

$^{13}\text{C}\text{-}\{^1\text{H}\}$ Nuclear Magnetic Resonance Spectroscopy of Poly(methyl methacrylate)

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ABSTRACT: The $^{13}\text{C}\text{-}\{^1\text{H}\}$ high-resolution nuclear magnetic resonance spectra were measured for poly(methyl methacrylate). The spectra clearly split corresponding to dyad, triad, tetrad, and pentad placements. The relative intensity of every peak for the spectrum of a polymer prepared with 9-fluorenyllithium in tetrahydrofuran/toluene (80/20) at -23°C was reasonably interpreted by the Bernoulli trial model.

The nuclear Overhauser effect due to total proton decoupling did not affect the relative intensities among the peaks assigned to chemically equivalent carbons except for the difference in stereochemical configuration. This was confirmed by comparison between the relative intensities of the above-mentioned polymer and by comparison between those of $^{13}\text{C}\text{-}\{^1\text{H}\}$ and of ^1H resonance of the polymer.

The microtacticity determined by $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of a polymer prepared with 9-fluorenyllithium in tetrahydrofuran/toluene (4/96) was fairly well interpreted by the stereobond model, but by neither first-order nor second-order Markovian model.

KEY WORDS Poly(methyl methacrylate) / $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR / Stereobond / Markovian Model / Bernoullian Model / Nuclear Overhauser Effect /

The $^{13}\text{C}\text{-}\{^1\text{H}\}$ high-resolution nuclear magnetic resonance spectroscopy is of great interest in the study of higher-order stereochemical placements of vinyl polymers, because carbon is the most elementary atom constituting the skeletal bonds and because chemical shift in ^{13}C resonance is much greater than that in ^1H resonance.

The sensitivity of ^{13}C resonance is extremely poor compared to that of proton. But by the multiple scan average technique and total proton decoupling one can overcome this poor sensitivity and effective signal-to-noise ratio can be improved.

Spectra of $^{13}\text{C}\text{-}\{^1\text{H}\}$ were successfully applied to ethylene oxide-maleic anhydride copolymers and propylene oxide homopolymer.^{1,2} Horsley, *et al.*, measured ^{13}C chemical shifts in amino acids and peptides.^{3,4} Duch, *et al.*, have reported a detailed study of the $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of polybutadiene and polyisoprene.⁵

Recently, Johnson, *et al.*, reported on a study of stereochemical placements in several vinyl polymers, including poly(methyl methacrylate), from $^{13}\text{C}\text{-}\{^1\text{H}\}$ resonance of the samples with

natural abundance.⁶

These reports all suggest the usefulness of $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra in the study of polymer solutions.

This paper is devoted to the assignment of the peaks due to dyad, triad, tetrad, and pentad stereochemical placements in $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of poly(methyl methacrylate)(PMMA). The triad tacticity determined from the $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of the α -skeletal carbon, α -methyl carbon, and carbonyl carbon were compared with that determined from the proton spectra of the α -methyl protons, in order to investigate whether the nuclear Overhauser effect affects the determination of tacticity or not in $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra. The data of the microtacticity determined from the $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra were used to examine the polymerization mechanisms of the polymers.

EXPERIMENTAL

Materials

Two types of PMMA were prepared with 9-fluorenyllithium. Polymer I was polymerized

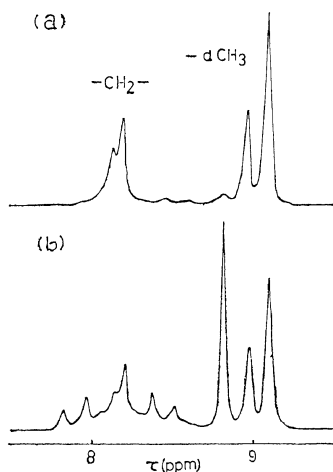


Figure 1. Methylene and α -methyl proton spectrum of poly(methyl methacrylate) observed at 100 MHz, in 10-% (w/v) solution in nitromethane at 110°C: (a) predominantly syndiotactic (polymer I); (b) stereoblock (polymer II).

