N.m.r. properties of tactic poly(*trans*-4-methacryloyloxyethylenoxyazobenzene)

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Poly(*trans*-4-methacryloyloxyethylenoxyazobenzene) was prepared by homopolymerization of the corresponding monomer, either by radical or anionic initiation, to give the first isotactic photochromic polymer. In the former case the ^{13}C n.m.r. spectrum exhibits, in the regions of the signals of several carbon atoms, multiplets attributable to pentad, triad or dyad stereosequences. Their intensity distribution closely fits Bernoullian statistics ($P_m = 0.21$) consistent with an atactic, predominantly syndiotactic, structure of the polymer backbone. On the other hand, in the spectrum of the sample prepared by anionic initiation, all the signals appear as sharp singlets in the region of the isotactic ennads of the radical sample. The intensity distribution of the very small peaks attributable to different stereosequences allows us to assign a 98% isotacticity to this sample and to rule out the occurrence of an enantiomorphic mechanism of polymerization. Molecular dynamics in solution, investigated by ^{13}C spin-lattice relaxation times and nuclear Overhauser enhancement factor measurements, indicate a comparable mobility for the two samples.

(Keywords: poly(*trans*-4-methacryloyloxyethylenoxyazobenzene); *trans*-4-isobutyryloxyethylenoxyazobenzene; tacticity; ^{13}C n.m.r.; NOEF; relaxation times)

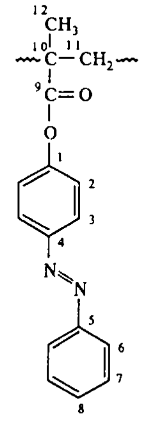
INTRODUCTION

For several years the photo and thermal isomerization of optically active polymers containing side chain photochromic groups has been the object of a thorough investigation with the aim of establishing useful correlations between photochromic properties and structural 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 u.v. and visible light irradiation[2–4]. It is well known, however, that polymer conformational properties depend on the main chain tacticity[5]. In order to gain a better insight into this aspect and its influence on polymer photochromism, a systematic ^{13}C n.m.r. investigation of photochromic polymer stereochemistry was started, to gain quantitative information on both macromolecular dynamics and main chain tacticity[6,7].

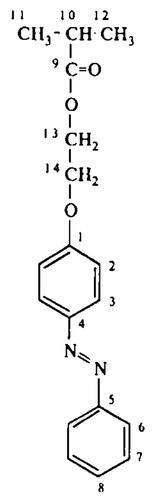
In this paper the results of the n.m.r. investigation of the stereochemistry of radically and anionically initiated homopolymers of *trans*-4-methacryloyloxyethylenoxyazobenzene (MEAB) are reported. Details of the synthesis, characterization and photochromism of MEAB are described in two forthcoming papers[8,9].

EXPERIMENTAL

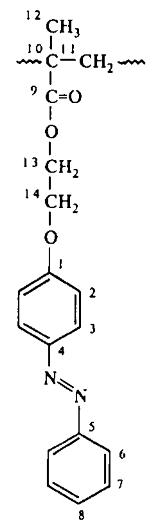
Trans-4-isobutyryloxyethylenoxyazobenzene (IEAB) was prepared as reported elsewhere[8]. Two samples of poly(*trans*-4-methacryloyloxyazobenzene) [poly(MEAB)] were prepared by homopolymerization in benzene at 60°C in the presence of AIBN (sample MER1) and in toluene at 20°C in the presence of phenylmagnesium bromide (sample MEA2), as reported elsewhere[8].



poly(MAB)



IEAB



poly(MEAB)

N.m.r. spectra were recorded using a Varian Gemini 200 spectrometer in 5 mm tubes on 10% (w/v) solutions, in either $CDCl_3$ at 50°C or toluene-d_8 at 100°C.

