

## $^{13}\text{C}$ NMR Study of Poly[(-)-menthyl methacrylate]

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**ABSTRACT:** Microtacticity and dynamics in solution of radically initiated radically poly[(-)-methyl methacrylate] was investigated by  $^{13}\text{C}$  NMR, in different solvents and at different field strengths. Resonance assignments were made from  $^{13}\text{C}$  dynamic measurements and by comparison with suitable high and low molecular weight model compounds. The correlation times evaluated from relaxation time ( $T_1$ ) and Nuclear Overhauser Enhancement Factors (NOEF) measurements are in agreement with an isotropic overall tumbling model. The splittings of the carbonyl signal, attributed to pentad stereosequences, allow to determine the main chain stereochemistry ( $P_m = 0.366$ ).

**KEY WORDS**  $^{13}\text{C}$  NMR / Poly[(-)-methyl methacrylate] / Relaxation Time / Stereoregularity / Nuclear Overhauser Enhancement Factors /

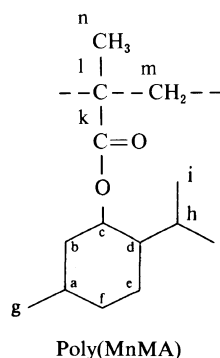
Chiroptical techniques have been particularly useful in establishing correlations between photochromic properties and structural parameters of optically active polymers containing side-chain photochromic groups.<sup>1</sup> In particular the copolymers of (-)-menthyl methacrylate (MnMA) with *trans*-4-methacroyloxyazobenzene (MAB) constitute at present the object of this study,<sup>2,3</sup> whereas information on the microstructure of the azobenzene containing homopolymer has been reported elsewhere.<sup>3</sup>

A straightforward determination of the main chain stereochemistry of poly(MnMA) and poly(MAB) is a prerequisite to the structural evaluation of the more complex poly(MnMA-*co*-MAB) samples. The poly(MAB) tacticity can be rather easily evaluated by  $^{13}\text{C}$  NMR.<sup>3</sup> On the other hand, even though the stereochemistry of poly(MnMA) prepared in the presence of different initiators has already been investigated,<sup>4</sup> the reported tacticity assignments have been derived from  $^{13}\text{C}$  NMR data relevant to the poly(methyl methacrylate) obtained by chemical transformation of poly(MnMA). This procedure is, however, time

consuming and, depending on reaction conditions, modification of the polymer microstructure may occur. As a consequence our efforts have been aimed at obtaining direct  $^{13}\text{C}$  NMR information on the main chain tacticity of poly(MnMA), whereas poly(MnMA-*co*-MAB) samples will constitute the object of a forthcoming paper.<sup>5</sup>

### EXPERIMENTAL

A radically initiated sample of poly[(-)-menthyl methacrylate] [poly(MnMA)] having  $M_n = 108,000$  and  $[\alpha]_D^{25} = -94.2$  ( $\text{CHCl}_3$ ) was prepared as reported in a previous paper.<sup>2</sup>



$^{13}\text{C}$  NMR spectra at 50.3 MHz were recorded at room temperature on 5% (w/v)  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  solutions by a Varian Gemini 200 spectrometer, under conditions of full proton decoupling, in 5 mm tubes. Spectral conditions were as follows: size, 11924 points; spectral width, 15000 Hz; pulse,  $70^\circ$ ; relaxation delay, 2 s; acquisition time, 0.4 s; number of scans, 30000. The  $T_1$  spin-lattice relaxation times were measured at room temperature by the inversion-recovery pulse sequence ( $\pi - \tau - \pi/2$ ) with a delay between the sequences of 4 s. Nuclear Overhauser Enhancement Factor (NOEF) were measured at room temperature by the inverse gated irradiation technique.  $^{13}\text{C}$  NMR spectra at 75.4 MHz were recorded at  $120^\circ\text{C}$  on 5% (w/v) 1,2,4-trichlorobenzene solutions by a Varian VXR-300 spectrometer, under conditions of full proton decoupling. Spectral conditions were as follows: spectral width, 15000 Hz; pulse,  $60^\circ$ ; relaxation delay, 2 s; acquisition time, 0.8 s; number of scans, 25000. In all cases a line broadening of 3 Hz was applied before the Fourier transformation.

