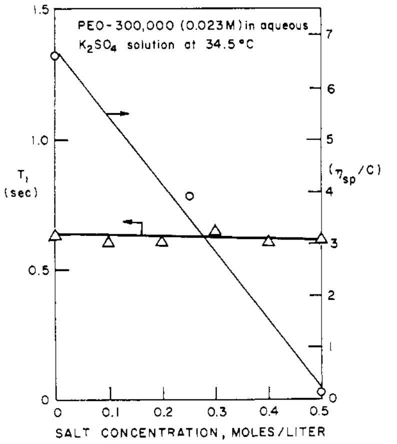

Figure 4. T_1 and reduced viscosity data for D_2O solutions of PEO-300,000.

duced viscosity of the polymer decreases more than 50 times passing from aqueous solution to 0.5 *M* K_2SO_4, where the polymer is on the verge of phase separation. No appreciable change in T_1 was observed over the same concentration range. These results indicate that the local segmental motion of the polymer chain is not affected by the presence of unbound ions.

We are now in possession of the following information: (1) the previously detected complex between K^+ and PEO in CD_3OD has a pronounced effect on T_1; (2) a looser polymer–salt interaction, such as that responsible for "salting out" in K_2SO_4–PEO–D_2O solutions, has no apparent effect on T_1; (3) the salting out interaction has a pronounced effect on solution viscosity. Complex formation may also affect polymer viscosity, but it is difficult to separate its influence from the salting-out process.

Of the above, only the relationship between salting out, T_1, and polymer viscosity merits further comment, or speculation—for it is, of course, extremely speculative to infer anything of a general nature from such meager knowledge. It may be somewhat difficult to understand how salting out can have such a pronounced effect on viscosity, and yet have no observable influence on T_1. The answer, we feel, is that η and T_1 are basically sensitive to different things, although both measure transport properties of polymers. It is well established[1,2] that nuclear relaxation of PEO in solution is mainly controlled by segmental rotameric transitions. For example, T_1 is influenced by the rates at which local *trans–trans–trans*, *trans–gauche–trans*, and other sequences interconvert. By altering these rates, through the introduction of a complexing agent like K^+, one produces changes in T_1. On the other hand, the viscosity of a polymer solution is governed primarily by polymer dimensions. Polymer dimensions can be theoretically expressed in terms of the numbers of *trans–gauche–trans*, *trans–trans–trans* sequences, etc.; and the way these sequences are arranged relative to one another along the macromolecular chain. Polymer dimensions do not reflect sequence interconversion rates directly although to be sure the equilibrium probability of each sequence is determined by the relative rates of transfer into, and out of, that local configuration. The present results suggest that addition of neutral salts to polymer solutions causes slight variations in the probabilities in these local sequences, or in their order along the chain. These changes need not be large to reduce the macroscopic chain dimensions, and lower the polymer viscosity. We can only speculate that any concurrent variations in the rates of rotameric transitions are too small to be detected in our T_1 measurements.

220-MHz Proton Magnetic Resonance Spectra of Polymers.

I. Poly(methyl methacrylate)

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Contribution No. 1530 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware. *Received January 27, 1969*

ABSTRACT: High resolution 220-MHz pmr spectra of a number of poly(methyl methacrylates) having grossly different tacticities have been measured on chlorobenzene solutions at 120°. The resonances associated with different tetrad and pentad configurational sequences have been resolved and identified. Broadening of the tetrad methylene and pentad α-methyl resonances, attributed to hexad and septad sequence effects, limits the reliability of tetrad and pentad distribution estimates. Nevertheless, more complete characterizations of stereoregularity and tests of statistical models for stereoregular polymerization are facilitated.

Since the discovery of configurational sequence (tactic placement) effects on the 40-MHz pmr spectra of poly(methyl methacrylates) by Bovey and Tiers,[1] nmr spectroscopy has been applied extensively to the characterization of PMMA and other vinyl polymers.[2] The increased resolution and sensitivity of nmr spectrometers operating at higher frequencies improved the ability to measure triad placements in PMMA, but the unexpectedly complex fine structure in the methylene region led to some difficulty in interpretation and analysis of dyad effects. This difficulty was correctly attributed by some workers to tetrad effects. Partial resolution of the tetrad methylene resonances[3,4] and de-

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(1) F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).