^1H n.m.r. spectra were recorded at 200 MHz. Spectral conditions were as follows: size, 11 968 points; spectral width, 3 kHz; pulse, 30°; acquisition time, 2 s; number of scans, 1. ^{13}C n.m.r. spectra were recorded at 50.3 MHz, under conditions of full proton decoupling. Spectral conditions were as follows: size, 23 936 points; spectral width, 15 kHz; pulse, 70°; relaxation delay, 2 s; acquisition time, 0.8 s; number of scans, 20 000. The 2D ^1H COSY spectra were recorded at 200 MHz on toluene-d_8 polymer solutions, using a sweep width of 1.6 kHz, 1024 data points and a delay time of 8 s between pulse sequences. A total of 256 spectra were used to provide the equivalent

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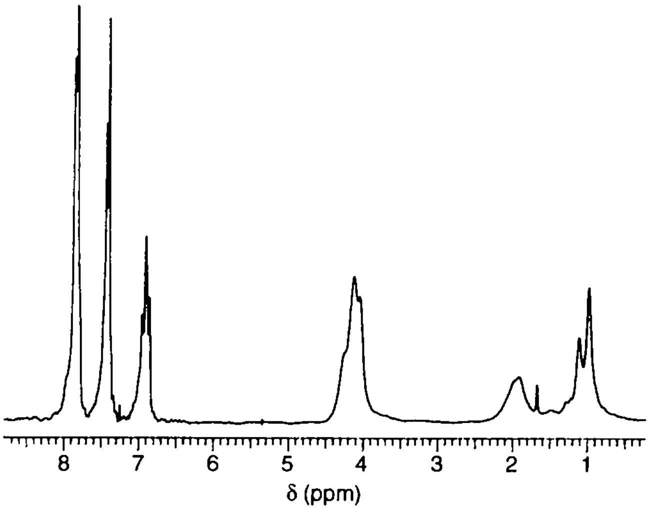


Figure 1 ^{1}H n.m.r. spectra in $CDCl_3$ at 50°C of radically initiated poly(MEAB)

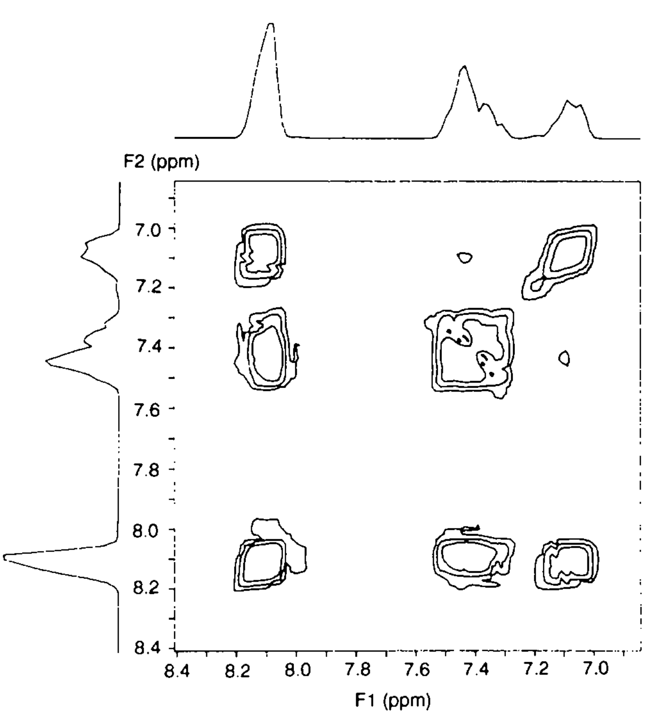


Figure 2 2D ^{1}H-COSY spectrum in the aromatic proton region of sample MER1 in toluene-d_8 at 100°C

