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High Resolution NMR Analysis of the Stereochemistry of Poly(methyl methacrylate)

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ABSTRACT: Spectra (400-MHz ^1H and 100.6-MHz $^{13}C\{H\}$) of poly(methyl methacrylate) have been obtained on a variety of polymers. First-order Markov statistics calculated from triad sequences were tested and confirmed with ^{13}C pentad and heptad sequence distribution data. Free radical polymerization gives moderately syndiotactic Bernoullian distributions. Bulk polymerization with sodium borohydride produces an unusual essentially random, but first-order Markov distribution. Anionic polymerization produces first-order Markov distributions, strongly dependent on solvent and other conditions.

Background

High-resolution proton and carbon-13 NMR spectra are widely used to determine the tacticity of poly(methyl methacrylate). The proton NMR literature to 1969 was reviewed by Bovey.[1] Triad tacticity estimates can be made at low frequencies. Studies of solvent and temperature effects on the proton chemical shifts provided useful information about polymer–solvent interactions[2,3] but did not significantly improve effective resolution. NMR shift reagents resolve the *O*-methyl resonances into triads or pentads,[4-8] but this technique has no significant advantage.

Tetrad methylene and pentad methyl sequence assignments have been made for 220-,[9] and 300-,[10,11] 360-,[12] and 500-MHz[13] spectra. Assignments for highly isotactic and syndiotactic PMMA were confirmed by two-dimensional techniques.[13] Some assignments are uncertain because conformational effects associated with large differences in tacticity cause significant chemical shift perturbations.[11] For this reason, also, model compound studies are not conclusive.[14]

Quantitative estimation of tetrad and pentad sequence distributions from proton NMR spectra is difficult because of superposition of spin–spin splitting on the methylene resonance patterns and incomplete resolution of the α-methyl patterns. Trial-and-error spectrum simulation has been used here and elsewhere[11] but is unsuitable for routine use.

Proton-decoupled carbon-13 spectra[15-21] have greater chemical shift dispersion, so that up to heptad effects are resolvable at higher frequencies.[11] In earlier work, assignments were based on only highly isotactic and syndiotactic PMMAs. Some of the sequences were not detectable and the assignments were incomplete. In this work, we have studied samples covering the complete range of tacticity, including random polymers in which all of the pentad sequences were detectable.

Experimental Section

Samples. The samples used in the study were coded as follows: (A) Polysciences PMMA, isotactic, catalogue no. 3370, lot no. 45114; (B) anionic polymerization in toluene at room temperature with 1,1-diphenylhexyllithium as initiator, M_n = 19 000, M_w = 304 000; (C) bulk polymerization with sodium borohydride initiation,[9] M_n = 8900; M_w = 16 400; (D) E3517-99C, Polysciences PMMA, catalogue no. 4552, lot no. 4488, bead polymer; (E) Polysciences PMMA, syndiotactic, catalogue no. 8729, lot no. 23491.

The molecular weights were determined by gel permeation chromatography on tetrahydrofuran solutions.

NMR. Spectra (400-MHz ^1H and 100.6-MHz $^{13}C\{^1H\}$) were run on $CDCl_3$ solutions of the polymers at ambient probe temperature (ca. 25 °C) on a Bruker WM400 NMR spectrometer. ^1H spectra have been published.[22] Nuclear Overhauser enhancement in the $^{13}C\{^1H\}$ spectra was suppressed by inverse gated decoupling. Pulses of 90° with ≥3-s time delays optimized sensitivity without significant differential magnetization recovery errors. (The relaxation times of PMMA are strongly solvent and temperature dependent and detectably concentration dependent. T_1s of highly isotactic PMMA are approximately twice those of syndiotactic PMMA.[23-30] The longest T_1s in $CDCl_3$ at 25 °C were estimated to be ca. 1 s. Integrals of the C=O and O—Me regions, having the longest T_1s, were essentially equal to integrals of the α-methyl, which has the shortest relaxation times, verifying that the conditions were satisfactory.)

Table I
Quaternary ^{13}C Triad Assignments for PMMA in $CDCl_3$ Solution at 25 °C

	chemical shift, ppm			
	sample			
sequence	A	C	D	mean[a]
mm	45.48	45.38		45.41
mr	44.88	44.74	44.76	44.79
rr		44.37	44.43	44.40

[a] Weighted mean from analysis of several samples covering full range of tacticities. Small differences in sequence chemical shifts as a function of tacticity were noted and were attributed to longer range conformational effects.

