^{13}C nuclear magnetic resonance study of poly(*trans*-4-methacryloyloxyazobenzene)

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The 50.3 MHz ^{13}C nuclear magnetic resonance of radically initiated poly(*trans*-4-methacryloyloxyazobenzene) was studied in $CDCl_3$ solution at room temperature. Resonance assignments were made by comparison with low-molecular-weight structural analogues and from dynamic measurements. Restricted internal rotation of the side-chain azobenzene group was found to be responsible for the splitting of some aromatic carbon signals. The carbonyl, methyl and main-chain quaternary carbons gave rise to multiplets attributable to pentad and triad stereosequences. Their intensity distribution closely fitted Bernoullian statistics ($P_m = 0.257$) consistent with a predominantly syndiotactic structure of the polymer backbone. Molecular dynamics in solution was investigated by measurements of ^{13}C T_1 and nuclear Overhauser enhancement factor.

(Keywords: ^{13}C nuclear magnetic resonance; poly(4-methacryloyloxyazobenzene); relaxation time; stereoregularity; nuclear Overhauser enhancement factor)

INTRODUCTION

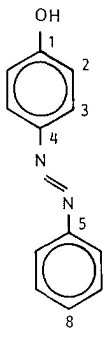
For several years the photo- and thermal isomerization of optically active polymers containing side-chain photochromic groups has been the subject of a thorough investigation aimed at establishing useful correlations between photochromic properties and structural and conformational parameters[1]. In this respect, when dealing with optically active systems, chiroptical techniques have been particularly fruitful, and in some cases they have suggested the occurrence of an extensive rearrangement of polymer conformation under light irradiation[2–4]. It is well known, however, that polymer conformational properties definitely depend on the main-chain tacticity[5]. Therefore, in order to get a better insight into polymer photochromism, we decided to start a systematic investigation of photochromic polymer stereochemistry by ^{13}C n.m.r. This technique is able to provide quantitative information on both macromolecular dynamics and main-chain tacticity[6–8].

In the present paper we report the results obtained in the ^{13}C n.m.r. investigation of the radical homopolymer of *trans*-4-methacryloyloxyazobenzene (MAB); the (−)-menthyl methacrylate homopolymer and the corresponding copolymers with MAB will constitute the subject of two forthcoming papers[9,10].

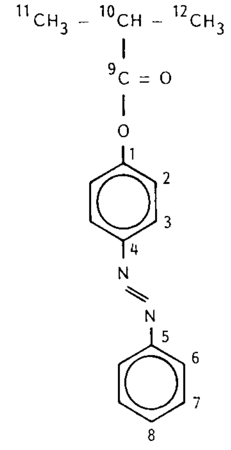
EXPERIMENTAL

Commercial *trans*-4-hydroxyazobenzene (HB) was used as received. A radically initiated sample of poly(*trans*-4-methacryloyloxyazobenzene) (poly(MAB)) having $M_n = 51\,000$ and *trans*-4-isobutyryloxyazobenzene (IAB) were prepared as reported in a previous paper[2].

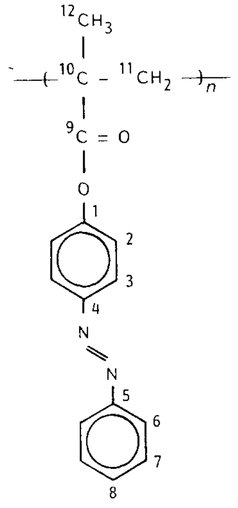
^{13}C n.m.r. spectra were recorded in 5 mm tubes at room temperature and at 60°C on 5% (w/v) $CDCl_3$ solutions by a Varian Gemini 200 spectrometer operating at 50.3 MHz, under conditions of full proton decoupling.