Table I. The microtacticity of polymers I and II obtained from the ^1H spectra reproduced in Figure 1

	Triad		
	(<i>mm</i>)	(<i>mr</i>)	(<i>rr</i>)
Polymer I	0.05	0.34	0.61
Polymer II	0.42	0.21	0.37

in tetrahydrofuran/toluene (80/20) at -23°C . Polymer II was polymerized in tetrahydrofuran/toluene (4/96) at 71°C . Details of the methods of preparation of these two polymers are described elsewhere.⁷

Their ^1H spectra are shown in Figure 1 and triad microtacticity determined from ^1H spectra are tabulated in Table I. ^1H spectra of PMMA were measured at 100 MHz, in 10-% (w/v) solution in nitromethane at 110°C , using a JNM PS-100 spectrometer. (The values of triad tacticity of polymer I are slightly different from those given in ref 7 as numbered B-4, because they were determined by the spectrum from a 100-MHz spectrometer; they are probably more accurate than the values in ref 7, which were determined from the 60-MHz spectrometer.)

Methods

The polymers were dissolved in *o*-dichloro-

benzene to prepare approximately 40-% (wt/vol) solution and observed at 140°C .

The $^{13}\text{C}\{-^1\text{H}\}$ spectra were obtained by field sweep in absorption mode at 25, 14 MHz using a JNM PS-100 spectrometer. Total proton decoupling was performed using JNM-IS-100 and JNM SD-HC (hetero spin decoupler) equipment.

The drift of the field was automatically corrected by the signal trigger or start point trigger technique using a JEC-5 spectrum computer. The samples were contained in 8 mm o.d. tubes including a capillary with $\text{CH}_3^{13}\text{COOH}$ as an external reference. Chemical shifts were represented in terms of parts per million, the positive values corresponding to upfield and *vice versa* from $\text{CH}_3^{13}\text{COOH}$. Effective signal-to-noise ratio was improved by means of the multiple scan average technique using a JEC-5 spectrum computer. The number of scans employed was indicated in the caption for each spectrum.

The microtacticity was determined from the relative intensities of the corresponding peaks. The experimental error in measured intensities is probably $\pm 1\%$ even for the smallest peak.

RESULTS AND DISCUSSION

$^{13}\text{C}\{-^1\text{H}\}$ spectra of each part of PMMA were shown in Figures 2–5.

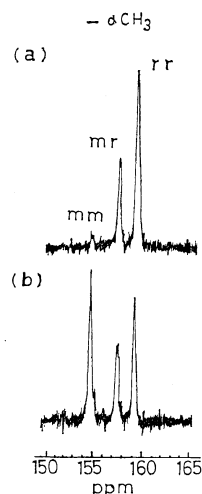


Figure 2. $^{13}\text{C}\{-^1\text{H}\}$ spectra of α -methyl group of poly(methyl methacrylate) observed at 25.14 MHz, in 40-% (w/v) solution in *o*-dichlorobenzene at 140°C (256 scans): (a) predominantly syndiotactic (polymer I); (b) stereoblock (polymer II).

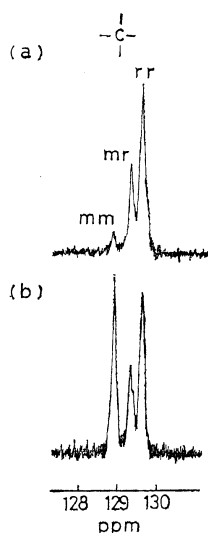


Figure 3. $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of α -skeletal carbon of poly(methyl methacrylate) observed at 25.14 MHz, in 40-% (w/v) solution in *o*-dichlorobenzene at 140°C (512 scans): (a) predominantly syndiotactic (polymer I); (b) stereoblock (polymer II).

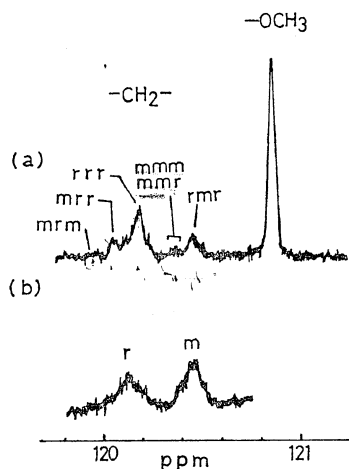


Figure 4. $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of methylene and methoxy group of poly(methyl methacrylate) observed at 25.14 MHz, in 40-% (w/v) solution in *o*-dichlorobenzene at 140°C (256 scans): (a) predominantly syndiotactic (polymer I); (b) stereoblock (polymer II).