Computer Analyses. Computer-fitting procedures (peak deconvolution and spectrum simulation) were applied. Deconvolution was accomplished by a nonlinear least-squares method on spectra transferred to a central computer.[31] Deconvolution has limitations, particularly in the estimation of weak lines in the wings of very strong lines. Therefore assignments and sequence distribution statistics were also tested by spectrum simulation using a program reported elsewhere.[32]

Results and Discussion

Representative 400-MHz ^1H spectra have been published elsewhere.[22] Diad and triad tacticity estimates were made from the methylene and α-methyl regions, respectively, as assigned in earlier work.[9] The *O*-methyl resonance was not resolved.

In the ^{13}C spectra, the CH_2 region reveals heptad effects but is not suitable for sequence analysis because of overlap with the *O*-methyl resonance (Figure 1a). The quaternary carbon pattern shows detectable pentad effects (with resolution enhancement, Figure 1b) but is useful only for triad estimates. The assignments are given in Figure 2 and Table I.

Pentad and heptad effects are resolved in the C=O and α-methyl regions (Figure 2 and 3). Some of the assignments were obvious by inspection, but careful analysis of observed vs. calculated intensity distributions was required to make complete assignments.

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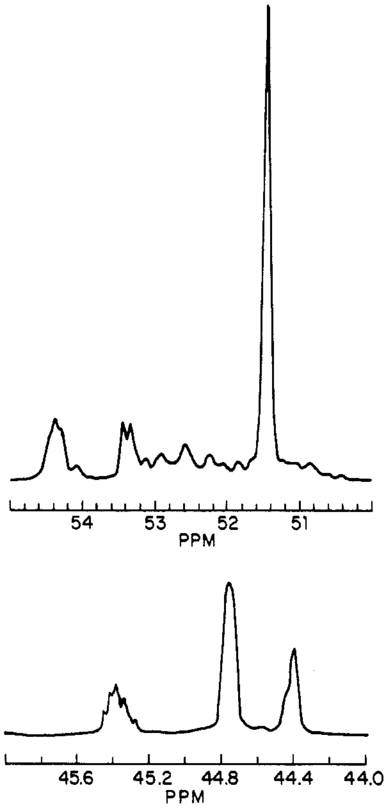

Figure 1. 100.6-MHz $^{13}C\{^1H\}$ spectrum of sample C in $CDCl_3$: upper, CH_2 and O–CH_3 region; lower, quaternary C region.

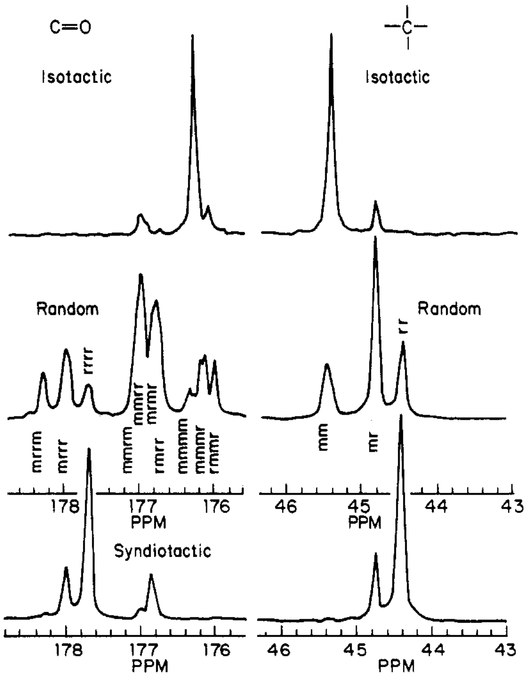

Figure 2. 100.6-MHz $^{13}\{^1H\}$ spectra of PMMA in $CDCl_3$, C=O and quaternary C regions: upper, sample A (isotactic); middle, sample C (random); lower, sample E (syndiotactic).

Triad estimates were made from integrals of α-methyl ^1H and α-methyl, quaternary, and carbonyl ^{13}C patterns. First-order Markov reactivity ratios were calculated from the triad data using well-known relationships.[1,33] $P(m/r) = 1 - P(m/m)$ is the probability that a racemic follows a meso placement and $P(r/m) = 1 - P(r/r)$ the probability that a meso follows a racemic. If the Sum $= P(m/r) + P(m/r) = 1$, the process is Bernoullian and only one probability, $P(r)$, is required.