HB



IAB



Poly(MAB)

Spectral conditions were as follows: size, 11 968 points; spectral width, 15 000 Hz; pulse, 70°; relaxation delay, 2 s; acquisition time, 0.4 s; number of scans, 20 000. The T_1 spin–lattice relaxation times were measured at room temperature by the inversion–recovery pulse sequence (π–t–$\pi/2$) with a delay between the sequences of 8 and 20 s in the case of poly(MAB) and IAB, respectively. Nuclear Overhauser enhancement factors (NOEFs) were measured at room temperature by the inverse gated irradiation technique with a delay between the sequences of 8 and 30 s in the case of poly(MAB) and IAB, respectively. In all cases a line broadening of 3 Hz was applied before the Fourier transformation.

RESULTS AND DISCUSSION

^{13}C n.m.r.: tacticity evaluation

The proton-decoupled ^{13}C n.m.r. spectrum of poly(MAB) was recorded at room temperature in $CDCl_3$

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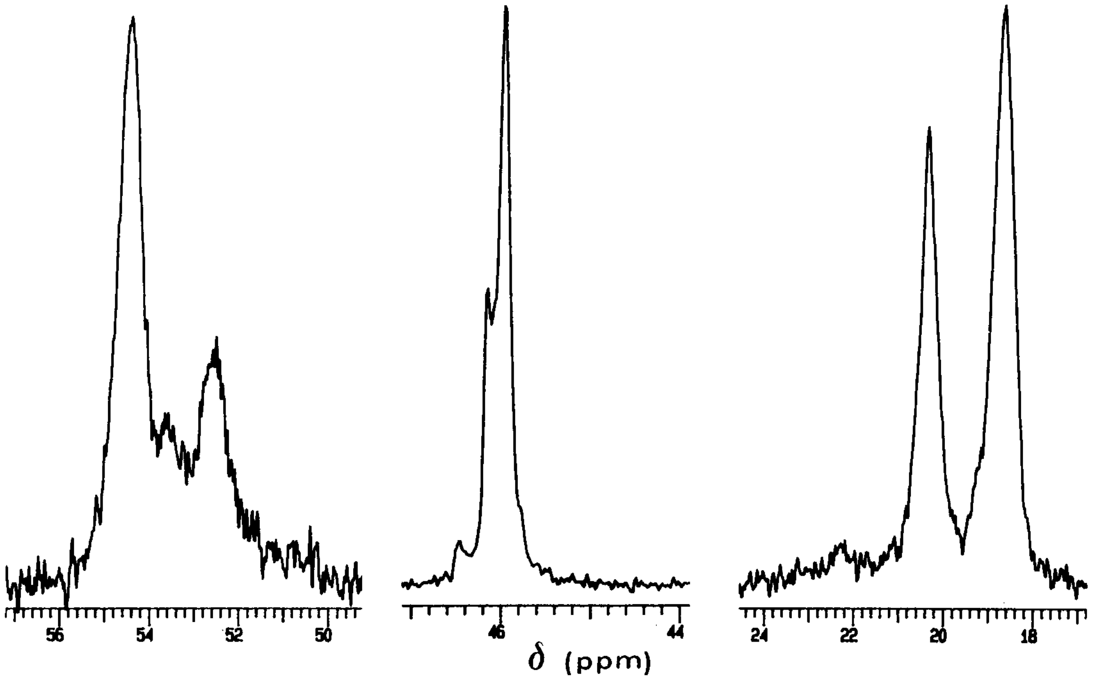

Figure 1 Proton-decoupled ^{13}C n.m.r. spectrum of poly(MAB) in the 57–15 ppm region

Table 1 ^{13}C n.m.r. experimental chemical shifts and relevant assignments for *trans*-4-hydroxyazobenzene (HB), *trans*-4-isobutyryloxyazobenzene (IAB) and poly(*trans*-4-methacryloyloxyazobenzene) (poly(MAB))

Carbon atom	Chemical shift (ppm)[a] HB	IAB	Poly(MAB)
C(1)	158.60	152.51	152.58
C(2)	125.13	122.04	121.79
C(3)	115.94	123.91	124.25
C(4)	147.40	150.07	150.58
C(5)	152.99	152.97	152.68
C(6)	122.70	122.77	123.05
C(7)	129.18	128.95	129.11
C(8)	130.56	130.89	131.13
C(9)	–	174.95	175.42
C(10)	–	33.67	45.94
C(11)	–	18.53	54.41
C(12)	–	18.53	18.53