The profile of the α -methyl carbon (Figure 2) and the α -skeletal carbon (Figure 3) give the same triad pattern as the α -methyl proton spectrum (Figure 1). The α -methyl carbon spectrum

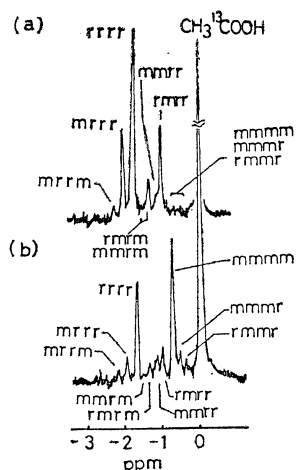


Figure 5. $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of carbonyl group of poly(methyl methacrylate) observed at 25.14 MHz, in 40-% (w/v) solution in *o*-dichlorobenzene at 140°C (512 scans): (a) predominantly syndiotactic (polymer I); (b) stereoblock (polymer II).

is spread over a five-fold greater range in chemical shifts than the α -skeletal one.

The peaks of the methylene carbon (Figure 4) of polymer I split into many peaks due to tetrad placements, but not clear in the spectrum of polymer II.

It is noteworthy that the methoxy carbon spectrum is rather broad but has a single peak. It is well known that the peaks of the methoxy proton splits into many peaks due to triad placements, if measured in aromatic solvents.⁸ This difference is interesting in the study of solvent effect.

The most interesting aspect is the carbonyl carbon spectra (Figure 5). These split into many peaks clearly due to pentad placements.

Assignments

The assignments written in the Figures are the most rational and consistent that we could provide at present. The microtacticity of the polymers I and II determined from the relative intensities of the peaks are shown in Tables II and III, respectively. The splitting due to tetrad placements was not observed in the spectrum of the methylene carbon of the polymer II, so that the tetrad microtacticity was calculated from the pentad intensities using the following relations.

Table II. The microtacticity of polymer I obtained from the ^{13}C - $\{^1\text{H}\}$ spectra reproduced in Figures 2-5

	Obsd			Calcd from Bernoulli trial
	$-\text{CH}_2-$	$\alpha\text{-C}$	$\alpha\text{-CH}_3$	
	>C=O			
Dyad				
(<i>m</i>)	0.20			0.21
(<i>r</i>)	0.80			0.79
Triad				
(<i>mm</i>)	0.05	0.05	0.04	0.04
(<i>mr</i>)	0.33	0.34	0.33	0.33
(<i>rr</i>)	0.62	0.61	0.63	0.63
Tetrad				
(<i>mmmm</i>)	} 0.06			0.01
(<i>mnmr</i>)				0.07
(<i>rmr</i>)	0.14			0.13
(<i>mrm</i>)	0.03			0.04
(<i>mrr</i>)	0.24			0.26
(<i>rrr</i>)	0.53			0.49
Pentad				
(<i>mmmm</i>)	} 0.04			0.002
(<i>mnmr</i>)				0.015
(<i>rmr</i>)				0.028
(<i>mrm</i>)	} 0.08			0.015
(<i>rmrm</i>)				0.055
(<i>mmrr</i>)	0.05			0.055
(<i>rmrr</i>)	0.20			0.207
(<i>mrrm</i>)	0.03			0.028
(<i>mrrr</i>)	0.18			0.207
(<i>rrrr</i>)	0.41			0.390

$$(mmn) = (mmmm) + \frac{1}{2}(mnmr) \quad (1)$$

$$(nmr) = (mnmr) + 2(rnmr) \quad (2)$$

$$(mrm) = \frac{1}{2}(mrmr) + \frac{1}{2}(mrmr) \quad (3)$$

$$(mrr) = 2(mrrm) + (mrrr) \quad (4)$$

$$(rmr) = \frac{1}{2}(mrmr) + \frac{1}{2}(rmrr) \quad (5)$$

$$(rrr) = (rrrr) + \frac{1}{2}(mrrr) \quad (6)$$

In these equations *m* and *r* denote *meso* and *racemic* dyads, respectively. The expressions enclosed by parentheses show observable tetrads and pentads, so that (*ijk*) means the sum of [*ijk*] and [*kji*] tetrads, if *k* is not equal to *i*.