(2) F. A. Bovey, *Accounts Chem. Res.*, **1**, 175 (1968).

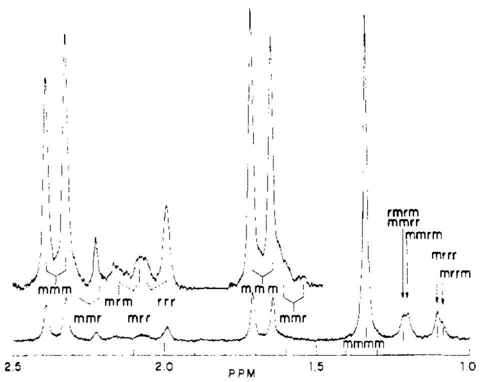

Figure 1. Methylene and α-methyl regions of the 220-MHz pmr spectrum of sample B, 18% w/v in chlorobenzene at 120°. The hatched peak at δ 2.22 is from an unidentified impurity.

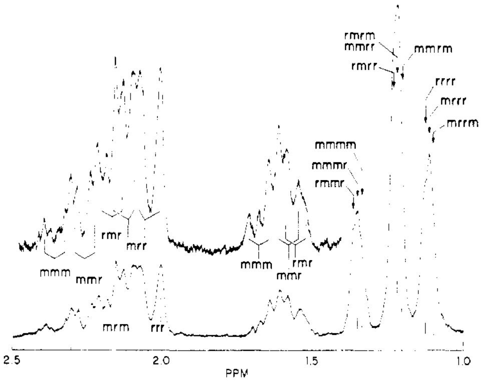

Figure 2. Methylene and α-methyl regions of the 220-MHz pmr spectrum of sample E, 10% w/v in chlorobenzene at 120°.

tectable, pentad effects[4] have been observed in 100-MHz spectra. In this work the 220-MHz spectra of several PPMA's having grossly different tacticities have been analyzed. The tetrad and pentad assignments are more complete and differ somewhat from those previously reported.[2,5,6,7]

Experimental Section

PMMA samples were obtained from various sources.[8] Samples A and B were polymerized in toluene by phenylmagnesium bromide initiation. Samples C, D, and F were prepared by anionic initiation in mixed solvent systems. Sodium borohydride was the initiator for polymerization of sample E.[9] Sample G was prepared by free radical initiation; several other free radical polymers from commercial sources were also studied.

The spectra were obtained with a Varian Associates HR-220 nmr spectrometer. The samples were run in chlorobenzene (5–20% w/v solutions) at 100–125°. Line frequencies relative to tetramethylsilane, internal, and relative intensities were measured by standard techniques. Proton–proton spin decoupling experiments were done by the field-sweep method.

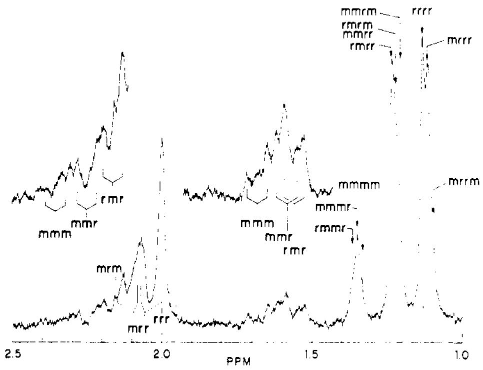

Figure 3. Methylene and α-methyl regions of the 220-MHz pmr spectrum of sample F, 7% w/v in chlorobenzene at 126°.

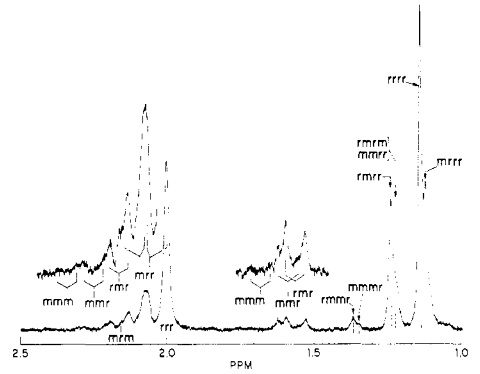

Figure 4. Methylene and α-methyl regions of the 220-MHz pmr spectrum of sample G, 12% w/v in chlorobenzene at 120°.

