Tacticity Determination of Poly(methyl Methacrylate) (PMMA) by High-Resolution NMR

One of the most important uses of HR NMR in the field of polymers is the determination of chain configuration. With the advent of superconducting magnets which produce fields of up to 100 kG, great simplification of the spectra can be achieved. As H_0 increases, there is a directly proportionate increase in the chemical differences between different nuclei, but the magnitude of the spin-spin J coupling does not change.

The study of stereoregularity of PMMA by proton NMR was first described by Bovey and Tiers (1) on a spectra taken at 40 MHz. In this study, the configuration of various forms of PMMA will be determined from the interpretation of a proton NMR spectra taken at 360 MHz.

Experimental

The high-resolution proton NMR spectra were taken on a Bruker WM 360 MHz spectrophotometer. The Bruker has a Low Loss Cryostats superconducting magnet with a field strength of 84,560 G. The solvents used were 99.96% deuterated acetone and chloroform. The various PMMA solutions were made to a concentration of approximately 0.01%.

Results

Table I shows the integrated peak intensities for isotactic, atactic, and 50/50 wt % mixtures of PMMA in $CDCl_3$ relative to the integrated peak of the ester methyl group. The number-average sequence lengths are also reported. The procedure described by Bovey and Tiers (2) was used to assign the chemical shift values, calculate the percent of tacticity, and determine the sequence lengths.

Figure 1 shows the β-methylene proton spectra at 360 MHz of predominantly (a) isotactic, (b) atactic, and (c) 50/50 wt % mixtures of the two in 0.01% solutions of $CDCl_3$. In these spectra, β-methylene tetrad resonances are distinguishable. The mmm tetrads in the form of an AB quartet at 1.5 and 2.1 ppm are clearly visible in Figures 1(a) and 1(c). In all three spectra, the eight racemic methylene resonances appear as fine structure between the meso resonances, but it is difficult to measure in integrated intensity for each of the eight since they are not well enough resolved.

Figure 2 shows the α-methyl proton spectra at 360 MHz of predominantly (a) isotactic, (b) atactic, and (c) 50/50 wt % mixtures of the two again in 0.01% solutions of $CDCl_3$. In all three spectra, the resonance centered at 1.2 ppm corresponds to mm triads (i), the resonance at 1.0 ppm to mr triads (h), and the resonance at 0.85 ppm to rr triads (s). In Figures 2(b) and 2(c), an additional resonance appears at 1.23 ppm. The mmmr and rmmr pentads for PMMA have been predicted to occur upfield of the mmmm pentad (b). However, since this

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TABLE I

Relative Intensity	Methyl Ester	β-Methylene	α-Methyl			
			s	h	i (mmmm)	i (mmmr, rmmr)
Isotactic (n_i=7.5)	2.989	2.00	0.250	0.417	2.355	
Atactic (n_s=5.8)	3.04	1.62	1.483	1.045	0.236	0.202
50/50	3.02	1.896	0.813	0.729	1.180	0.280

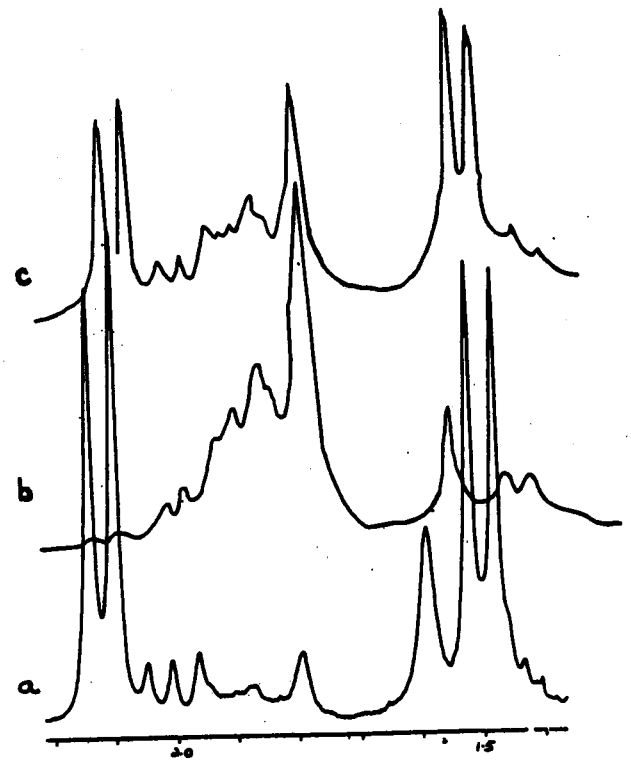

Fig. 1. β-Methylene proton spectra of (a) isotactic, (b) atactic, and (c) 50/50 wt % mixtures.