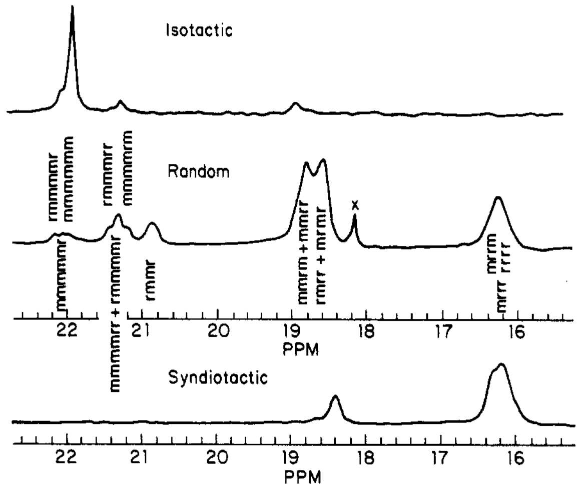

Figure 3. 100.6-MHz $^{13}C\{^1H\}$ spectra of PMMA in $CDCl_3$, α-methyl region: upper, sample A (isotactic); middle, sample C (random); lower, sample E (syndiotactic).

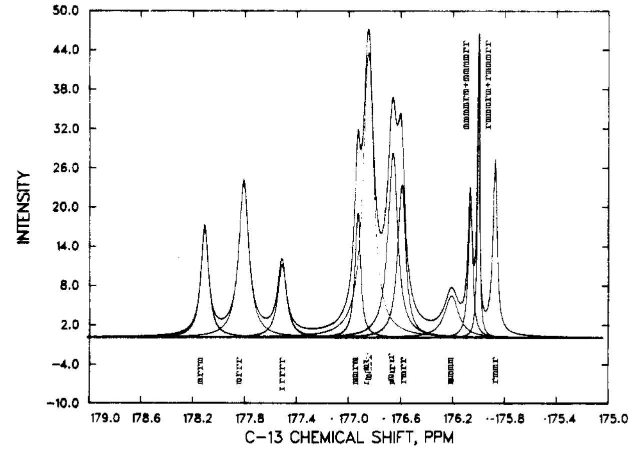

Figure 4. Computer deconvolution of the $^{13}C{=}O$ pattern of sample C. The calculated rmmr peak is omitted from this plot but was included in the analysis, and the fit was good.

Table II
NMR Triad Tacticity Data for PMMA

	sample				
	A	B	C	D	E
mm	0.85_8	0.76_9	0.21_9	0.05_9	0.02_3
mr	0.13_7	0.16_1	0.53_1	0.38_5	0.26_1
rr	0.00_5	0.07_0	0.25_0	0.55_6	0.71_6
$P(m/r)$	0.07_4	0.09_5	0.54_8	0.76_5	0.86_8
$P(r/m)$	0.94_4	0.53_4	0.51_6	0.25_7	0.15_7
Sum	1.01_8	0.62_9	1.06_5	1.02_3	1.02_5
r(calcd)	0.07_4	0.15_0	0.51_5	0.74_8	0.84_7
r(obsd)	0.08_1		0.54_6	0.77_4	0.77_5

There is some error in all estimates using integrals because of incomplete resolution. When no obvious interferences were evident, the estimates were averaged (Table II). Fifteen samples covering the full range of tacticity were analyzed and statistical tests run on the data. Standard deviations of the reactivity ratios were 3–6% of the estimates. Thus, up to 10% deviations from Sum = 1.0 may not be statistically significant. When first-order Markov effects are this weak, the distributions can be approximated as Bernoullian.

Sequence distributions through heptads were calculated from the first-order Markov reactivity ratios using a computer program obtained from Harwood.[34] The calculated distributions were used in making assignments and to test the statistics.