If the polymer I was assumed to be controlled by Bernoulli trial⁹ as in a previous paper,⁷ each order of tacticity can be calculated from the statistical parameter P_m to be 0.21. These values are shown in the last column of Table II.

Table III. The microtacticity of polymer II obtained from the ^{13}C - $\{^1\text{H}\}$ spectra reproduced in Figures 2-5

	Obsd			Calcd from Stereo-blend model
	$-\text{CH}_2-$	$\alpha\text{-C}$	$\alpha\text{-CH}_3$	
	>C=O			
Dyad				
(<i>m</i>)	0.52			0.52
(<i>r</i>)	0.48			0.48
Triad				
(<i>mm</i>)	0.43	0.42	0.43	0.42
(<i>mr</i>)	0.21	0.22	0.22	0.21
(<i>rr</i>)	0.36	0.36	0.35	0.37
Tetrad				
(<i>mmmm</i>)				0.39 ^a
(<i>mnmr</i>)				0.07 ^a
(<i>rmr</i>)				0.08 ^a
(<i>mrm</i>)				0.05 ^a
(<i>mrr</i>)				0.13 ^a
(<i>rrr</i>)				0.28 ^a
Pentad				
(<i>mmmm</i>)				0.37
(<i>mnmr</i>)				0.04
(<i>rmr</i>)				0.02
(<i>mrm</i>)				0.02
(<i>rmrm</i>)				0.04
(<i>mmrr</i>)				0.06
(<i>rmrr</i>)				0.10
(<i>mrrm</i>)				0.03
(<i>mrrr</i>)				0.08
(<i>rrrr</i>)				0.24

^a Calculated from the relative intensities of the pentads.

The intensities of experimental triad, tetrad, and pentad coincide with those of theoretical values within the probable experimental error. Furthermore, the intensities of the triad determined from the ^{13}C - $\{^1\text{H}\}$ spectra coincide with those from the proton spectra as shown in Table I.

These facts show that the nuclear Overhauser effect caused by the total proton decoupling did not affect the relative intensities among the peaks assigned to the same chemical species except for stereochemical placements even for ^{13}C - $\{^1\text{H}\}$ resonance. These facts also support our assignments having been rational.

But the line ordering between (*mrm*) and (*mmrr*) is not conclusive, because the theoretical

intensities expected from the Bernoulli trial model of these two are equal to each other. A more detailed discussion is as follows.

In the analyses of the 220-MHz proton magnetic resonance spectra of PMMA, both (*mmrr*) and (*rmrm*) were observed in essentially the same chemical shift in the α-methyl resonance.¹⁰

If this is also the case in the ¹³C-¹H} spectra of the polymer I, the relative intensities of (*rmrr*), (*mmrr*+*rmrm*), and (*mmrm*) should be observed as 0.207, 0.110, and 0.015 respectively. But corresponding values cannot be found in the experimental values for relative intensities. This lead to the conclusion that the chemical shifts of (*mmrr*) and of (*rmrm*) must be different in the ¹³C-¹H} spectrum.

Identical relations,

$$(mmmr) + 2(rmnr) = (mmrm) + (mmrr) \quad (7)$$

$$2(mrrm) + (mrrr) = (rmrr) + (mmrr) \quad (8)$$

must be held when the propagation reaction is carried out under conditions of statistical stationarity.¹¹ In polymer II, these relations are satisfied slightly better if we put (*mmrr*)=0.06 and (*rmrm*)=0.04 than if we put (*mmrr*)=0.04 and (*rmrm*)=0.06.

Then we have the assignment as shown in Figure 5. Of course, the difference between the intensities of the peaks assigned to (*mmrr*) and (*rmrm*) are comparable to the order of the experimental error, so that the above assignments may not be conclusive.

