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Carbon-13 Relaxation Study of Stereoregular Poly(methyl methacrylate) in Solution

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Abstract: Carbon-13 spin–lattice relaxation times (T_1) have been determined for pyridine and for $CDCl_3$ solutions of both predominantly isotactic and predominantly syndiotactic poly(methyl methacrylate), PMMA, at 38 and 100 °C. The T_1's of both backbone and side-chain carbons are longer in the isotactic chain configuration. The relative T_1 data for both quaternary and methylene backbone carbons suggest the isotactic chain skeleton is more flexible than that of the syndiotactic polymer. In addition, spin–spin relaxation data (T_2) and $^{13}C\{^1H\}$ nuclear Overhauser enhancements for the CH_2 carbon indicate that backbone motion in the PMMA systems is characterized by a distribution of correlation times. Both Cole–Cole and log χ^2 distributions were found to provide reasonable fits of the experimental data; however, a broader distribution was required to fit the syndiotactic results than the isotactic results. Finally, the T_1 results for the α-methyl carbons in the different stereoforms of the polymer suggest that the constraint to methyl internal rotation in the isotactic chain is less than in the syndiotactic chain.

Introduction

Recently, Hatada and co-workers[1] have reported a dependence of the proton spin–lattice relaxation times, T_1, of poly(methyl methacrylate), PMMA, on the polymer chain configuration. From their study, the relaxation times of the various protons of the repeat unit were found to be (1) shorter in a highly syndiotactic PMMA relative to a highly isotactic PMMA, and (2) shorter in a syndiotactic triad relative to isotactic triad in atactic PMMA. Thus, differential relaxation times were found for the case of two stereoregular polymers and for the case of local regions of stereoregularity (stereochemical triads) in a nonstereoregular polymer.

Hatada et al.[1] suggest that, unlike the proton results, the corresponding carbon-13 relaxation times in PMMA should be *independent* of chain configuration. Evidence cited for this conclusion includes the results that (1) in *o*-dichlorobenzene solutions of polystyrene, the T_1 results are the same for the atactic and isotactic polymers;[2] and (2) in atactic polyacrylonitrile, poly(vinyl chloride), and poly(vinyl alcohol),[3] the methine carbon resonances corresponding to syndiotactic, heterotactic, and isotactic stereochemical triads have equal T_1 values. The physical basis cited for the equivalency of the C-13 T_1 values is that[1] "the mechanism of ^{13}C relaxation is mainly a dipole–dipole interaction between the carbon and the directly bonded protons". There is of course ample evidence to support this relaxation mechanism for carbons with attached hydrogens;[4-6] however, this alone does not preclude differences in ^{13}C T_1 occurring between different stereoforms of the same polymer. Indeed, such differences can arise in two ways: (1) from differences in the chain segmental motion between stereoregular polymers or between regions of stereoregularity in an atactic polymer; and (2) from differences in preferred conformations between the stereoforms which lead to different "average distances" for the interaction of a carbon with a proton of a neighboring repeat unit. This latter mode is largely precluded for a carbon with a directly attached proton,[7] the

Table I. Carbon-13 Motional Parameters for PMMA Solutions at 38 °C

Polymer configuration	Solvent	Parameter	Carbon in monomer unit $-CH_2-$	α-CH_3	-C-	OCH_3	C=O
Isotactic	Pyridine	T_1[a]	64	124	940	630	1840
		T_2[a]	52(6.1)[b]	95(3.3)			
		NOE	2.5[c]	2.9			
Isotactic	$CDCl_3$	T_1	63	122			
Syndiotactic ($M_{\overline{w}} \sim 6000$)	Pyridine	T_1	42	46	581	448	1100
		T_2	22(14.5)	33(9.6)			
		NOE	2.1[c]	2.6			
Syndiotactic ($M_{\overline{w}} \sim 6000$)	$CDCl_3$	T_1	40	47			
Syndiotactic ($M_{\overline{w}} \sim 500\,000$)	Pyridine	T_1	41	51	533	400	*d*
		T_2	23(13.9)	33(9.6)			
		NOE	2.0	2.8			

[a] In milliseconds, ±8%. [b] Line width in hertz. [c] ±0.15. [d] Not determined.