## RESULTS AND DISCUSSION

### $^{13}\text{C}$ NMR Tacticity Evaluation

The proton decoupled  $^{13}\text{C}$  NMR spectrum of a radical sample of poly(MnMA) was recorded at 50.3 MHz in  $\text{CDCl}_3$  and in  $\text{C}_6\text{D}_6$  solution at room temperature. Resonance assignments (Table I) were made from  $^{13}\text{C}$   $T_1$  relaxation times and by comparison with those already reported for (–)-menthol,<sup>5</sup> poly[(–)-menthyl vinyl ether]<sup>5</sup> and poly(methyl methacrylate).<sup>4</sup>

Several carbon atoms give rise to multiplets in the region 10–80 ppm, due to their sensitivity to tacticity. However, the individual components severely overlap, particularly in  $\text{CDCl}_3$ , thus preventing unequivocal assignments of the stereosequences. In order to improve the spectral resolution a  $^{13}\text{C}$  NMR spectrum of poly(MnMA) was run at 75.4 MHz, in 1,2,4-trichlorobenzene solution at

**Table I.**  $^{13}\text{C}$  NMR experimental chemical shifts and relevant assignments for [poly[(–)-menthyl methacrylate] in different solvents

Carbon atom	Chemical shift/ppm <sup>a</sup>		
	$\text{CDCl}_3^b$	$\text{C}_6\text{D}_6^b$	$\text{C}_6\text{H}_3\text{Cl}_3^c$
$\text{C}_a$	31.27	31.38	30.16
$\text{C}_b$	39.99	40.41	39.16
$\text{C}_c$	75.91	75.89	74.37
$\text{C}_d$	47.22	47.48	46.33
$\text{C}_e$	22.70	22.85	22.02
$\text{C}_f$	34.20	34.23	33.26
$\text{C}_g$	21.99	22.13	20.68
$\text{C}_h$	25.48	25.78	24.56
$\text{C}_i$	15.64	15.99	14.79
$\text{C}_j$	21.26	21.40	19.92
$\text{C}_k$	176.9	176.8	174.87
$\text{C}_l$	45.57	46.17	45.04
$\text{C}_m$	52.31	53.03	51.72
$\text{C}_n$	17.75	18.40	17.61

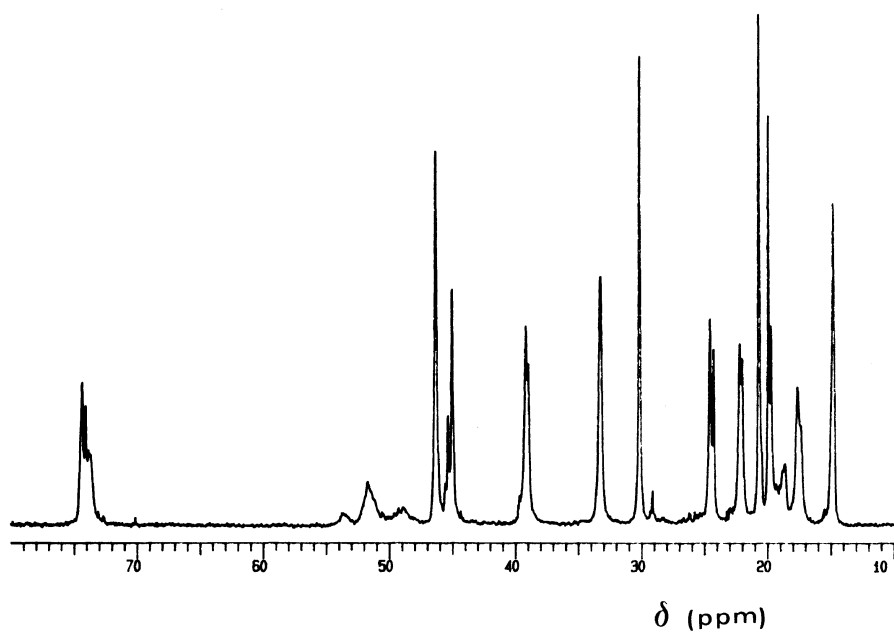
<sup>a</sup> In ppm from TMS.

<sup>b</sup> At room temperature and 50.3 MHz.

