at least partially controlled by transport of the degradation products (by bubbles and diffusion) through the softened PMMA. For example, when 200-μm-thick PMMA was degraded in air, the latter regime was observed with heating rates above 3 °C/min for TG and at temperatures above 237 °C for isothermal heating.

3. There are two reaction stages of weight loss from PMMA degraded in nitrogen. Both reactions are apparently first order with respect to sample weight. The first reaction stage is due to end initiation but also includes some effects of impurities in the commercial PMMA used in this study. The activation energy of the first reaction stage is 31 kJ/mol as determined by isothermal heating. The second reaction stage is due to random scission initiation. The activation energy of the second reaction stage is 210 kJ/mol as determined by TG and 224 kJ/mol as determined by isothermal heating.

4. There are four reaction stages of weight loss for the commercial PMMA degraded in air in both TG and isothermal heating experiments. The first three of these reaction stages are apparently first order with respect to the sample weight. Activation energies of the first three reaction stages are much less than that of random scission initiation of PMMA degraded in nitrogen. These four reaction stages are mainly caused by impurities in the sample. The weight loss of the purified PMMA shows a single oxidative step.

5. The effects of purification of the commercial PMMA on its weight loss are small for samples degraded in nitrogen except for the threshold of the weight loss at low temperatures, but they are significant for the sample degraded in air. This indicates that thermal oxidative degradation of PMMA is very sensitive to the impurities in the sample.

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Observation of the Stereochemical Configuration of Poly(methyl methacrylate) by Proton Two-Dimensional *J*-Correlated and NOE-Correlated NMR Spectroscopy

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ABSTRACT: We report the one-dimensional and two-dimensional (2D) *J*-correlated (COSY) and nuclear Overhauser effect correlated (NOESY) 500-MHz spectra of isotactic and atactic poly(methyl methacrylate). The 2D spectra permit unambiguous association of nonequivalent methylene protons and thereby materially aid the assignment of resonances to configurational sequences. We also observe in the COSY spectra correlations of α-methyl and methylene protons, assumed to arise from weak (1–2 Hz) *J*-couplings through four bonds. This information is consistent with the assignments of the resonances of both types of protons.

Introduction

Conventional one-dimensional (1D) proton NMR spectroscopy has made major contributions to our understanding of the microstructure—particularly the stereochemical configuration—of synthetic macromolecules, but during the past decade has been largely eclipsed by carbon-13 NMR because of the much greater range of carbon-13 chemical shifts and consequent greater sensitivity to structural detail. Proton NMR has certain inherent advantages, however, among them the ability to measure

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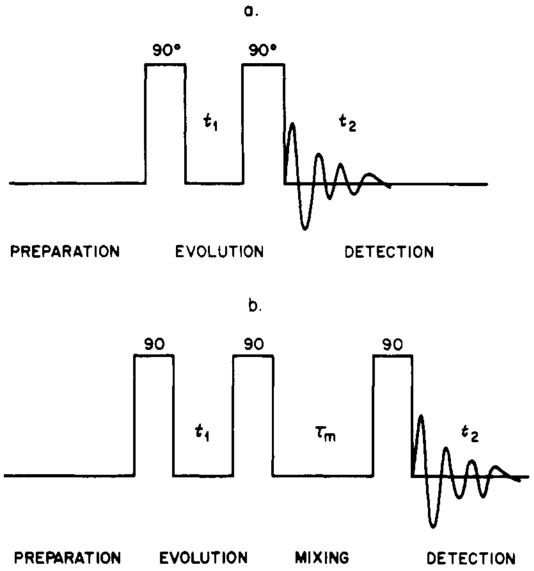


Figure 1. (a) Pulse sequence for COSY experiment; (b) pulse sequence for NOESY experiment. (See Experimental Section.)

J couplings—which may in turn be related to conformation—and to provide fundamental symmetry information. We believe these features should lead to a renaissance in its use, particularly at high field and in the 2D mode, for the study of synthetic polymers. It has never fallen out of fashion for the study of biological polymers.