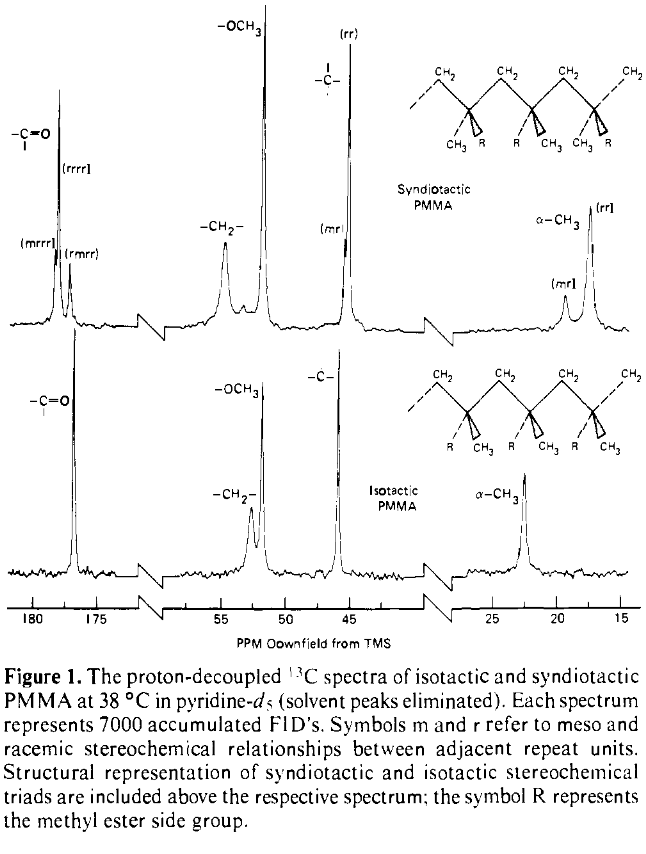

Figure 1. The proton-decoupled ^{13}C spectra of isotactic and syndiotactic PMMA at 38 °C in pyridine-d_5 (solvent peaks eliminated). Each spectrum represents 7000 accumulated FID's. Symbols m and r refer to meso and racemic stereochemical relationships between adjacent repeat units. Structural representation of syndiotactic and isotactic stereochemical triads are included above the respective spectrum; the symbol R represents the methyl ester side group.

former is not. For carbons without attached protons but relaxed via a dipolar process with neighboring protons, differences in T_1's can arise from either or both modes.

Based on the above arguments, neither differences in segmental motion nor significant differences in distances between interacting C and H nuclei appear to occur in the polystyrenes or the various atactic polymers discussed above. In PMMA, however, the proton relaxation data[1] directly indicate differences in chain segmental motion for the two stereoforms. This result is also supported by dielectric[8a] and acoustic[8b] relaxation data and by calculations of chain configurations[8c] which suggest the isotactic PMMA chain is more flexible than the syndiotactic chain. It would seem such differences in segmental motion would lead to *different* T_1 values for carbons in a predominantly isotactic PMMA relative to a predominantly syndiotactic polymer and, in this paper, we report the results of a ^{13}C relaxation study of these two stereoregular forms of PMMA.[9]

Results and Discussion

In Figure 1 are shown the equilibrium C-13 spectra[10] of the isotactic ($M_w \sim 28\,000$) and syndiotactic ($M_w \sim 6000$) PMMA's employed in this investigation. The presence of only one resonance line in both the α-methyl and carbonyl resonance regions of the spectrum of the isotactic polymer indicates a highly stereoregular chain[11] (meso dyad, m, content > 98%). In each of the corresponding resonance regions of the spectrum of the syndiotactic polymer, there is, in addition to the major resonance line, one or more less intense resonances, whose presence indicate a small number of meso dyads in a polymer chain composed primarily (ca. 90%) of racemic dyads, r. In addition to these PMMA's, a commercially prepared polymer of relatively high racemic content (ca. 80%) and high molecular weight ($M_w \sim 500\,000$) was included in the study. Further details of the stereoregularity of the samples are provided in the Experimental Section.