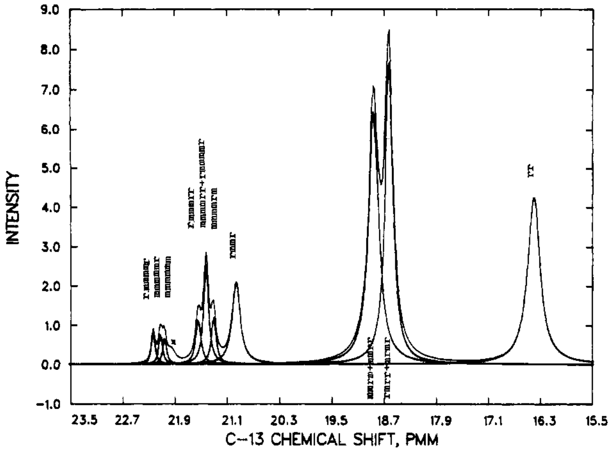

Figure 5. Computer deconvolution of the α-$^{13}CH_3$ region of sample C. × indicates an unknown impurity.

Table III
^{13}C Carbonyl Shifts in $CDCl_3$

sequence	shift, ppm	probability^a calcd	probability^a obsd
mrrm	178.27	0.066	0.068
mrrr	177.98	0.125	0.123
rrrr	177.69	0.058	0.056
mmrm	177.21	0.124	0.104
mmrr	177.00	0.116	0.187
mrmr	176.82	0.150	0.146
rmrr	176.72	0.141	0.122
mmmm	176.50	0.045	0.037
mmmmrm	176.32	0.025	0.045
mmmmrr	176.32	0.024	
rmmmrm	176.18	0.031	0.054
rmmmrr	176.18	0.029	
rmmr	176.00	0.066	0.057

^{a}Data for sample C: $P(m/r) = 0.55$, $P(r/m) = 0.52$.

With strong resolution enhancement, heptad effects were detectable in all triad regions of the C=O and α-methyl patterns.[22] Computer deconvolution, however, converged reliably and to statistically significant results at about the resolution shown in Figures 4 and 5. Thus, pentad assignments were adequate for all except the mm triad regions.

Both Lorentzian and Gaussian line shapes were used in computer deconvolution of the C=O and α-methyl regions. Lorentzian line shapes gave somewhat better fits (Figures 4 and 5), but intensity distribution estimates were not markedly dependent on the line-shape function.

The assignments best fitting the patterns of all samples are given in Tables III and IV. The agreement between calculated and observed probabilities for sample C appeared to be within the experimental error of the deconvolution method. Similar tests for the remaining samples confirmed the first-order Markov statistics of Table II. We have found no PMMAs that required higher order statistics.

First-order Markov statistics were calculated from triad tacticity data in the literature and unpublished data on a large variety of research samples from our laboratories.

Free radical polymerization is reportedly Bernoullian, with $P(r)$ being polymerization temperature dependent.[35-38] Apparent first-order Markov effects were observed, particularly in earlier work at low frequencies.[35,37] We attribute these deviations to errors (often systematic) in integral ratios.

Anionic polymerizations are characterized by strong terminal diad (apparent first-order Markov) effects, which are solvent and temperature dependent.

Table IV
^{13}C α-Methyl Shifts in $CDCl_3$

sequence	shift, ppm	probability^a calcd	probability^a obsd
rmmmmr	22.18	0.013	0.013
mmmmmr	22.09	0.022	0.015
mmmmmm	22.19	0.009	0.017
rmmmrr	21.38	0.029	0.026
mmmmrr	21.35	0.024	0.053
rmmmmr	21.35	0.013	
mmmmrm	21.31	0.025	0.025
rmmr	20.88	0.066	0.060
mmrm	18.99	0.124	0.258
mmrr	18.84	0.116	
mrmr	18.60	0.150	0.282
rmrr	18.59	0.141	
rrrr	16.40	0.058	0.251
mrrr	16.29	0.125	
mrrm	16.20	0.066	

^{a}Data for sample C: $P(m/r) = 0.55$, $P(r/m) = 0.52$.

Multistate statistics have been reported for anionic systems, especially with mixed solvents.[10] Tests of the statistics require higher order (tetrad or pentad) sequence distribution data. For the limited number of anionic PMMAs studied here, first-order Markov statistics adequately described pentad distributions. Bulk polymerization with solid borohydride gave an unusual essentially random tacticity, with a weak terminal diad effect.

Registry No. PMMA, 9011-14-7.