Two-dimensional NMR techniques have been applied extensively to biological macromolecules. Two-dimensional Overhauser effect spectroscopy—termed NOESY for NOE-correlated spectroscopy—has been applied by Wüthrich, Ernst, and others to proteins,[1-7] cyclic peptides,[8,9] micelle-bound glucagon,[10] nucleic acids,[11,12] and synthetic biopolymers.[13] Applications to vinyl and related polymers have as yet been very limited. Macura and Brown[14] have applied 2D *J*-resolved proton spectroscopy to poly(vinyl chloride), and Gippert and Brown[15] have reported a closely related study of poly(vinyl alcohol). Gerig[16] has applied ^{19}F–^{1}H 2D chemical shift correlated NMR to poly(*p*-fluorostyrene) and Bruch et al.[17] have used ^{19}F *J*-correlated 2D spectroscopy, termed COSY, to establish resonance assignments for poly(vinyl fluoride). Bruch and Bovey[18] have applied proton NOESY to interpret the spectrum of a vinylidene chloride–isobutylene copolymer, and Bruch et al. have employed *J*-resolved proton spectroscopy to the study of the structure of poly(propylene oxide).[19]

In this paper we report for the first time the use of proton COSY and NOESY at 500 MHz to establish with greater certainty than heretofore the stereochemical microstructure of isotactic and atactic poly(methyl methacrylate). We also report certain unexpected observations concerning long-range *J*-couplings in these polymers.

Experimental Section

NMR Methods. The COSY pulse sequence is shown in Figure 1a. The preparation period is a relaxation delay to ensure that the spin system is in equilibrium. The first 90° pulse causes each proton to precess at its characteristic frequency during the evolution period of length t_1. The second 90° pulse, or mixing pulse, causes coherent magnetization exchange between all protons which are *J* coupled to each other. The final precession frequency is observed during the evolution period of length t_2. The evolution time t_1 is systematically incremented and the resultant free induction decay is detected in t_2 for a series of t_1 values. A two-dimensional Fourier transform is performed on the resultant data matrix to yield a 2D spectrum as a function of two frequencies, ω_1 and ω_2, the precession frequencies during t_1 and t_2, respectively. Those protons which do not exchange magnetization have a final frequency, ω_2, which is the same as the initial frequency, ω_1. The COSY spectrum therefore contains the normal spectrum along the diagonal corresponding to $\omega_1 = \omega_2$. The protons which exchange magnetization due to *J* coupling have a final frequency differing from the initial precession frequency. This gives rise to off-diagonal contours or *cross peaks* connecting coupled protons. These contain the useful information in the 2D spectrum. By matching all pairs of off-diagonal peaks, the complete network of connectivities via *J* coupling can be seen in a single COSY spectrum.

The NOE-correlated or NOESY pulse sequence is shown in Figure 1b. Unlike scalar coupling, the NOE, which depends on direct, through-space dipole–dipole coupling, is a relaxation phenomenon which takes a time of the order of the spin–lattice relaxation time, T_1, of the poly(methyl methacrylate) protons to manifest itself. This is provided by the mixing time τ_m following the second 90° pulse, during which dipolar-coupled protons exchange noncoherent magnetization. Following the third 90° pulse the free induction decay is acquired in the detection time t_2. In the final 2D spectrum, cross peaks identify those protons which are close enough in space to experience measurable dipole–dipole interaction. Since the NOE varies as the inverse sixth power of the internuclear distance, it becomes negligible beyond approximately 4 Å.

NMR Measurements. The 500-MHz ^{1}H NMR spectra were recorded on a JEOL GX-500 spectrometer using 10% (w/v) solutions in chlorobenzene-d_5 with hexamethyldisiloxane (HMDS) as internal reference. All spectra were recorded at 100 °C. For the 1D spectra 100 scans were collected with a pulse interval of 8.0 s. The COSY and NOESY experiments employed a recycle time of 4.0 s, with 8 transients being collected for each t_1 value. A total of 512 spectra, each consisting of 2048 data points, were accumulated, and the data matrix was zero-filled to 1024 by 2048 points with a frequency range of 2500 Hz in both dimensions. The pulse sequences included a four-step phase-cycling routine. For quadrature detection the phase cycles together with the receiver reference phase are incremented by $\pi/2$ every four accumulations to compensate for phase and amplitude errors in the receiver channels.

For the NOESY experiment a mixing time of 300 ms was employed. The methyl and methylene proton T_1 values are in the range 0.3–0.5 s at 100 °C.[21] For the COSY experiment on the atactic polymer we were able to obtain better spectral quality by using a 60° mixing pulse. This has the effect of reducing the intensity of the diagonal resonances relative to the cross peaks.[22] As a result artifacts due to "t_1 noise" (vide infra) and overlapping of star patterns are significantly reduced.