[a] ppm from TMS

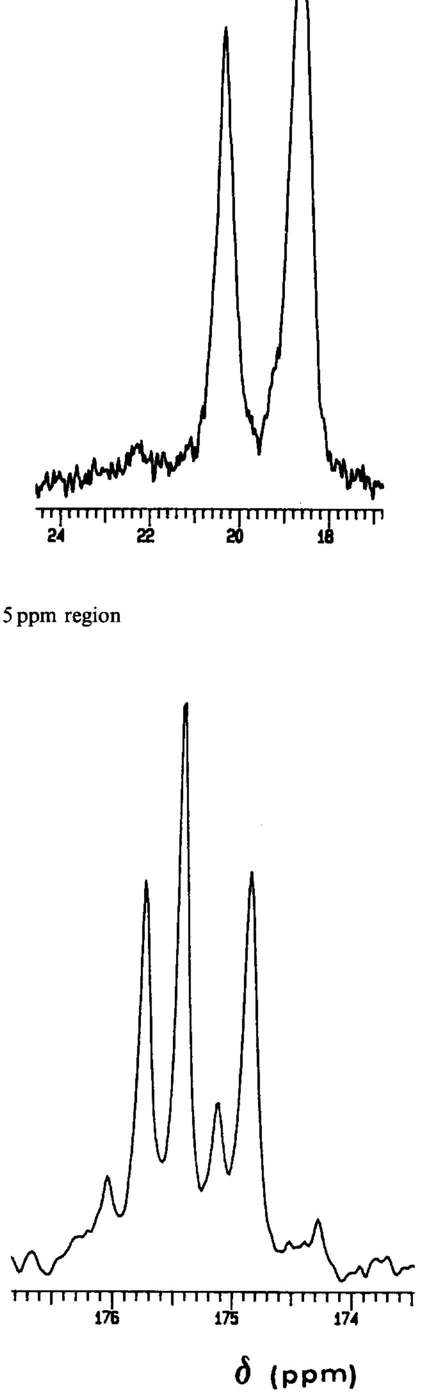

Figure 2 Proton-decoupled ^{13}C n.m.r. spectrum of poly(MAB) in the 177–174 ppm region

solution. Resonance assignments were made by comparison with model compounds (*trans*-4-isobutyryloxyazobenzene (IAB) and *trans*-4-hydroxyazobenzene (HB)) and by using ^{13}C T_1 relaxation times. Chemical shifts of carbon atoms of poly(MAB), IAB and HB, and the corresponding assignments, are summarized in *Table 1*.

The spectrum of poly(MAB) is consistent with a regular head-to-tail enchainment of monomeric units; within the limits of instrumental sensitivity, no signal corresponding to either head-to-head or tail-to-tail linkages can be observed.

Several signals in the poly(MAB) spectrum appear as multiplets. In particular, the signals corresponding to both quaternary and methyl carbon atoms are split into triplets (*Figure 1*), whereas the C(9) signal exhibits six well resolved lines (*Figure 2*). Taking into account the accepted mechanism of radically initiated polymerization[11], the triplet peaks have been attributed to racemic (*rr*), atactic (*mr*) and isotactic (*mm*) triads, in going from high to low field (*Table 2*). Analogously, the six resonances of the carbonyl carbon atom can be attributed to *mrrm*, *rrrm*, *rrrr*, *rmrm* + *mmrm*, *rmrr* + *mmrr* and *mmmm* + *mmmr* + *rmmr* pentads, respectively (*Table 3*). It is fair to mention that in the case of pentads other attributions can fit the experimental data. The proposed assignments, however, are in keeping with those reported for poly(methyl methacrylate)[12] and poly(α-methylstyrene)[13].