In Table I are listed the T_1 values (at 38 °C) for the various carbons of the PMMA repeat unit obtained for pyridine solutions of the polymers. The interesting facet of the data is that the spin-lattice relaxation times at both backbone and side-chain sites are longer in the isotactic polymer than in the predominantly syndiotactic polymers. The good agreement in the relaxation data for the two syndiotactic systems is consistent with the molecular weight independence of T_1 generally found for a given polymer (of the same chain configuration) when $M_{\overline{w}} > 3000$.[3,12] To explore the possibility that the relaxation time differences between these two stereoregular forms of PMMA might be associated with a solvent effect specific to pyridine, T_1 data were obtained for the backbone and α-methyl carbons of the two low molecular weight polymers dissolved in $CDCl_3$. As the results (Table I) are consistent in each solvent, it appears that the differences in relaxation results arise from effects associated with the configurational characteristics of the polymer chains.

Since the proton relaxation data[1] on the stereoregular PMMA's were obtained at 110 °C (in toluene-d_8), ^{13}C T_1 values (in pyridine) were also measured under similar thermal conditions (100 °C). The results and, for comparative purposes, the corresponding proton relaxation data are given in Table II. As in the case for the data obtained at 38 °C, a given carbon in the isotactic polymer has a longer T_1 value than in the syndiotactic polymer. Not only does the carbon relaxation data parallel the proton data in this manner but, for both nuclei, the spin-lattice relaxation times in a given chain configuration follow the order: methoxy > α-methyl > methylene. Thus, it is quite apparent that the suggestion by Hatada and co-workers[1] that the relaxation times for corresponding carbons in stereoregular PMMA's would be equal is *not* the case. We now turn to a discussion of the implication of the relaxation

Table II. ^1H and ^{13}C Spin-Lattice Relaxation Times of Syndiotactic and Isotactic PMMA's

	T_1[a]							
	Proton[b]			Carbon				
Configuration	α-CH_3	CH_2	OCH_3	α-CH_3	CH_2	OCH_3	-C-	C=O
Syndiotactic	177	125	541	200[c]	130	1120	1530	*d*
Isotactic	321	206	745	377[c]	210	1500	1870	*d*

[a] In milliseconds. [b] In toluene-d_8, temperature = 110 °C, data taken from ref 1. [c] In pyridine-d_5, temperature = 100 °C, our data. [d] Not measured.

times with respect to the molecular motion in the two stereoregular polymers.

Backbone Motion

Previous ^{13}C relaxation studies on polymers[6] have shown that T_1's are largely determined by rapid motions of the chain while to some extent the ^{13}C-$^1\{H\}$ nuclear Overhauser enhancement, NOE, and to a greater extent T_2 are affected by lower frequency motions. Thus to provide a fuller characterization of the chain segmental motion and to supplement the T_1 measurements, values of T_2 and NOE were determined for the methylene carbons at 38 °C. As indicated in Table I, these motional parameters were also found to differ between the two PMMA's.

The ca. 50% increase in methylene T_1 in isotactic relative to syndiotactic polymer is indicative of an increase in backbone segmental motion in the isotactic chain. A change of similar magnitude occurs in the T_1 data for the quaternary carbon of the polymer backbone. Thus, this set of results is in accord with the dielectric[8a] and acoustic[8b] relaxation data for the various tactic forms of PMMA which, as noted earlier, suggest the isotactic chain to be more flexible than the syndiotactic chain.

