resolution ^{13}C and ^{1}H NMR spectra provide rich monomer tacticity information, which should often allow expanded use of proton NMR to study the tacticity of complex polymers.

Acknowledgment. We thank Mr. August J. Lentz for his consultation on sample preparation and assistance in running the 1D NMR spectra.

References and Notes

(1) Tonelli, A. E. *NMR Spectroscopy and Polymer Microstructure: The Conformational Connection*; VCH: New York, 1989.
(2) Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic Press, New York, 1972.
(3) Randall, J. C. *Polymer Sequence Determination: C-13 Method*; Academic Press: New York, 1977.
(4) Schilling, F. C.; Bovey, F. A.; Bruch, M. D.; Kozlowski, S. A. *Macromolecules* **1985**, *18*, 1418.
(5) Mirau, P. A.; Bovey, F. A. *Macromolecules* **1986**, *19*, 210.
(6) Kotyk, J. J.; Berger, P. A.; Remsen, E. E. *Macromolecules* **1990**, *23*, 5167.
(7) Frisch, H. L.; Mallows, C. L.; Heatley, F.; Bovey, F. A. *Macromolecules* **1968**, *1*, 533.
(8) Ferguson, R. C. *Macromolecules* **1969**, *2*, 237.
(9) Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, *14*, 1359.
(10) White, A. J.; Filisko, F. E. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20* (10), 525.
(11) Crowther, M. W.; Szeverenyi, N. M.; Levy, G. C. *Macromolecules* **1986**, *19*, 1333.
(12) Ferguson, R. C.; Ovenall, D. W. *Macromolecules* **1987**, *20*, 1245.
(13) Tsuruta, T.; Makimoto, T.; Kanai, H. *J. Macromol. Chem.* **1966**, *1*, 31.
(14) Niezette, J.; Desreux, V. *Makromol. Chem.* **1971**, *149*, 177.
(15) Junquera, J.; Cardona, N.; Figueruelo, J. E. *Macromol. Chem.* **1972**, *160*, 159.
(16) Ivin, K. J.; Pitchumani, S.; Rami Reddy, C.; Rajadurai, S. *Eur. Polym. J.* **1981**, *17*, 341.