Results and Interpretation

The 220-MHz nmr spectra of the methylene and α-methyl regions of selected samples are shown in Figures 1–4. Figures 1 and 4 are the spectra published as Figure 7 of ref 2. They are repeated here to clarify and substantiate more detailed assignments, and to point out apparent chemical shift differences relative to the spectra of the same (or essentially identical) polymers run on a different spectrometer.

The spectra of Frisch, *et al.*,[7] show apparent shifts to high field of about 0.04–0.1 ppm for most of the assigned resonances of the syndiotactic polymer (comparable to sample G, Figure 4) *vs.* the isotactic polymer (comparable to sample B, Figure 1). No such difference was found here, nor were systematic tacticity-dependent trends in the line frequencies of the assignable tetrad and pentads observed. The 100-MHz spectra of syndiotactic and isotactic PMMA in chloroform[4] and in *o*-dichlorobenzene,[5] and particularly the superimposed spectra of a mixture of the syndiotactic and isotactic polymers *vs.* the spectra of the individual polymers,[5] tend to confirm that the triad and tetrad line positions are essentially constant.

The chemical shifts for the resonances associated with the various tetrad and pentad sequences were deduced

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(3) K. Hatada, K. Ota, and H. Yuki, *Polym. Sci. Lett.*, **5**, 225 (1967).

(4) K. C. Ramey, *ibid.*, **5**, 859 (1967).

(5) R. C. Ferguson, *Trans. N. Y. Acad. Sci.*, **29**, 495 (1967).

(6) R. C. Ferguson and W. D. Phillips, *Science*, **157**, 257 (1967).

(7) H. L. Frisch, F. Heatley, and F. A. Bovey, *Macromolecules*, **1**, 533 (1968).

(8) Samples were kindly contributed by Dr. R. R. Minesinger, Du Pont (A); Dr. F. A. Bovey, Bell Telephone Laboratories (B, G); Professor M. Goodman, Brooklyn Polytechnic Institute (C, D, F); and Dr. W. S. Zimmt, Du Pont (E).

(9) W. S. Zimmt and C. T. Arkens, to be published.

by (1) symmetry considerations, (2) systematic intensity variations with tacticity for the entire series of samples studied, and (3) spin-decoupling experiments.

For head-to-tail vinyl polymers of the general structure $(\text{-CH}_2\text{CXY-})_n$, the relative configurations of sequences of the pseudoasymmetric centers can have measurable effects on the chemical shifts (time averaged over all conformations) of the nuclei. The chemical shifts of the methylene (β) protons are affected by even-numbered configurational sequences (dyads, tetrads, hexads, . . .); the shifts of magnetic nuclei in the α-carbon substituents are affected by odd-numbered sequences (triads, pentads, . . .).

The theoretical significance and statistical treatment of *n*-ad configurational sequences, as measured by nmr spectroscopy, have been covered by Frisch, *et al.*[10] In their notation the dyad placements are designated *m* for *meso* (isotactic) and *r* for racemic (syndiotactic). The triads producing different nmr shifts of the α-carbon substitutents are *mm*, *mr* (= *rm*), and *rr* (formerly designated isotactic, heterotactic, and syndiotactic). The six tetrads expected to produce different methylene resonances are *rrr*, *rrm* (= *mrr*), *mrm*, *mmm*, *mmr* (= *rmm*), and *rmr*. Pentad and longer sequences are designated analogously.

For PMMA, where X = CH_3 and Y = COOCH_3, the ester methyl resonances at about δ 3.55 are only slightly sensitive to triad placements; triad effects were not resolved at 220 MHz. The α-methyl resonances, for which the triad effects are resolvable at lower frequencies, show additional fine structure at 220 MHz, attributable to pentad effects. The triad sequence distributions were determined from the relative areas of the α-methyl resonances centered at δ 1.10, 1.22, and 1.35 (Table I). To aid in making assignments, the tetrad and pentad distributions were estimated from the triad data, assuming Bernoullian statistics.[2,7,10] This assumption is rigorously applicable only to the free radical PMMA's.[2] and was used only as a rough guide for making assignments. More weight was given to the assumption that the tetrad and pentad line frequencies were essentially constant, and that the relative concentrations of the various sequences changed monotonically in the series progressing from highly isotactic to highly syndiotactic polymers.