The processing of the data matrix included the use of a trapezoidal filter function in both directions to improve resolution and signal-to-noise ratio. The absolute value spectrum ("power spectrum") was calculated in both dimensions. Following the Fourier transformation, the data matrix was symmetrized to eliminate the band of "t_1 noise" running parallel to the ω_1 (vertical) axis. This noise results from instabilities in the electronic components over the experimental accumulation time—approximately 13 h.[23]

Materials. The isotactic poly(methyl methacrylate) was prepared with the anionic initiator fluorenyllithium in toluene at −40 °C, according to the method described by Sorenson and Campbell.[24] The atactic polymer was produced in a suspension polymerization[25] initiated with 2,2′-azobis(2-methylpropionitrile) at 82 °C. Analysis of the proton and carbon-13 spectra indicated a P_m value of ca. 0.25 for the free radical polymer and an isotactic content of ca. 0.95 as triads for the isotactic polymer.

A determination of molecular weights by gel permeation chromatography indicated the $\bar{M}_n$ of the isotactic and atactic materials to be 5.49×10^4 and 9.04×10^4, respectively, while $\bar{M}_w$ was found to be 3.45×10^5 and 2.5×10^5.

Results and Discussion

The first quantitative observations of the stereochemical configuration of a vinyl polymer were made by proton NMR on poly(methyl methacrylate).[26-33] As we have said, from about 1970 onward carbon-13 NMR became the

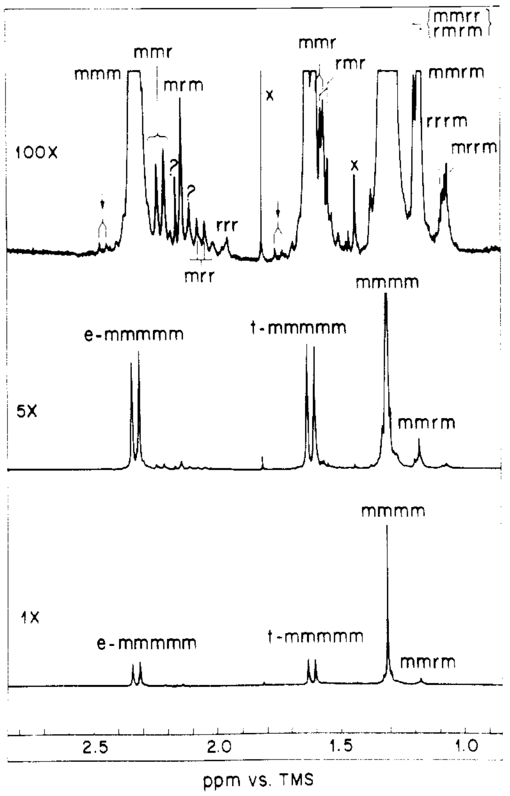
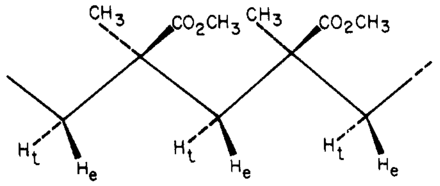


Figure 2. 500-MHz proton spectrum of isotactic poly(methyl methacrylate) at three values of gain observed in 10% (w/v) solution in chlorobenzene-d_5 at 100 °C. Resonances marked by arrows may correspond to end groups or oligomers (see text).

method of choice for the observation of synthetic polymer microstructure although for the protonated carbons in poly(methyl methacrylate) it is no more discriminating than high-field proton NMR.

In Figure 2 is shown the 500-MHz proton spectrum of isotactic poly(methyl methacrylate)—ca. 95% isotactic as triads (see Experimental Section)—observed at 100 °C in chlorobenzene-d_5. (The methoxyl proton region at ca. 3.6 ppm is omitted.) The spectrum is observed at three values of gain. At 1× the spectrum appears to be that of a nearly purely isotactic polymer with AX doublets for the methylene protons and a singlet for the methyl mmmm resonance. The e and t notations for the methylene protons refer to erythro and threo protons, respectively, which are syn and anti to the ester group in the trans–trans conformation.



(This is in fact the preferred conformation of the isotactic chain;[34,35] vide infra). This identification has been demonstrated for acrylates by Yoshino et al.[36] and has been extended to methacrylates,[37] but for the latter it cannot be regarded as firmly established.