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Main-Chain Dynamics of Sodium Poly(acrylate) As Probed by NMR: A Comparison of Models

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ABSTRACT: Nuclear magnetic relaxation rates of sodium poly(acrylate) are analyzed and used to test two different models of polymer motion, i.e., the damped diffusion and the anisotropic rotation diffusion models. The spectral density function of ^{2}H methylene motion of sodium poly(acrylate) at various concentrations has recently been determined[1] in the range 0–80 MHz. A sharp increase of the low-frequency part of the spectral density function was observed in the semidilute regime, which could be ascribed to an enhanced electrostatic stiffness of the poly(acrylate) chains. Whereas in the more concentrated regime both models fit the data equally well, it is found that in the semidilute regime the rotation diffusion description seems more appropriate.

Introduction

A long-standing question in polymer physics is the relation between the rigidity of a polymer chain and its dynamic behavior.[1-4] The dynamic behavior of a polymer chain may be probed by techniques such as dielectric relaxation,[5] fluorescence depolarization,[6] and nuclear magnetic relaxation,[7-8] whereas the rigidity (cf. persistence length) may be determined by elastic light scattering experiments[9]—provided that the excluded volume parameter is known—or by small-angle neutron scattering experiments.[10]

Recently, Yamakawa[11] pointed out that for dielectric relaxation experiments[5] a clear correlation exists between the dynamic behavior and the rigidity of various flexible-chain polymers. For nuclear magnetic relaxation[12] experiments a less direct correlation was found. Generally, the relaxation rates do not depend solely on the rigidity of the polymer. They depend strongly on individual polymer characteristics. Instead of studying the effect of the rigidity on the dynamic behavior of a number of geometrically different polymers, it is preferable to study this effect on only one type of polyelectrolyte yet under different circumstances. The rigidity of a polyelectrolyte chain may be varied over a considerable range by changing the degree of neutralization and/or the ionic strength.

The total persistence length[13-15] of a polyelectrolyte chain is the sum of two contributions, the intrinsic persistence length and the electrostatic persistence length. The former is a measure of the rigidity of the uncharged chain while the latter is the additional contribution to the stiffness originating from the repulsive forces of the charges along the chain. The electrostatic persistence length is strongly influenced by the screening of the polyion charges by the small mobile counterions. In general the electrostatic persistence length will depend on many parameters like the solvent, the concentration, the degree of neutralization, the ionic strength, and the temperature.

In order to interpret the measurements correctly one must realize that in general the altered dynamic behavior as probed by nuclear magnetic relaxation will not originate solely from the altered electrostatic persistence length of the polyelectrolyte chain. When a polyelectrolyte chain is charged, an enhanced interaction of counterions and water molecules with the charged carboxylate groups will occur. This implies that effects due to the changed solvent and counterion mobility may influence the conformational transition rates.

Normally, the relaxation rates are not only determined by persistence-dependent segmental motions but also by limited reorientational movements (rotameric jumps) occurring on a subnanosecond time scale. The latter process contributes to both the longitudinal and the transverse nuclear magnetic relaxation rate. Fortunately, the effect of an altered persistence is observed by studying the movements of more extended backbone segments, and these occur on a much slower time scale (>10 ns). At moderate NMR frequencies (10–100 MHz) this means that the effect of an altered persistence will be mainly probed by the transverse relaxation rate via the spectral density value at frequency zero.

In studying the total spectral density function these two effects can be separated. In earlier work the different time scales of the polymer motion were characterized in relatively concentrated solutions of poly(methacrylic acid) (>0.2 monomol/L) as a function of the polymer charge.[16,17] Comparison of the rotation diffusion model and the damped diffusion model[18,19] for main-chain motion showed that only the former could describe the spectral density function. Surprisingly realistic persistence lengths were obtained with a primitive representation of the motional unit by a rotational ellipsoid.

In a previous paper[1] the dynamic behavior of poly(acrylic acid) was studied. As this is an intrinsically more flexible polymer with concomitant smaller relaxation rates, the experiments could be extended to lower concentrations (~0.01 monomol/L) where an important increase of the transverse rate occurs due to the increasing persistence length of the charged polyelectrolyte.

In the present paper the applicability of the rotational diffusion and damped diffusion models will be investigated for poly(acrylate) solutions at relatively low concentrations where the spectral density function shows a pronounced frequency dependence.

Motional Models for Polymers

The description of the motion of a linear macromolecule

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