The same line ordering has been concluded in the analyses of the 220-MHz proton magnetic resonance spectra of the α-methyl group of PMMA, apart from wholly reversing the line ordering from the lower to the upper field.¹²

We now consider what order of Markovian statistics controls the propagation reaction in the polymer II.

If the propagation reaction is controlled by first-order Markovian statistics, the following relations must hold.¹³

$$4(mmmm)(rmnr)/(mmmr)^2 = 1 \quad (9)$$

$$4(mrm)(rrr)/(mrr)^2 = 1 \quad (10)$$

Similar relations must hold if the reaction is controlled by second-order Markovian statistics as follows

$$4(mmmm)(rmnr)/(mmmr)^2 = 1 \quad (11)$$

$$(mrrm)(rmnr)/(mmrr)(rmrm) = 1 \quad (12)$$

$$4(mrrm)(rrrr)/(mrrr)^2 = 1 \quad (13)$$

On the other hand, we have next values from the experimental data of polymer II.

$$4(mmm)(rmr)/(mmr)^2 = 25$$

$$4(mrm)(rrr)/(mrr)^2 = 3$$

$$4(mmmm)(rmnr)/(mmmr)^2 = 19$$

$$(mrrm)(rmnr)/(mmrr)(rmrm) = 0.83$$

$$4(mrrm)(rrrr)/(mrrr)^2 = 5$$

These results suggest that both first- and second-order Markovian models are not appropriate to the propagation mechanism of polymer II.

In the polymerization of methyl methacrylate with 9-fluorenyllithium, the polymers polymerized in a polar medium were highly syndiotactic and were controlled by Bernoulli trial, while the polymers polymerized in a nonpolar medium were highly isotactic, and in an intermediate medium in its polarity the polymers were stereoblock.⁷

These facts had possibly assumed that polymer II was a stereoblend comprising the highly syndiotactic polymer {A} and the pure isotactic polymer {B}, of which the former has been controlled by the Bernoulli trial model.

If polymer II were composed of blends of polymer {A} and {B} in the ratio (1-w): w, and the statistical parameter relating to the former was *P_m*, triad intensities are expressed as follows

$$(mm) = w + (1-w)P_m^2 \quad (14)$$

$$(mr) = 2(1-w)P_m(1-P_m) \quad (15)$$

$$(rr) = (1-w)(1-P_m)^2 \quad (16)$$

$$(mm) + (mr) + (rr) = 1 \quad (17)$$

If this model is applied to polymer II, we have w=0.39 and *P_m*=0.22 from the experimental data listed in Table I.

Provided that these parameters are used to calculate the relative intensities of every order of microtacticity the values listed in the last column (designated as "stereoblend model") of Table III are obtained.

These values show fairly close agreement with those obtained experimentally.

It may be concluded that the polymer II is

stereoblend within the accuracy of the experiments and the calculations. There is some kind of deviation between the experimental and the calculated values, and it may well be interpreted by the possibility of the stereoblend model being composed of more than two polymers, each of which have different tacticities.

The above-mentioned stereoblend model is regarded as an extreme case of the Coleman—Fox model.¹⁴

Liquori, *et al.*,¹⁵ and Inagaki, *et al.*,¹⁶ divided anionically polymerized PMMA's into two tactically different polymers. These facts also support the stereoblend model.

CONCLUSION

The ¹³C-¹H} NMR analysis of polymer configuration may possibly provide the most suitable means of studying the configurational sequences of PMMA similar to or over the 220-MHz ¹H NMR, and its future in polymer chemistry is promising.

The totally spin decoupled spectra are rather simple because of the well discriminated chemical shifts over a wide range, and thus analyses of spectra are able to be carried out more easily.

It was shown that the nuclear Overhauser effect caused by total proton decoupling did not affect the relative intensities among the peaks assigned to the same chemical species, except for stereochemical placements, even for ¹³C-¹H} resonance.

The relative intensities of the polyad configurational sequences obtained from the ¹³C-¹H} spectra made it possible to test the model describing the propagation reaction more precisely.

As a result, it can be concluded from the consideration of the pentad microtacticities that the PMMA polymerized with 9-fluorenyllithium

in polar solvent is described by the Bernoulli trial model, while that in a nonpolar solvent is described by the stereoblend model.

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