As the gain is increased to 5× and 100× residual chain irregularities become evident. The indicated assignments to tetrad and pentad configurational sequences have been made with the aid of the 2D results to be described. They do not differ significantly from those made earlier[28-33] but are now more certain. The methylene resonances at 1.75 and 2.50 ppm—indicated by arrows—are outside the chemical shift range for normal chain units. They are somewhat too large to correspond to the reported $\bar{M}_n$ (see Experimental Section) and may correspond at least in part to oligomers not detected by GPC.

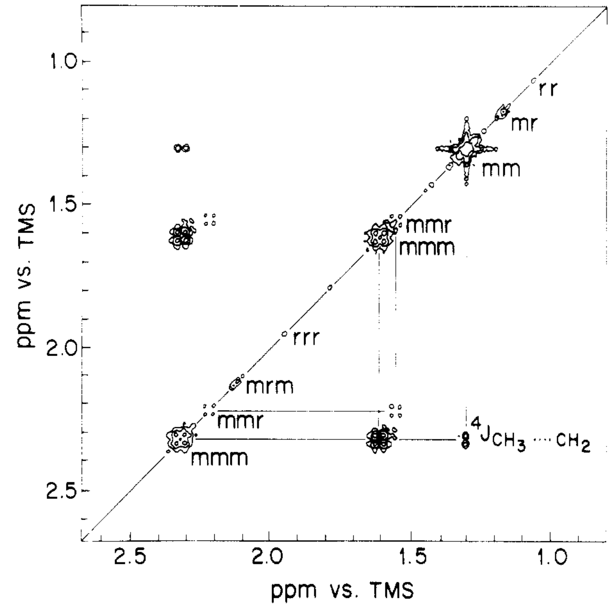


Figure 3. 500-MHz proton COSY spectrum of isotactic poly(methyl methacrylate) observed in 10% (w/v) solution in chlorobenzene-d_5 at 100 °C.

Figure 3 shows the 500-MHz COSY spectrum of the isotactic polymer, observed under the same conditions as in Figure 2. The methoxyl proton is again omitted. The principal correlating influence is the geminal coupling, J_{gem}, of the methylene protons, which has a magnitude of −15 Hz. This is manifested as diagonal resonances composed of four peaks arranged in a square pattern with frequency spacing parallel to the axes (and along the diagonal) equal to J_{gem} and as cross peaks of the same form and nearly equal intensity. The latter unambiguously identify the coupled protons even for very weak resonances where the correlation is not obvious. Thus, each methylene group exhibits a total of 16 peaks. The methyl protons and those methylene protons which appear as singlets (or nearly so)—rrr and mrm—of course do not exhibit cross peaks. The rrr methylene tetrad resonance is relatively prominent and the position of the rr methyl triad resonance corresponds to that of the mrrm and rrrm pentads. These observations suggest a fairly marked deviation from Bernoullian statistics, in agreement with previous findings.[38]

In Figure 4 the NOESY spectrum of the isotactic polymer is shown. It is virtually identical with the COSY spectrum. This at first sight is somewhat unexpected but is in conformity with the fact that in this polymer protons which are close in space are also strongly J coupled. This pattern of behavior should be common but not necessarily universal.

In the COSY spectrum of the isotactic polymer (Figure 3) we observe a cross peak between the mmmm CH$_3$ resonance and the mmm erythro proton but not the threo proton. This evidently reflects a four-bond coupling, probably of ca. 1–2 Hz, which is observable only in the 2D spectrum. It may be noteworthy that in the trans–trans main-chain conformation (vide supra) only the erythro proton is capable of forming with an α-methyl proton (one-third of the time for each) a "W"-shaped four-bond path of the kind generally thought to be favorable for such long-range coupling. Expressed somewhat differently, the methyl group and the erythro proton exhibit in the trans–trans main-chain conformation the 180° dihedral angle corresponding to maximum coupling according to