Assuming the methylene carbons relax only via a dipolar mechanism with the directly attached protons, a single effective rotational correlation time, τ_r, for backbone segmental motion can be calculated from an isotropic reorientational model,[5] i.e.

$$\frac{1}{T_1} = \frac{N_H K}{10 r_{CH}^6} (J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)) \qquad (1)$$

where $J(\omega) = \tau_r/(1 + \tau_r^2\omega^2)$, N_H is the number of attached protons, K is a constant equal to 3.56×10^{10} Å^6 s^{-2}, and r_{CH} is the internuclear C-H distance (1.09 Å). For the isotactic polymer, a value of $\tau_r = 0.38$ ns is calculated from eq 1 while for the syndiotactic polymer a corresponding analysis yields a value of 0.60 ns. In terms of the isotropic reorientation model, these values of τ_r fall to the high frequency side of the T_1 minimum,[13] but are in a region of the frequency spectrum where some deviation from the motional narrowing condition (i.e., $\omega^2\tau_r^2$ is not $\ll 1$) is occurring for the $J(\omega_H + \omega_C)$ spectral density term in eq 1. In this region small deviations from $T_1 = T_2$ and maximum NOE (2.987) would be expected for the methylene carbon; i.e., for $\tau_r = 0.38$ ns, T_2 is predicted to be 63 ms and NOE = 2.94, while for $\tau_r = 0.6$ ns, values of 42 ms and 2.86 are predicted for T_2 and NOE, respectively. However, the measured values (Table I) of the parameters are found to differ considerably from the values predicted. Indeed, it is found that the experimental T_2 and NOE results for the isotactic chain are consistent with τ_r values of 0.51 and 1.4 ns, respectively; while the corresponding parameters for the syndiotactic chain produce τ_r values of 1.4 and 2.0 ns. Collectively, the motional parameters suggest that a distribution of correlation times rather than a *single* effective correlation time characterizes the backbone segmental motion in PMMA. This situation has been found by Schaefer[6,14] to be the case in isotactic polystyrene, *cis*-polyisoprene, and *cis*-polybutadiene, by Lyerla and Torchia[15] in the biopolymer, elastin, and as just recently reported, by Heatley and Begum[16] in poly(propylene oxide), polystyrene, and atactic PMMA.

Because the atactic PMMA ($M_n = 90\,000$) used in the study by Heatley and Begum contained >50% syndiotactic triads, it is of interest to compare their relaxation results on 10% w/v *o*-dichlorobenzene solutions with those obtained for the syndiotactic polymer in this study. When differences in magnetic field[17] are taken into account, the T_1's for CH_2 and α-CH_3 carbons (the only T_1's of the PMMA repeat unit measured by Heatley and Begum) at 38 °C are in good agreement; however, the NOE for the CH_2 was measured to be greater (2.1 vs. ca. 1.5)[18] in our study.

Heatley and Begum observed the minimum in the temperature dependence of T_1 occurred at a T_1 value approximately twice that predicted by the single correlation time model. Such T_1 behavior is indicative of a distribution of correlation times and these authors found that both Cole-Cole[19] and log χ^2 distributions[14] provided suitable fits of the T_1 and NOE data. Each distribution is characterized by an average correlation time τ_0 and a width parameter for the distribution. The Cole-Cole distribution (symmetrical about τ_0) is governed by width parameter, γ, which lies in the range 0 to 1 with 1 being equivalent to a single correlation time model. The log χ^2 distribution (unsymmetrical about τ_0 with a tail toward long correlation times) is characterized by width parameter p with $p > 100$ being essentially equivalent to a single correlation time model. These distributions were applied[20] to the data in Table I for the CH_2 carbons and the τ_0 and p values for the log χ^2 distribution parameters which gave simultaneous good fits of all three dynamical parameters (T_1, T_2, and NOE) are listed in Table III as are the τ_0 and γ values for the Cole-Cole distribution which provided good fits of T_1 and NOE parameters.[20]

For the Cole-Cole distribution, the width parameter and τ_0 for syndiotactic PMMA (Table III) are in reasonable agreement with the results of Heatley and Begum. However, for the log χ^2 results, the data obtained in this study are fit with a narrower distribution (larger p value) than required by Heatley and Begum. These authors could not obtain values of T_2 from line widths because of the potential for line broadening arising from chemical shift dispersion due to irregular tacticity of the polymer. However for their reported log χ^2 distribution parameters at 30 and 50 °C, methylene line widths would be predicted to be ca. 300 and 100 Hz, respectively. Although the syndiotactic PMMA used in this study is of lower $M_{\overline{w}}$, the T_2 value (Table I) found for the CH_2 in the PMMA of $M_{\overline{w}} \sim 500\,000$ is comparable to the lower $M_{\overline{w}}$ polymer. Thus, the distribution width of $p = 19$ and $\tau_0 = 0.6$ ns which produces a CH_2 line width of 14.3 Hz seems a more appropriate description of syndiotactic PMMA. A value of $p = 18$ was obtained by Schaefer for isotactic polystyrene in solution and in view of the similar temperature for the T_1 minimum (~30 °C)