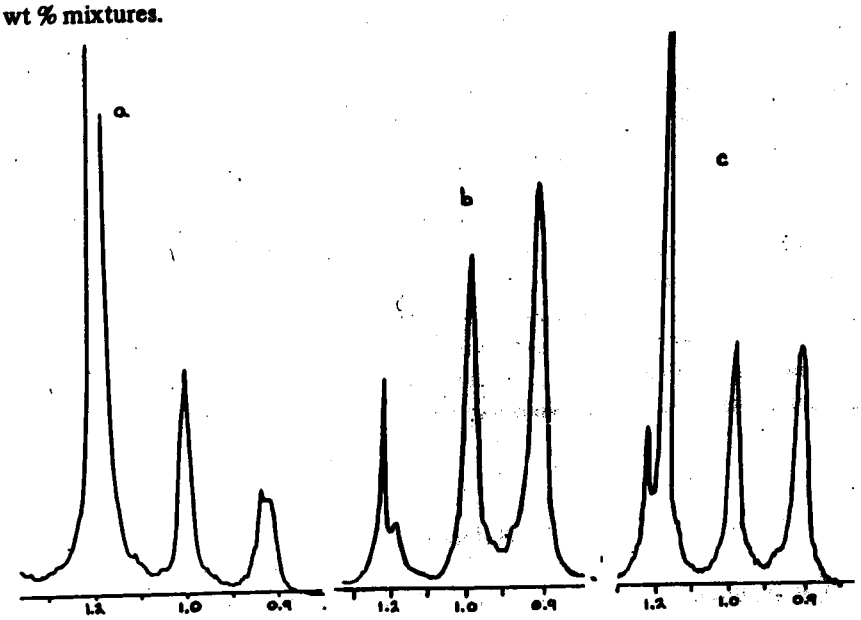

Fig. 2. α-Methyl proton spectra of (a) isotactic, (b) atactic, and (c) 50/50 wt % mixtures.

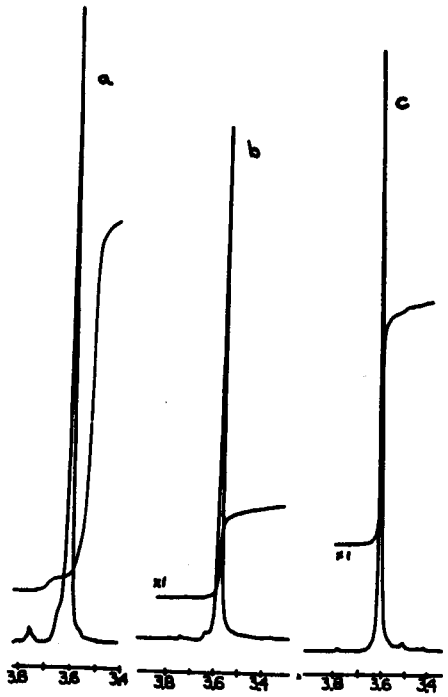

Fig. 3. Ester methyl proton spectra of (a) isotactic, (b) atactic, and (c) 50/50 wt % mixtures.

peak at 1.23 ppm increases with the addition of atactic polymer at the expense of the resonance at 1.20 ppm, it appears that the resonance at 1.20 ppm corresponds to the mmmm pentads, while the resonance downfield at 1.23 ppm corresponds to either the mmmr or rmmr pentads. This is contrary to the prediction that the mmmr and rmmr pentads will occur at higher field than mmmm pentads.

Figures 3(a), 3(b), and 3(c) show the ester methyl proton spectra of the same three PMMA samples. In all cases the ester methyl resonance was a sharp singlet occurring at 3.59 ppm (2).

Note: The ester methyl resonance was a singlet because the spectra was run in $CDCl_3$. In solvents that promote syndiotactic/isotactic stereocomplex formation (benzene, acetone, toluene), an additional ester methyl resonance can be seen that is due to associated syndiotactic/isotactic sequences.

References

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(3) F. Bovey, "High Resolution NMR of Macromolecules," Academic, New York, 1972.

A. J. White
F. E. Filisko

Department of Macromolecular Science
and Engineering
The University of Michigan
Ann Arbor, Michigan 48104

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