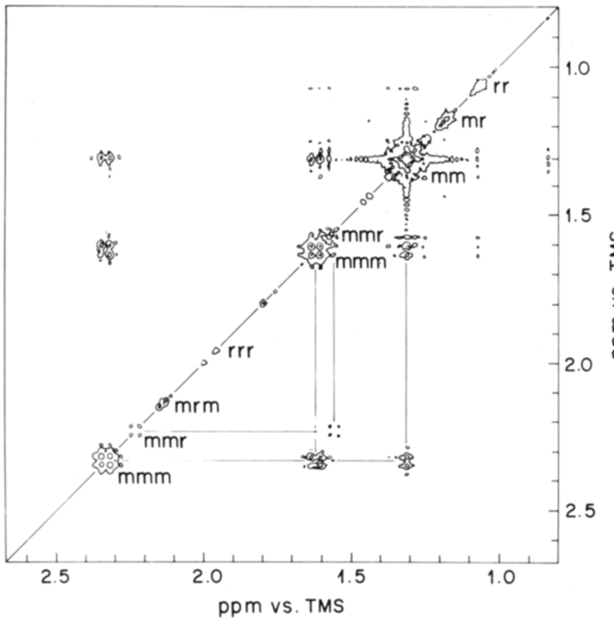


Figure 4. 500-MHz proton NOESY spectrum of isotactic poly(methyl methacrylate) observed in 10% (w/v) solution in chlorobenzene-d_5 at 100 °C.

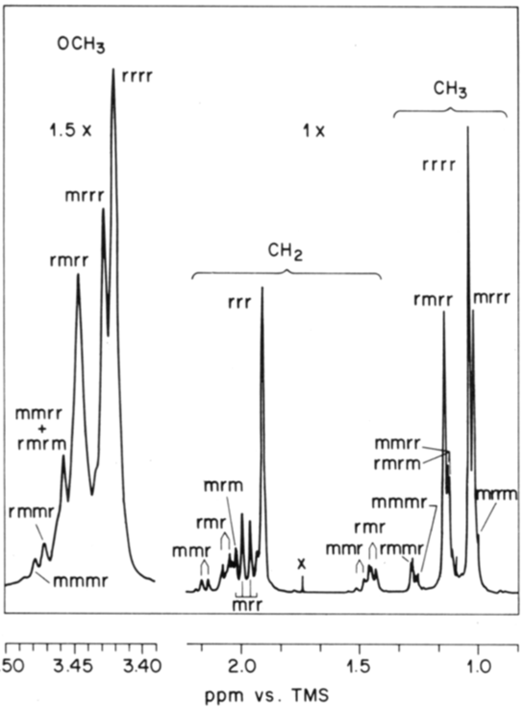
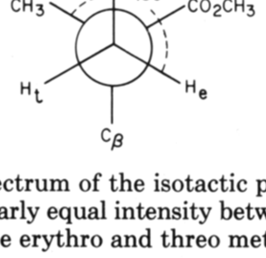


Figure 5. 500-MHz proton spectrum of free radical (atactic) poly(methyl methacrylate) observed in 10% (w/v) solution in chlorobenzene-d_5 at 100 °C.

the correlation of Barfield,[39] whereas the threo proton is near a minimum:



The NOESY spectrum of the isotactic polymer exhibits cross peaks of nearly equal intensity between the mmmm CH_3 and both the erythro and threo methylene protons.

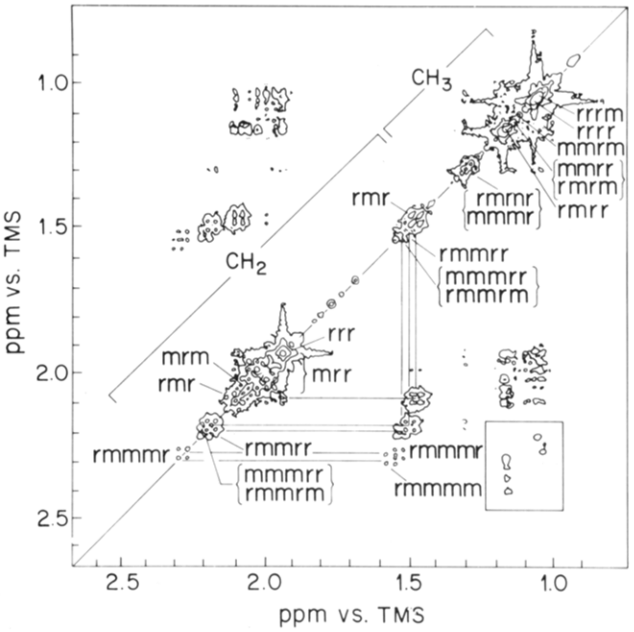


Figure 6. 500-MHz proton COSY spectrum of free radical (atactic) poly(methyl methacrylate) observed in 10% (w/v) solution in chlorobenzene-d_5 at 100 °C. The small inset spectrum shows the appearance of the CH_3–CH_2 cross-peak region, moved downward by 0.30 ppm on the vertical axis, when a 60° mixing pulse is employed. (See Experimental Section.)