Table III. Correlation Times, Distribution Width Parameters, and Predicted Relaxation Parameters for PMMA at 38 °C

Distribution	Polymer	Distribution width γ	Correlation time[a] τ_0	Predicted ^{13}C parameters T_1[b]	T_2[b]	NOE
Cole–Cole	Isotactic	0.75	0.25	64	c	2.5
	Syndiotactic	0.58	0.54	42	c	2.1
	(Syndiotactic)[d,e]					
	30 °C	0.57	1.6			
	50 °C	0.57	0.8			
		p	τ_0	T_1	T_2	NOE
log χ^2	Isotactic[e]	25	0.24	64	53	2.5
	Syndiotactic[e]	19	0.6	39	22	2.2
	(Syndiotactic)[d,e]					
	30 °C	8	2.5			
	50 °C	10	0.9			

[a] In nanoseconds. [b] In milliseconds. [c] Not determined. [d] Data from ref 16 at the indicated temperature. [e] Log base (parameter b in Schaefer's[14] equations) = 1000.

(indicative of similar flexibilities of the chains) for this polymer and PMMA,[16] it would seem a similar distribution width would characterize the motion of the two polymers in solution. Also supportive of this value of p are T_1 data at 40 °C obtained for a predominantly syndiotactic PMMA at a magnetic field of 14.1 kG.[21] The measured methylene T_1 is 33 ms and the predicted T_1 at this field from the log χ^2 distribution with $p = 19$, $\tau_0 = 0.6$ ns is 34 ms.

The dynamical parameters for the methylene of the isotactic polymer are fit by log χ^2 distribution with p value = 25 and $\tau_0 = 0.24$ ns. (This solution is probably not unique as p values between 23 and 28 give reasonable fits of the data when the experimental error in measurement of each of the dynamical parameters is considered.) Thus, the isotactic chain is characterized by a narrower distribution and shorter average correlation time than the syndiotactic polymer. The best data fits from the Cole–Cole distribution indicate a narrower width and shorter τ_0 for the isotactic polymer. It could be argued that a smaller distribution width should characterize the isotactic chain relative to syndiotactic chain because the greater segmental mobility would be consistent with a lesser degree of cooperative (slower) motions among repeat units. In the absence of a complete temperature profile for the relaxation parameters, however, any definitive conclusions other than a distribution of correlation times is required to adequately explain the ^{13}C relaxation data in both isotactic and syndiotactic PMMA are somewhat speculative.[22]

The quaternary carbons have much longer T_1 values than the methylenes, since they are not relaxed via directly bonded dipolar interactions. The relative values of the quaternary T_1's in the two stereoforms are in approximately the same ratio as the CH_2 carbon T_1 data, which presumably indicates that the backbone motion is reasonably isotropic in each polymer and that there are not major differences in "average" C–H distances for the quaternary and the neighboring protons between the polymers. Indeed, if it is assumed these carbons are relaxed only by the methylene and methyl protons of the same repeat unit and the methylene protons of the neighboring repeat unit, there are no populated conformations that would alter the interaction distance between the two polymers. The only deviations of the ratio of quaternary T_1's from that of methylene T_1's would be due to effects arising from the different internal reorientation rates of the α-methyl groups in the two stereoregular compounds.[23]