Pentad Assignments. Of the ten possibly distinguishable pentad sequences, two (*mmrr* and *rmrm*) may reasonably be expected to produce essentially the same chemical shift for the central α-methyl resonance. Thus, nine singlets are identified on the figures and in Table II. These assignments are more complete, but are consistent with the recent assignments of Frisch, *et al.*,[7] except as follows. They have indicated that *rmrr* and *mmrr* are unresolved, as are *rmrm* and *mmrm*. Note, however, that the environments of the central methyl groups should be more perturbed by replacing a flanking *r* with an *m* configuration than by merely changing the orientation of the central *mr* triad to *rm* in the sequence *m–r*. This assumption predicts three, rather than two, resonances in the *mr* (= *rm*) triad region. In Figures 3 and 4 (as well as in Figure 1a of ref 7) there are two shoulders on the high-field side of the line designated *rmrr*. In these highly syndiotactic polymers, the probabilities (whether rigorously Bernoullian or not) are such that the concentrations of *rmrr* > (*rmrm* + *mmrr*) > *mmrm*, consistent with the observed line shape. In addition, the spectra of the isotactic polymers A and B (Figure 1), for which the probability of *rmrr* must be quite low, had no detectable absorption at the frequency assigned to *rmrr*. Finally, the assignments of this work show a consistent trend of upfield shifts in the order *m–m* > *m–r* > *r–r* for each of the sets of pentads having the same central triad.

TABLE I

TRIAD DISTRIBUTIONS FROM α-METHYL RESONANCES

Sample	Fraction of triads: mm	mr	rr
A	⩾0.96	⩽0.02	⩽0.02
B	0.79	0.11	0.10
C	0.59	0.26	0.15
D	0.61	0.29	0.11
E	0.22	0.49	0.29
F	0.15	0.40	0.45
G	0.03	0.24	0.73

TABLE II

CHEMICAL SHIFTS[a] OF PMMA TETRAD (METHYLENE) AND PENTAD (α-METHYL) RESONANCES OF PMMA

Tetrad	Confign	Methylene group, ppm	Pentad	α-Methyl Group, ppm
rmr	*t*[b]	1.56	*mrrm*	1.09
	e	2.16	*mrrr*	1.10
mmr	*t*	1.59	*rrrr*	1.13
	e	2.25	*mmrm*	1.20
mmm	*t*	1.67	*mmrr*	1.22
	e	2.37	*rmrm*	1.22
rrr		2.00	*rmrr*	1.24
mrr		2.05	*mmmm*	1.34
		2.10	*mmmr*	1.35
mrm		2.15	*rmmr*	1.37

[a] Average values for eight samples covering range from highly isotactic to highly syndiotactic. Estimated accuracy δ ±0.01. [b] Identification of the methylene protons as *t* = *threo* and *e* = *erythro* is based on work discussed in ref 2.

(A reviewer has noted the absence of the peak labeled *mmmr* in Figure 7b of ref 2. This peak was erroneously identified as a spinning side band and omitted in preparing that figure. The pair of peaks *rmmr* and *mmmr* shown in Figure 4 were also observed in commercial syndiotactic PMMA's.)

Tetrad Assignments. Because of symmetry, the two β protons in each of the *rrr* and *mrm* tetrads should be magnetically equivalent; the resonances most reasonably assigned to these tetrads are singlets, as expected. The remaining tetrads should give AB-type (four-line) methylene resonances because of nonequivalence of the β protons. At 220 MHz, the *mmm*, *mmr*, and *rmr* methylene patterns in fact approach the *AX* limit $(\nu|\delta_A - \delta_B| \approx 150\ \text{Hz} \gg J_{AB} = 14.5\ \text{Hz})$. For the AB-type methylene pattern of the *mrr* tetrad, $\nu|\delta_A - \delta_B| = 8\text{–}13$ Hz. $|J_{AB}| = 14.5$ Hz is expected, but the outer weak lines of the pattern are obscured.