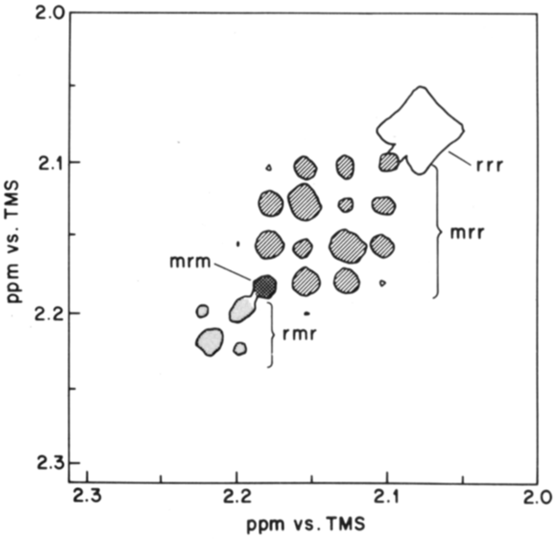


Figure 7. Expansion of a portion of Figure 6 showing a single-contour COSY spectrum of the region centered on the mrr multiplet (hatched). The mrm singlet (crosshatched) coincides with one diagonal peak of the mrr multiplet.

In Figure 5 is shown the 500-MHz proton spectrum of free radical (atactic) poly(methyl methacrylate) of P_m equal to ca. 0.25 (see Experimental Section). The methyl protons are resolved to the pentad level and the methylene protons to the hexad level. This fine structure is more clearly evident in the COSY spectrum (Figure 6), in which overlapping four-peak methylene proton patterns can be seen in both the diagonal and off-diagonal resonances. In fact, the hexad resonance assigned to rmmmm can be seen as a cross peak but is not evident on the diagonal in Figure 6; this diagonl resonance can be seen when lower contours are employed (not shown). Again, the association of nonequivalent methylene protons is made unambiguous by the cross peaks.

The resonances are assigned to configurational sequences on the basis of Bernoullian intensities (which can be only semiquantitatively estimated in the COSY spectrum), by cross-peak correlations, and by reference to the spectra of the isotactic polymer. No resonances are observed which can be plausibly assigned to end groups or oligomers. The r-centered methylene proton tetrad resonances are singlets with the exception of mrr; this exhibits an AB pattern in which the separation of chemical shifts $\Delta\nu$ is such that $J_{gem}/\Delta\nu$ is ca. $3^{1/2}/3$, so that the peaks are equally spaced. This gives the regular 4 × 4 pattern at ca. 2.0 ppm. This 16-peak pattern is expanded in Figure 7, in which the mrm and rrr resonances may also be more clearly seen.

We again see cross peaks between the CH_3 and CH_2 resonances, arising in part from four-bond coupling but also in part from a combination of "t_1 noise" and overlapping of star patterns of prominent peaks. By use of a 60° mixing pulse in the COSY experiment (see Experimental Section) true cross peaks are enhanced and diagonal resonances, together with associated artifacts, are suppressed. The inset spectrum of the CH_3–CH_2 cross-peak region is the result of such an experiment. These resonances now show the expected correlation of CH_3 pentad and CH_2 tetrad sequences, based on four-bond coupling, and confirm the assignments given.

Conclusion

Two-dimensional proton NMR spectroscopy of isotactic and atactic poly(methyl methacrylate) at 500 MHz permits an unambiguous assignment of *J*-coupled methylene proton pairs. This is particularly useful for weaker resonances, where assignment in the 1D spectrum may be difficult. Hexad splittings of methylene tetrad resonances are clearly discriminated.

In addition, the COSY spectrum of the isotactic polymer shows cross peaks between the mmmm methyl singlet and the erythro methylene proton doublet but not to the threo proton doublet. This arises from a long-range (four bond) *J* coupling which is not detectable in the 1D spectrum. This finding appears to be consistent with the all-trans main-chain conformation which isotactic poly(methyl methacrylate) is believed, from rotational isomeric state calculations, to prefer in solution. Similar cross peaks in the COSY spectrum (using a 60° mixing pulse) of the atactic polymer permit correlation of CH_3 and CH_2 resonances and are consistent with the assignments of these peaks.

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Registry No. Isotactic poly(methyl methacrylate), 25188-98-1; atactic poly(methyl methacrylate), 9011-14-7.

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