of 1.6 kHz sweep width in the second frequency dimension. Final COSY spectra were symmetrized and displayed in the absolute value mode. The 2D ^{13}C–^{1}H COSY spectra were measured at 50.3 MHz on $CDCl_3$ polymer solutions at 50°C, using a sweep width of 3 kHz and 1024 data points. A total of 256 spectra were used to provide the equivalent of a 1.5 kHz sweep width in the ^{1}H frequency dimension. The spin-lattice relaxation times (T_1) were measured at room temperature on $CDCl_3$ polymer solutions by the inversion–recovery pulse sequence (π-τ-$\pi/2$) with a delay between the sequences of 12 and 20 s in the case of poly(MEAB) and IEAB, respectively. Nuclear Overhauser enhancement factors (NOEF) were measured at room temperature on $CDCl_3$ polymer solutions by the inverse gated irradiation technique with a delay between the sequences of 15 and 30 s in the case of poly(MEAB) and IEAB, respectively. No weighting function was applied before the Fourier transformation.

RESULTS AND DISCUSSION

Samples of poly(MEAB) were prepared both by radical initiation in benzene at 60°C (sample MER1) and by anionic initiation in toluene at 20°C (sample MEA2)[8]. These experimental conditions are known to provide, respectively, mainly atactic and isotactic poly(alkyl methacrylate)s[10].

The ^{1}H n.m.r. spectrum of poly(MEAB) in $CDCl_3$ at 50°C exhibits three sets of multiplets at about 7, 4 and 2 ppm, attributable to aromatic, oxyethylene, and aliphatic protons, respectively (*Figure 1*). The three signals at 6.9, 7.4 and 7.8 ppm (relative intensity 3:4:5) can be attributed to protons *ortho* to oxygen, *meta* and *para* to nitrogen, and *ortho* to nitrogen, respectively. This assignment is confirmed by the appearance of the 2D ^{1}H–COSY (*Figure 2*) and 2D ^{13}C–^{1}H COSY (*Figure 3*) spectra.

Comparison of the spectra of radical and anionic samples, recorded either in toluene-d_8 or in $CDCl_3$, highlights some significant differences that allow for quantitative evaluation of the main chain stereochemistry. In fact, in toluene solution the signals at about 1.5, 4 and 4.4 ppm, relevant to methyl and oxymethylene groups, appear as unresolved triplets in the radical sample and as rather sharp singlets in the case of the anionic sample (*Figure 4*). Correspondingly, the signals of main chain methylene are constituted by a broad unresolved multiplet at about 2.3 ppm and by two doublets centred at 1.8 and 2.5 ppm. These last two signals can be attributed to *threo* and *erythro* protons which are respectively *anti* and *syn* to the ester group in the planar zig-zag conformation[11].

The individual components of the triplets can be attributed to *mm*, *mr* and *rr* triads in going from low to high field and their intensity distribution allows us to

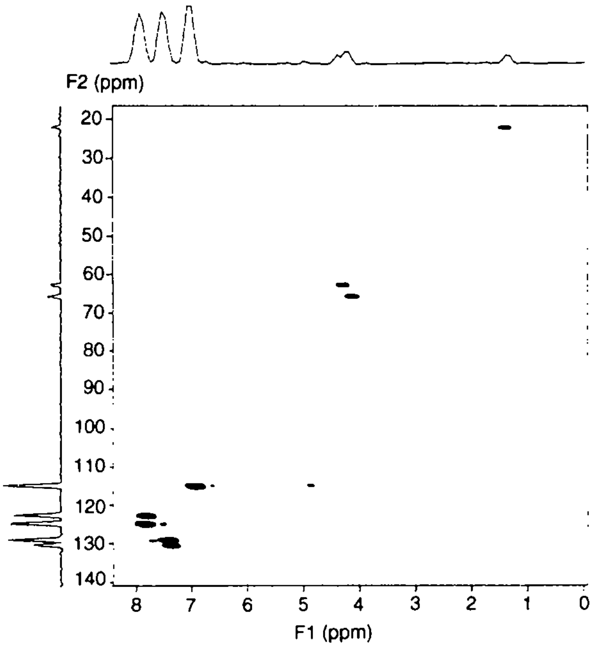
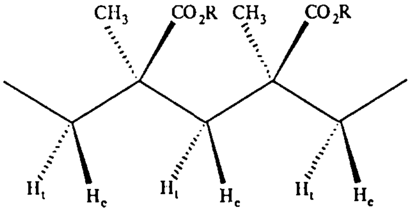


Figure 3 2D ^{13}C–^{1}H COSY heteronuclear spectrum of anionic poly(MEAB) in $CDCl_3$ at 50°C



assign an isotacticity degree of about 20 and 95% to radical and anionic samples, respectively. Poor peak resolution prevents more precise evaluation.

