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APPLICATION OF ^{13}C MAGNETIC RESONANCE SPECTROSCOPY TO THE DETERMINATION OF THE TACTICITY OF STEREOREGULAR POLY(METHYL METHACRYLATE)

I. R. Peat and W. F. Reynolds

Department of Chemistry, University of Toronto, Toronto 181, Canada

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While it is well established that proton magnetic resonance spectroscopy can be used to determine tacticity of stereoregular polymers (1) and consequently to test theories of stereoregular polymerization (2,3), the information which can be obtained is often limited. For example, for poly(methyl methacrylate) (PMMA), both tetrad methylene and pentad methyl proton peaks are only partially resolved at 220 MHz (4,5). Relatively crude ^{13}C magnetic resonance (c.m.r.) spectra of PMMA have indicated that the ability to determine tacticity by this technique is at least as good as by p.m.r. spectroscopy (6,7). We present evidence here that c.m.r. is distinctly superior to p.m.r. for PMMA. This allows more detailed testing of models for stereoregular polymerization.

Samples I and II were prepared by polymerization of 3.5 M solutions of methyl methacrylate in tetrahydrofuran and toluene respectively, at -78°C with n-butyllithium as catalyst. Random noise-decoupled ^{13}C spectra were obtained on a Varian XL-100-15 n.m.r. spectrometer with 620 i computer (16 K memory) at 32°C, using Fourier transform techniques and 10% W/V samples of polymer in $CDCl_3$.

Spectra are shown in Figures 1-4. Six of the ten possible pentad peaks are clearly resolved in the $^{13}C{=}O$ spectra of the ester groups. Assignments are based on triad probabilities and the assumption that I fits Bernoullian statistics (see below). This requires assignment of the rmrr pentad as part of the high field peak in the heterotactic (mr) region. The assignment of other heterotactic pentads is unproven, but is consistent with the data. Triad probabilities estimated by integration of $^{13}CH_3$ and CH_2-^{13}C- peaks agree closely with those obtained from $^{13}C=O$ peaks (see Table I). This strongly suggests that nuclear Overhauser effects, where present, affect different triad (and pentad) peaks for a given carbon (e.g. methyl) equally and that relative peak areas within a group are accurate. Tetrad probabilities have been calculated from pentad probabilities using necessary relationships (3).

In Table I, n(ad) probabilities are compared with those calculated for models of stereoregular polymerization. I obeys Bernoullian (3) statistics with only minor deviations for tetrads and pentads. II clearly does not obey Bernoullian or first order Markov (3) statistics. The fit is better for second order Markov (4) and Coleman-Fox (4,8) models. However, in both cases, the relative probabilities for rrrm and rrrr pentads and probably also for mmmm, mmmr and rmmr pentads differ from experimental results in what may be a significant fashion. A two state mechanism has been suggested for the polymerization of methyl methacrylate in toluene with n-butyllithium (9,10). However, one or both of the states may not obey Bernoullian statistics, as required by the Coleman-Fox model (8). A systematic testing of models for stereoregular polymerization is being undertaken, using c.m.r. spectroscopy.

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TABLE I

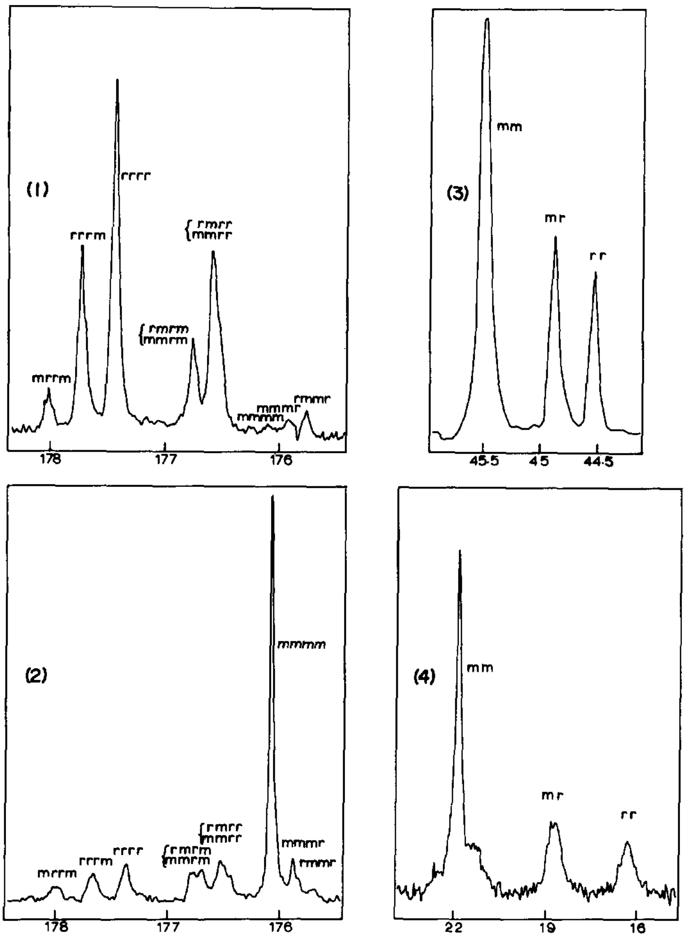
Experimental and Calculated n(ad) Probabilities for Poly(Methyl Methacrylate) Samples

n(ad)	I EXP. C=0	I EXP. CH_3	I EXP. $-\overset{|}{\underset{|}{C}}-$	I CALC. BERN[b]	II EXP. C=0	II EXP. CH_3	II EXP. $-\overset{|}{\underset{|}{C}}-$	II CALC. BERN.
m[a]	.235	.238	.240	-	.706	.707	.709	-
r[a]	.766	.762	.760	-	.294	.293	.291	-
mm	.051	.051	.060	.055	.591	.590	.592	.499
mr	.367	.374	.361	.359	.230	.229	.231	.415
rr	.582	.575	.579	.586	.178	.181	.177	.086

n(ad)	I EXP. C=0	I CALC. BERN[b]	II EXP. C=0	II CALC. BERN.	II CALC. MARKOV 1st Order	II CALC. MARKOV 2nd Order	II CALC. COLEMAN-FOX
mmm[a]	.019	.013	.545	.352	.495	-	-
mmr	.064	.084	.092	.293	.193	-	-
mrm	.053	.042	.057	.147	.045	-	-
rmr	.155	.137	.067	.061	.019	-	-
rrm	.264	.275	.127	.122	.140	-	-
rrr	.450	.449	.115	.025	.109	-	-
mmmm	.010	.003	.518	.248	.414	.501	.526
mmmr	.018	.020	.054	.206	.161	.085	.038
rmmr	.023	.032	.019	.043	.016	.004	.027
mmrm	.106	.020	.113	.206	.075	.066	.058
rmrm		.064		.086	.015	.045	.053
mmrr	.261	.064	.117	.086	.117	.051	.038
rmrr		.210		.036	.023	.066	.087
mrrm	.037	.032	.033	.043	.027	.023	.023
rrrm	.191	.210	.062	.036	.084	.082	.081
rrrr	.355	.343	.084	.007	.065	.074	.077

a) Calculated from necessary relationships.

b) Bernoullian statistics calculated from C=0 diads.



(1) Sample I, $^{13}C{=}O$ spectrum of ester group

(2) Sample II, $^{13}C{=}O$ spectrum of ester group

(3) Sample II, $CH_2{-}^{13}C{-}$ (quaternary carbon) spectrum

(4) Sample II, $C{-}^{13}CH_3$ spectrum

Chemical shifts are given in p.p.m. to low field of tetramethylsilane at 25.2 MHz.