The tetrad assignments in this work are essentially in agreement with those of Frisch, *et al.*, except for differing chemical shift values arising from (1) the afore-

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(10) H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).

mented systematic shift differences between their two spectra, and (2) the assumption of this work that the tetrad shifts remained essentially constant in the entire series of polymers. The assignments which are not identical are *mrm* of the syndiotactic polymer (Figure 4) and the high field doublets of *mmr* and *rmr* (1.5–1.6-ppm region) of the isotactic polymer (Figure 1). It is notable that the apparent increase in chemical shift difference between the nonequivalent protons of the *mmr* tetrad, progressing from 8 Hz in the syndiotactic polymer (Figure 4) to 13 Hz in the isotactic polymer (Figure 1), was also observed by Frisch, *et al.*

Discussion

Sample E (Figure 2) is particularly interesting, since it apparently has an essentially random distribution of sequences: dyad (*r*:*m* ≈ 1:1), triad (*mm*:*mr*:*rr* ≈ 1:2:1), and pentad (*rmmr*:*mmmr*:*mmmm* ≈ 1:2:1, etc.) The methylene patterns of this and other samples prepared by the same method showed some additional reproducible fine structure. Since these polymers were known to have molecular weights of approximately 20,000,[9] it was concluded that the observed fine structure and/or broadening of the resonances was due to hexad placement effects, rather than end effects. The exact positions of the *mmm*, *mmr*, *rmr*, and *mrm* resonances in the spectrum were difficult to deduce because of the overlapping fine structure. Spin-decoupling experiments involving irradiation of the X region (δ 1.56–1.6) while observing the A region (δ 2.16–2.3), and *vice versa*, confirmed the chemical shift assignments made by analysis of the other spectra in the series. The spin-decoupling experiments gave indicative, but not conclusive, evidence that the observed fine structure was real and associated with the basic tetrad resonance patterns.

The resonances of all the less stereoregular samples were consistently broader than those of the most stereoregular PMMA's. This observation is consistent with a general phenomenon found in our work on other polymers. In general, the spectra of highly stereoregular or otherwise structurally regular homopolymers give resonances with line widths approaching those of low molecular weight organic liquids (or the homogeneity-controlled resolution of the spectrometer). For less regular homopolymers and copolymers, the resonances are invariably broader. This broadening was formerly attributed to viscosity, *i.e.*, relaxation time, effects. However, it is now apparent that broadening, often also accompanied by unsymmetrical line shapes, is at least in part a consequence of higher *n*-ad effects upon chemical shifts. Thus, the broadening of the tetrad methylene and pentad α-methyl resonances of PMMA, and the observation of a more complicated fine structure in the methylene region (particularly in Figures 2 and 3) than predicted for tetrad effects suggest that hexad effects, at least, are not negligible.

These higher *n*-ad effects, along with the low signal-to-noise ratios for the weakest resonances in the spectra, readily account for minor differences in the detailed tetrad and pentad assignments reported here and by Frisch, *et al.* In this work, it was possible to fit the spectra of all seven samples, broadly covering the tacticity range, with tetrad and pentad line positions deviating no more than 0.01 ppm from the values in Table II. Because of the line widths, the incompletely interpreted additional fine structure, and the inability to apply adequate statistical criteria to the relative line intensities, the assignments are not all conclusive.

Conclusions

The improved resolution and sensitivity of 220-MHz pmr spectroscopy has made it possible to resolve and identify the tetrad methylene and pentad α-methyl resonances of PMMA. Dyad and triad sequence distributions can be estimated more accurately, and estimates of tetrad and pentad distributions, even if only approximate, make more exacting comparisons of samples possible. Quantitative estimation of tetrad and pentad distributions with sufficient accuracy for rigorous and unambiguous tests of statistical models for stereoregular polymerization has proved to be difficult, because of line broadening and additional fine structure due to hexad and septad sequence effects.

Acknowledgments. The contributions of Drs. F. A. Bovey, M. Goodman, W. Zimmt, and R. R. Minesinger in providing samples and helpful information are gratefully acknowledged. Mr. F. W. Barney and Mrs. Jean Read rendered valuable assistance in the experimental work.