It is interesting to observe that in the main chain proton region of the 2D ^{1}H-COSY spectrum of the anionic sample (*Figure 5*) two small cross peaks are present off the diagonal, implying a long-range coupling between the *erythro* methylene proton and the methyl group. Conversely, no corresponding cross peak can be seen for the *threo* proton. A similar behaviour has previously been observed for poly(methyl methacrylate)^{12} and it has been proposed that the isotactic polymer assumes in solution a *trans trans* main chain conformation in which only the *erythro* methylene proton is capable of forming, with the α-methyl proton, a W-shaped path of the kind generally thought to be favourable for long-range coupling.

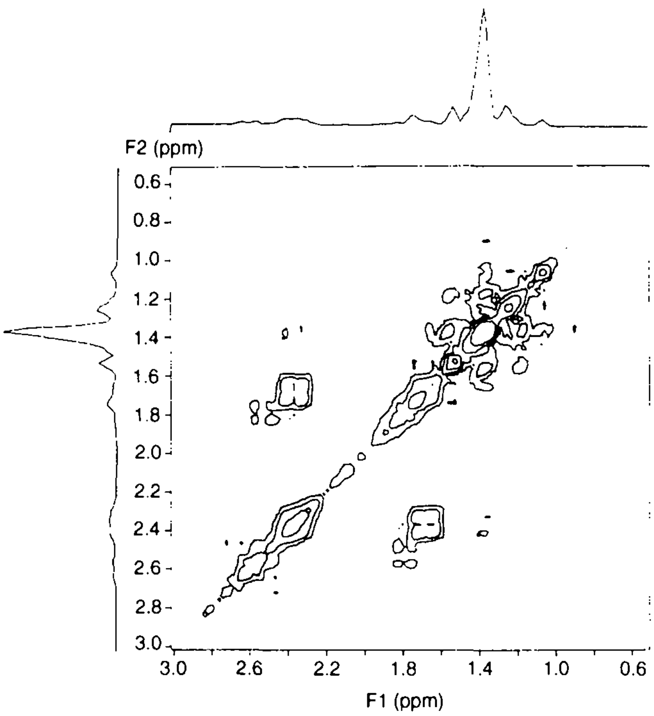


Figure 5 2D ^{1}H COSY spectrum in the 1–3 ppm region of sample MEA2, in toluene-d_8 at 100°C

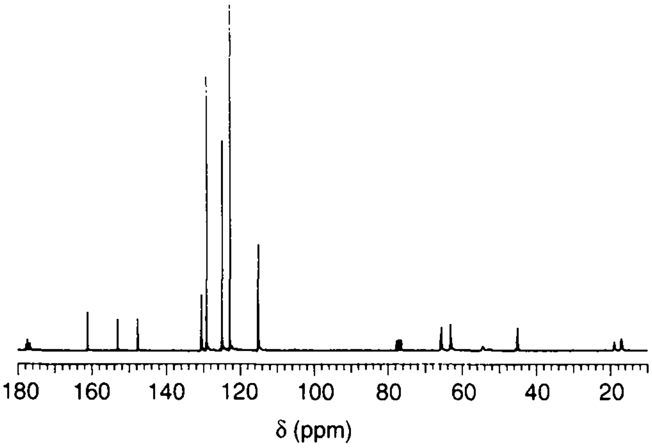


Figure 6 Proton decoupled ^{13}C n.m.r. spectrum in $CDCl_3$ at 50°C of radically initiated poly(MEAB)