The distribution of the relative intensities into the three groups of lines fits a Bernoullian distribution of stereosequences having $P_m = 0.257$ (*Tables 2* and *3*) and

Table 2 Assignments of the splittings relevant to methyl and main-chain quaternary carbon signals in terms of triad sequences in poly(MAB)

Quaternary carbon		Methyl carbon			
Chemical shift (ppm)	Relative intensity	Chemical shift (ppm)	Relative intensity	Assignment	Calculated intensity[a]
46.5	0.07	22.3	0.07	*mm*	0.07
46.2	0.35	20.3	0.38	*mr*	0.38
45.9	0.58	18.6	0.55	*rr*	0.55

[a] Assuming Bernoullian statistics ($P_m = 0.257$)

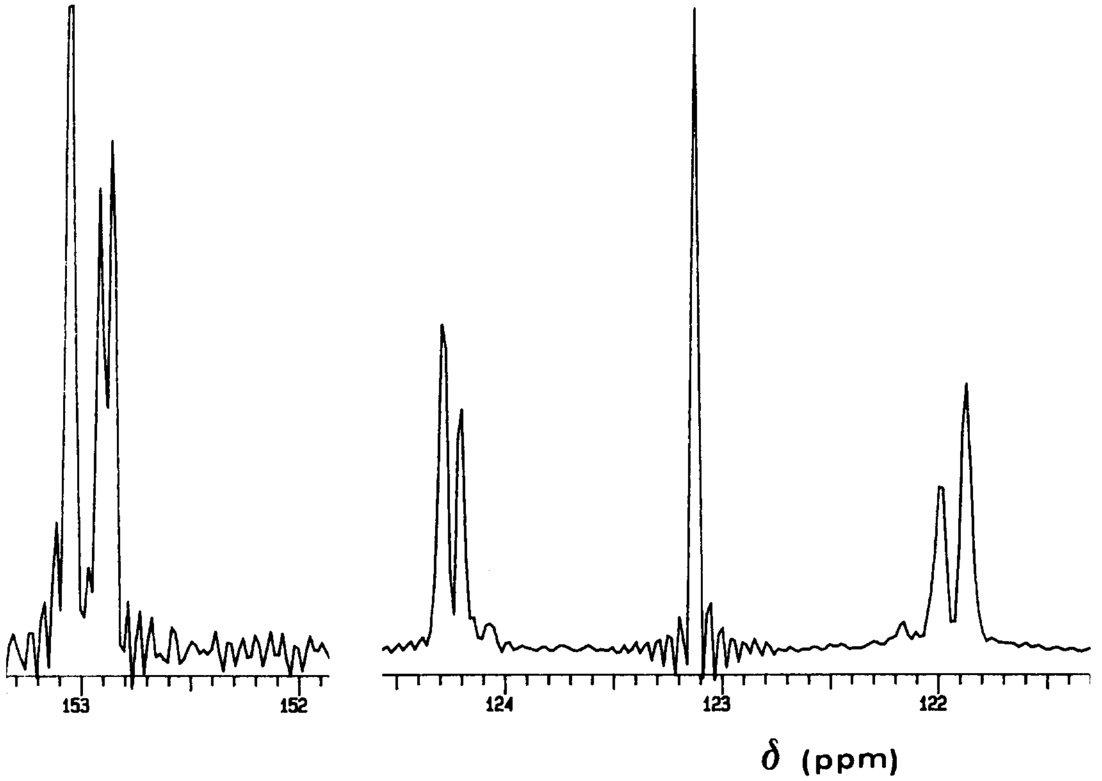

Figure 3 Proton-decoupled ^{13}C n.m.r. spectrum at 60°C of poly(MAB) in the 155–120 ppm region

Table 3 Assignments of carbonyl signal splittings in terms of pentad sequences in poly(MAB)

Chemical shift (ppm)	Assignment	Intensity	
		Calculated[a]	Found
176.1	*mrrm*	0 04	0.04
175.8	*rrrm*	0.21	0.21
175.4	*rrrr*	0.31	0.31
175.1	*rmrm* + *mmrm*	0.10	0.11
174.8	*rmrr* + *mmrr*	0.28	0.28
174.3	*mmmm* + *mmmr* + *rmmr*	0.07	0.05