Side-Chain Motion

The 2.7 increase in T_1 value for the α-methyl carbon in the isotactic chain relative to the corresponding carbon in the syndiotactic chain indicates that greater reduction in motional constraints occurs for side-chain reorientation than backbone reorientation in isotactic relative to syndiotactic chain configuration. The differences in T_1 values between α-methyl and methylene (taking into account the differences in number of C–H interactions) suggest the α-methyl carbon in the syndiotactic polymer has rotational freedom about the methyl–quaternary carbon bond. Thus, the much longer T_1 for the α-methyl carbon in the isotactic form implies that this carbon is subject to a reduced intramolecular potential barrier for methyl internal rotation relative to its counterpart in the syndiotactic chain. Indeed, the V_3 potential barrier for methyl group reorientation obtained from neutron scattering studies[24] is 23 kJ/mol in the isotactic polymer and 33 kJ/mol in the syndiotactic polymer. In addition, the ^{13}C studies on atactic PMMA by Heatley and Begum[16] indicate different activation energies for the α-methyl internal reorientation of the center unit of a syndiotactic triad (25 kJ/mol) and a heterotactic triad (20 kJ/mol). The longer T_2 and larger NOE values for the isotactic α-CH_3 carbon also emphasize the greater motional freedom in this chain relative to the syndiotactic chain. A more quantitative description of the α-methyl relaxation requires a complete temperature profile of the T_1 and T_2 relaxation times and the NOE parameter and is presently being undertaken.

The much longer T_1's of the methoxy carbons relative to the α-methyl carbon in each respective stereoregular polymer primarily reflects the very low barrier (ca. 4 kJ/mol)[24] to internal rotation of the methoxy group. The reorientation of a methoxy carbon C–H vector can be considered to arise from chain segmental motion (ester side group fixed), rotation of the ester side group about the backbone–carbonyl bond, and internal rotation of the methoxy group. Which one of these sources gives rise to the difference in methoxy T_1 between stereoforms (Tables I and II) is uncertain; however, the long methoxy T_1 values relative to the methylene carbon suggest that differences in backbone motion would have small effects. Perhaps the most likely source of difference would be hindrance to methoxy internal rotation in some populated conformations of the syndiotactic polymer.

The longer carbonyl T_1's with respect to the quaternary carbon T_1's (the other carbon without attached protons) in each polymer reflect the longer "average interaction distance" for the C–H dipolar interactions for the carbonyl. The ratio of carbonyl T_1's in isotactic to syndiotactic polymer is approximately equal to that of the quaternary carbons. This might be expected if internal reorientation of the ester side group does not differ greatly in the two chains. However, as with the case of the other side-chain carbons, temperature dependent T_1 results are required before firm conclusions can be drawn.[25]

Experimental Section

A. Relaxation Parameters. Experiments were performed on a Varian CFT-20 pulse Fourier transform spectrometer operating at 18.7 kG. The T_1 determinations at 38 °C were carried out using the 10-mm o.d. probe, while the determinations at 100 °C required use of the variable temperature probe (8-mm o.d.). The pulse power delivered to the single coil probes was sufficient to rotate the ^{13}C magnetization by 90° in 16 μs for the 10-mm probe and 14 μs for the 8-mm probe. T_1 values for the carbonyl carbons were determined in one set of experiments and those for the various upfield resonance lines in another set. This procedure enabled 2-kHz spectral widths to be employed so that upon 8K Fourier transformation of data (via the Varian 620I-16K computer), the digital resolution was ca. 0.5 Hz.

Relaxation experiments were carried out using the standard 180–τ–90 pulse sequence with a $(5T_1 + \tau)$ repetition rate. Free induction decays (2500) were accumulated for each value of τ in the relaxation experiment sequence (8–10 values of τ were employed to determine T_1). The T_1 values were determined by least-squares analysis of time-dependent peak intensities and were reproducible to ±8%.

NOE and T_2 parameters were measured only at 38 °C. The NOE's were evaluated from comparison of integrated line intensities of spectra obtained under continuously proton-decoupled and appropriately decoupler-gated (proton decoupler on only during FID accumulation) conditions.[26] Spin–spin relaxation times were determined for methylene and α-methyl carbons from resonance line widths (LW) at half-height ($1/T_2 = 1/\pi(\mathrm{LW})$) corrected for instrument and digital broadening contributions (1.5 Hz).