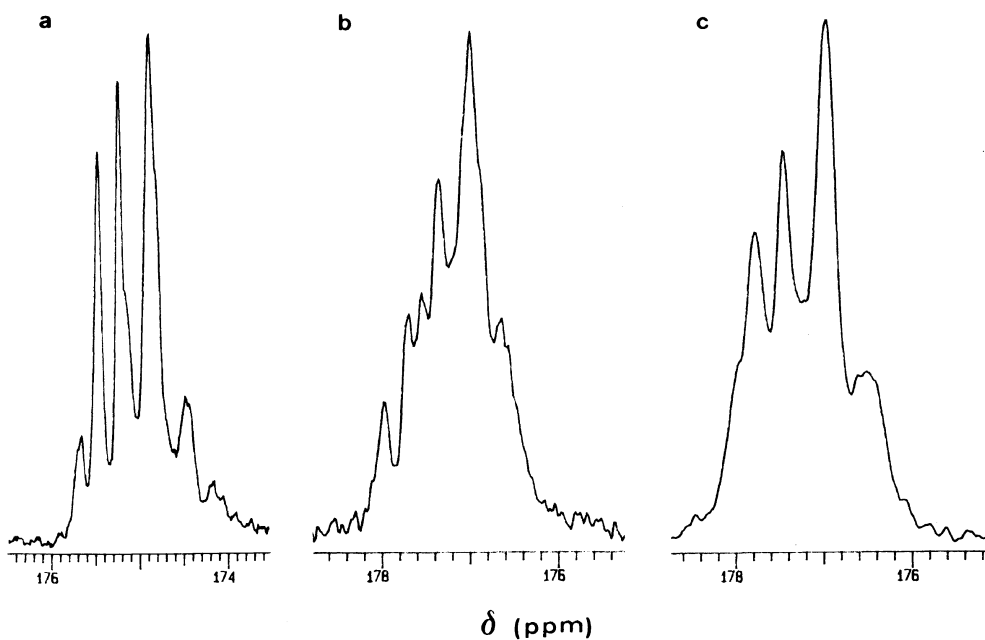
<sup>c</sup> At  $120^\circ\text{C}$  and 75.5 MHz.

$120^\circ\text{C}$ . Even in this case (Figure 1) no definite quantitative correlation can be established between signal multiplicity and backbone stereochemistry. However, in the  $\text{C}_6\text{H}_3\text{Cl}_3$  spectrum the peak relevant to the carbonyl carbon atom appears as six distinct resonances (Figure 2a) that can be attributed to *mrrm*, *rrrm*, *rrrr*, *rmrm* + *mmrm*, *rmrr* + *mmrr* and *mmmm* + *mmmr* + *rmmr* pentads, respectively. Similarly the less resolved splittings observed in benzene solution (Figure 2b) have been tentatively assigned to *mrrm*, *rrrm*, *rrrr*, *rmrm*, *mmrm* + *rmrr* + *mmrr* and *mmmm* + *mmmr* + *rmmr* pentads. In  $\text{CDCl}_3$  solution the carbonyl resonance is not resolved enough to allow unambiguous attributions (Figure 2c). Analogous assignments have been reported for poly(methyl methacrylate),<sup>7</sup> poly(MAB)<sup>3</sup> and poly( $\alpha$ -methylstyrene).<sup>8</sup>

Only qualitative information on main chain tacticity can be drawn from the intensity profile of the carbonyl resonance in  $\text{CDCl}_3$  solution. On the contrary the relative intensities of the



**Figure 1.** Proton decoupled 75.5 MHz  $^{13}\text{C}$  NMR spectrum of poly(MnMA) in 1,2,4-trichlorobenzene at 120°C in the 80–10 ppm region.



**Figure 2.** Proton decoupled  $^{13}\text{C}$  NMR spectrum of poly(MnMA) in the carbonyl region: a, at 75.4 MHz in 1,2,4-trichlorobenzene at 120°C; b, at 50.3 MHz in  $\text{C}_6\text{D}_6$  at room temperature; c, at 50.3 MHz in  $\text{CDCl}_3$  at room temperature.

**Table II.** Assignments in terms of pentad sequences of carbonyl signal splittings of poly(MnMA) in different solvents

$C_6H_3Cl_3^a$				$C_6D_6^b$			
Chemical shifts	Assignment	Intensity		Chemical shift	Assignment	Intensity	
		Calcd <sup>c</sup>	Found			ppm	Calcd <sup>c</sup>
175.65	<i>mrrm</i>	0.05	0.07	177.94	<i>mrrm</i>	0.05	0.06
175.45	<i>rrrm</i>	0.19	0.18	177.75	<i>rrrm</i>	0.19	0.19
175.22	<i>rrrr</i>	0.27	0.27	177.42	<i>rrrr</i>	0.16	0.17
	<i>mrrm</i>			177.19	<i>mrrm</i>	0.11	0.10
174.87	<i>mmrm</i>	0.36	0.36	176.91	<i>mmrm</i>	0.36	0.34
	<i>rmrr</i>				<i>rmrr</i>		
	<i>mmrr</i>				<i>mmrr</i>		
174.45	<i>mmmm</i>	0.08	0.09	176.50	<i>mmmm</i>	0.13	0.14
	<i>mmmr</i>				<i>mmmr</i>		
174.15	<i>rmmr</i>	0.054	0.04		<i>rmmr</i>		

<sup>a</sup> At 120°C and 75.5 MHz.