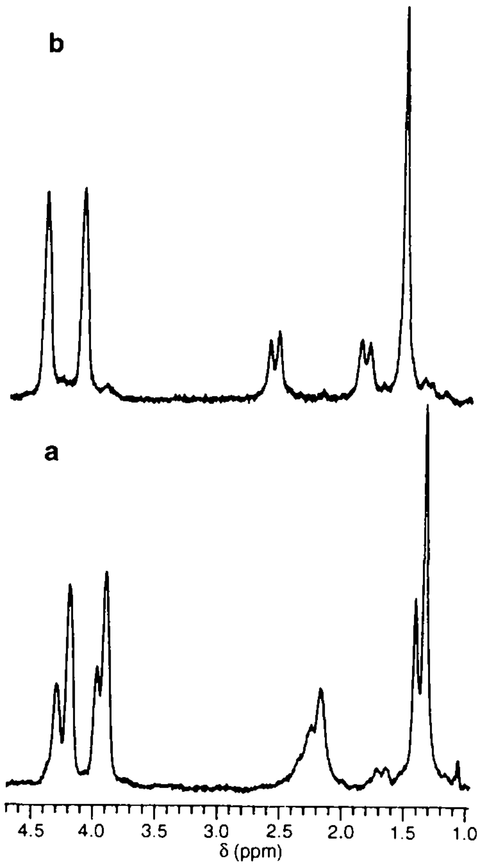


Figure 4 ^{1}H n.m.r. spectra in the aliphatic proton region of (a) radical and (b) anionic poly(MEAB), in toluene-d_8 at 100°C

The proton decoupled ^{13}C n.m.r. were recorded at 50°C in $CDCl_3$ solution (*Figure 6*). Resonance assignments (*Table 1*) were made by comparison with a low molecular weight model compound, *trans*-4-isobutyryloxyethylenoxyazobenzene (IEAB), from the known assignments of poly(*trans*-4-methacryloyloxyazobenzene) [poly(MAB)]^{6}, and by using ^{13}C T_1 data. The reported attributions are confirmed by the 2D ^{13}C-^{1}H COSY heteronuclear spectrum (*Figure 3*).

The ^{13}C n.m.r. spectra of poly(MEAB)s are 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 spectrum of radically initiated poly(MEAB) appear as multiplets. In particular the signals corresponding to C_1, C_{10} and C_{12} carbon atoms are split into triplets (*Figure 7*), whereas the C_9 signal exhibits 10 rather well resolved lines (*Figure 8*). Taking into account the accepted mechanism of radically initiated polymerization^{13}, 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 10 resonances of the carbonyl carbon atom can be attributed to *mrrm*, *rrrm*, *rrrr*, *rmrm*, *mmrm*, *rmrr*, *rmrm*, *mmmm*, *mmmr* and *rmmr* pentads, respectively (*Table 3*).

It is fair to mention, however, that some of these signals are very small; moreover, in the case of the *mr* centred pentads, reversal of the *mmrr* and *rmrm* attributions still fits the experimental data. Therefore, significant assignments have been made only by comparison with the spectrum of poly(MEAB) prepared in the presence of an anionic initiator.

Table 1 ^{13}C n.m.r. experimental chemical shifts and relevant assignments for IEAB and for radically initiated poly(MEAB) and poly(MAB)

	Chemical shift[a]		
Carbon atom	Poly(MEAB)	IEAB	Poly(MAB)
C_1	161.01	161.42	152.58
C_2	115.02	115.25	121.79
C_3	124.85	124.88	124.25
C_4	147.61	147.92	150.58
C_5	153.06	153.34	152.68
C_6	122.75	122.78	123.05
C_7	129.09	129.14	129.11
C_8	130.46	130.49	131.13
C_9	177.36	177.09	175.42
C_{10}	44.97	33.87	45.94
C_{11}	54.47	18.71	54.41
C_{12}	16.97	18.71	18.53
C_{13}	63.10	62.42	-
C_{14}	65.63	66.58	-

[a] In ppm from TMS, only the chemical shift of the most intense peak has been reported in the case of multiplets