B. Sample Preparation and Characterization. The two stereoregular PMMA samples were synthesized by anionic polymerization techniques. Isotactic polymer, $M_w = 28\,000$, was prepared in toluene at 0 °C with phenylmagnesium bromide as catalyst while the syndiotactic polymer, $M_w = 6\,000$, was synthesized in THF using a fluorenyllithium/N-methylpyrrolidone co-catalyst system. Molecular weights were determined by GPC (modified Waters Associates Model 200). Samples for relaxation studies were prepared as 10% w/v solutions in pyridine-d_5 or $CDCl_3$. Sample volumes were confined to heights of ca. 9 mm in the NMR tubes by vortex plugs. This procedure ensured the entire sample was contained within the volume of the single coil (9 mm in height) of the probes.

Previous work[11] on determining the sensitivity of ^{13}C NMR to the stereochemistry of PMMA has shown that the α-methyl, quaternary, and carbonyl carbon regions of the ^{13}C spectrum provide information on triad tacticity. In addition, the carbonyl region yields data on pentad structure. As indicated earlier, only resonance lines corresponding to mm and mmmm triad and pentad relationships, respectively, between repeat units could be found in the isotactic polymer and thus the system was of very high stereoregularity (>98% meso). For the syndiotactic polymer, triad analysis gave a 78/21/1 distribution for rr/mr/mm repeat unit relationships. From these data the average length of racemic blocks ($\overline{N}_r$) in the chain was found to be 8.5 as determined from the expression[27]

$$\overline{N}_r = 1 + 2(\mathrm{rr})/(\mathrm{mr})$$

The triad analysis indicates the meso relationships in the syndiotactic polymer occur largely as isolated defects. This is further evidenced by the fact that the only resonances in the carbonyl region in addition to the rrrr resonance line (177.19 ppm) are those which have been previously assigned[11] to rrrm (178.22 ppm) and rmrr (177.06 ppm) pentads. Thus the syndiotactic polymer was highly stereoregular. Triad analysis for the commercial PMMA (prepared by free-radical polymerization) was 59/35/6 for rr/mr/mm, respectively. This distribution is near Bernoullian with a racemic dyad content of ca. 77% and $\overline{N}_r = 4.4$.

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References and Notes

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(10) That is, spectra were obtained with a pulse delay long enough for all carbons to recover equilibrium magnetization and with the proton-decoupler gated-on only during data collection to avoid differential nuclear Overhauser enhancements (delay time > $7T_1$).

(11) The α-methyl, quaternary, and carbonyl carbon regions of the ^{13}C spectrum provide information on triad tacticity in PMMA. In addition, the carbonyl region provides information on pentad structure. For details of such analyses, the reader is referred to the following: (a) I. R. Peat and W. F. Reynolds, *Tetrahedron Lett.*, **14**, 1539 (1972); (b) Y. Inoue, A. Nishioka, and R. Chûjô, *Polym. J.* **4**, 535 (1971); (c) L. F. Johnson, F. Heatley, and F. A. Bovey, *Macromolecules*, **3**, 175 (1970).

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(21) Data obtained on Nicolet TT-14 spectrometer.

(22) The distribution calculations assume reorientation is isotropic; if this is not the case, the relaxation parameters depend on several correlation times. In general, the distribution function which determines the contribution of each correlation time to the spectral density will depend upon the orientation of the CH vector with respect to the rotation axes. Hence, the use of a single distribution function for different carbons in the backbone *approximately* characterizes the *average* chain motion.

(23) This assumes only a C–H dipolar relaxation mechanism and isotropic backbone motion. That the T_1 ratio for the quaternary carbons is slightly greater than for methylene is in accord with the faster α-methyl reorientation (reduced efficiency for the interactions of these protons with the quaternary) in the isotactic polymer.

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(26) The ratio of the pulse delay to T_1 was greater than 10 in all cases for the gating experiment, thus the problems noted by Opella et al. in determining NOE's from gated-decoupled spectra [S. J. Opella, D. J. Nelson, and O. Jardetzky, *J. Chem. Phys.*, **64**, 2533 (1976)] were avoided.

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