[a] Assuming Bernoullian statistics ($P_m = 0.257$)

substantiates a predominantly syndiotactic structure with only isolated *meso* placements. Number-average sequence lengths for *meso* and *racemic* additions are 1.3 and 3.9, respectively. By applying a resolution enhancement function ($e^{t/RE}e^{-t/AF}$, $RE = 0.1$ s, $AF = 0.2$ s) to the free induction decay (FID) before the Fourier transformation (*FT*), analogous triad splittings can be observed in the corresponding C(1), C(2) and C(3) signals in the spectrum recorded at 60°C (*Figure 3*).

The splittings of the methylene signal (*Figure 1*) can be tentatively assigned to mixed dyad and tetrad stereosequences, analogous to what has been suggested by several authors for poly(methyl methacrylate)[6]. In the present case, however, the individual components are not resolved well enough to allow any significant attribution.

^{13}C *n.m.r.: dynamic parameters*

To obtain information about molecular mobility, ^{13}C n.m.r. relaxation times (T_1) and nuclear Overhauser enhancement factors (NOEFs) have been measured at 50.3 MHz, in $CDCl_3$ solution at room temperature, for both poly(MAB) and IAB (*Table 4*).

Apart from the quaternary carbon signals, the NOEFs observed for IAB are close to the maximum theoretical value (1.98), indicating an overall isotropic tumbling of the molecule and a dipolar mechanism of relaxation. On the other hand, the rather low NOEF of the quaternary carbons seems to suggest that the dipolar relaxation mechanism is quite inefficient for these carbon atoms, analogously to what is observed for instance in the case of pyrene[14].

The correlation times reported in *Table 4* have been

Table 4 ^{13}C n.m.r. spin–lattice relaxation time (T_1), nuclear Overhauser enhancement factor (NOEF) and correlation time (τ) for IAB and poly(MAB) in $CDCl_3$ solution at 50.3 MHz

	IAB			Poly(MAB)		
Assignment	T_1[a] (s)	NOEF[a]	τ (10^{-11} s)	T_1[a] (s)	NOEF[a]	τ (10^{-11} s)
C(1)	>20.0	0.57	–	2.5	0.14	–
C(2)	1.7	1.73	2.4	0.33	1.15	8.2
C(3)	1.8	1.98	2.6	0.33	1.26	9.0
C(4)	9.5	0.79	–	2.7	0.17	–
C(5)	>20.0	0.82	–	2.5	0.14	–
C(6)	2.0	1.58	1.9	0.66	1.14	4.1
C(7)	2.0	1.98	2.3	0.63	1.20	4.5
C(8)	0.54	1.84	7.3	0.14	0.45	7.6
C(9)	>8.7	0.58	–	1.3	0.26	–
C(10)	2.6	1.77	–	1.1	0.57	–
C(11)	2.0	1.59	0.6	0.15	0.51	4.0
C(12)	2.0	1.59	0.6	0.04	0.87	17

[a] ±5%

evaluated from the corresponding T_1 and NOEF values[7], under the assumption that only directly bonded hydrogens contribute to the relaxation process. In spite of the crudeness of this assumption, the reported correlation times are roughly self-consistent, the significantly smaller values of the methyl groups being due to their fast internal rotation[15]. On the other hand, the rather large τ value obtained for C(8) points to the occurrence of preferred rotation of the IAB molecule around the long axis[16].

An isotropic overall tumbling model with a single correlation time does not agree with the different τ values (*Table 4*) evaluated for the individual carbons of poly(MAB). The reported data, however, allow one to draw some qualitative conclusions concerning the mobility of the MAB units in the polymer as compared with low-molecular-weight model compounds. As expected, the main-chain mobility is rather limited and the very long correlation time of the methyl group can be tentatively attributed to the steric crowding along the polymer backbone, due to chain folding.

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