<sup>b</sup> At room temperature and 50.3 MHz.

<sup>c</sup> Assuming Beroullian statics ( $P_m=0.366$ ).

more resolved individual components, in both  $C_6H_3Cl_3$  and  $C_6D_6$  solution, fit a Bernoullian distribution of stereosequences having a  $P_m$  of 0.366 (Table II) and substantiates a slightly predominant syndiotactic structure. Number average sequence lengths for *meso* and *racemic* placements are 1.6 and 2.7, respectively. The degree of stereoregularity thus evaluated closely matches that reported for the poly-(methyl methacrylate) derived from radical poly(MnMA) by chemical transformation.<sup>4</sup>

The content of isotactic dyads evaluated for radical poly(MnMA) is significantly higher than that expected by comparison with several poly(alkyl methacrylates).<sup>10</sup> In fact the menthyl group is rather bulky and it is well recognized that the tendency to form syndiotactic sequences in the radical polymerization depends mainly on the bulkiness of the side chain substituent and to a minor extent on other thermodynamic parameters.<sup>9,10</sup> Therefore we must once more stress the tendency of

the highly dissymmetric (–)-menthyl group to somewhat favor isotactic arrangement of monomeric units independent of the polymerization conditions, as already observed in the cationic homopolymerization and copolymerization of (–)-menthyl vinyl ether.<sup>6,11</sup>

#### <sup>13</sup>C NMR Dynamic Parameters

To gain information about molecular mobility <sup>13</sup>C NMR relaxation times ( $T_1$ ) and Nuclear Overhauser Enhancement Factors (NOEF) have been measured at 50.3 MHz, in  $CDCl_3$  solution at room temperature.

The dipolar relaxation mechanism <sup>13</sup>C–<sup>1</sup>H has been found to be dominant in polymer solutions,<sup>12</sup> even if the extreme narrowing conditions are not usually met.<sup>13</sup>

The correlation times listed in Table III have been evaluated from the measured  $T_1$  and NOEF values, under the assumption that only directly bonded hydrogens contribute to the relaxation process.<sup>14</sup> In spite of the crudeness

**Table III.**  $^{13}\text{C}$  NMR spin-lattice relaxation times ( $T_1$ ), Nuclear Overhauser Enhancement Factors (NOEF) and correlation times ( $\tau$ ) of poly(–)-menthyl methacrylate]

Carbon atom	$T_1^a$	NOEF <sup>a</sup>	$\tau$
	s		$10^{-11}$ s
C <sub>a</sub>	0.22	0.84	9.0
C <sub>b</sub>	0.11	0.69	7.4
C <sub>c</sub>	0.22	0.49	5.3
C <sub>d</sub>	0.21	0.76	8.5
C <sub>e</sub>	0.13	1.07	9.7
C <sub>f</sub>	0.11	0.90	9.7
C <sub>g</sub>	0.38	1.37	2.8
C <sub>h</sub>	0.20	0.70	8.3
C <sub>i</sub>	0.39	1.38	2.8
C <sub>j</sub>	0.42	1.36	2.5
C <sub>k</sub>	2.08	0.34	—
C <sub>l</sub>	1.26	0.71	—
C <sub>m</sub>	0.11	0.61	6.7
C <sub>n</sub>	0.06	1.45	19

<sup>a</sup> +5%.

of this assumption, the data thus evaluated are in agreement with an isotropic overall tumbling model with a single correlation time ( $\tau = 9 \times 10^{-11}$  s). The rather large value of C<sub>n</sub> has been tentatively imputed to the steric crowding along the polymer backbone, whereas the lower values observed for the C<sub>g</sub>, C<sub>i</sub>, and C<sub>j</sub>, methyl carbons arise from the fast internal rotation typical of the methyl group. This last behavior has been assessed also on theoretical

grounds.<sup>15</sup>

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