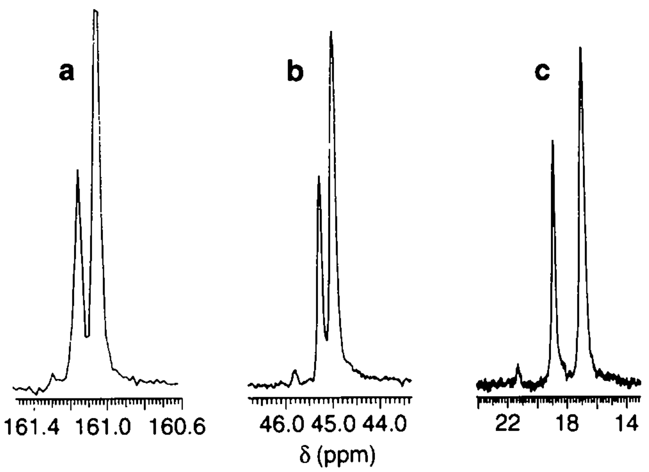


Figure 7 (a) C_1, (b) C_{10}, and (c) C_{12} signals in the proton decoupled ^{13}C n.m.r. spectrum of radical poly(MEAB), in $CDCl_3$ at 50°C

The methylene signal (*Figure 9*) is split into two broad, partially overlapping peaks at 54.5 and 52.5 ppm (relative intensity 0.64:0.36) that can be tentatively assigned either to *rr* and *mm* dyads or to unresolved, mixed tetrads.

The distribution of the relative intensities into these five groups of lines fits a Bernoullian distribution of stereosequences having a P_m of 0.21 (sample MER1, *Tables 2* and *3*) and substantiates a predominantly syndiotactic structure with isolated meso placements. Number average sequence lengths[14] for meso and racemic additions are 1.3 and 4.9, respectively.

In the case of the MEA2 sample, most of the signals appear as sharp singlets. The frequency of the peaks due to carbon atoms sensitive to triad (C_1, C_{10} and C_{11}) and

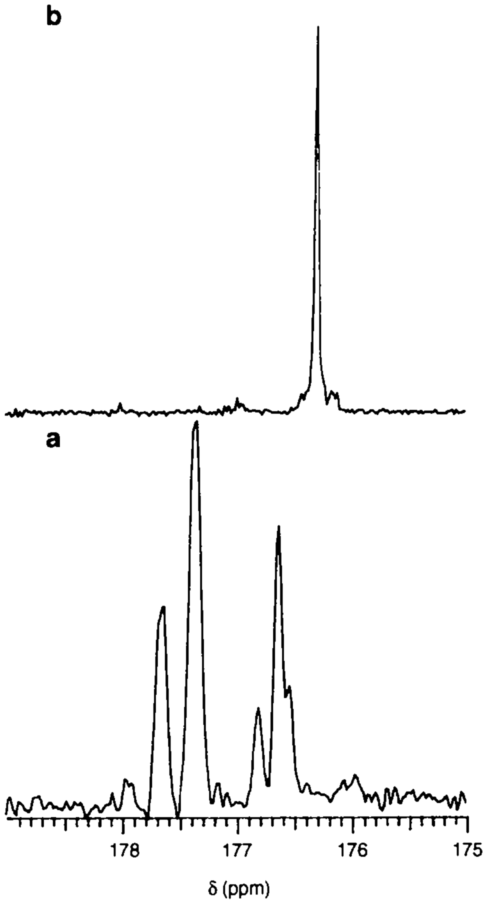


Figure 8 C_9 signal in the proton decoupled ^{13}C n.m.r. spectrum of (a) radical and (b) anionic poly(MEAB), in $CDCl_3$ at 50°C

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

	C_1		C_{10}		C_{12}			
Sample	ppm	I[b]	ppm	I[b]	ppm	I[b]	Assignment	Calculated intensity[a]
MER1	161.25	0.03	45.76	0.03	21.30	0.03	*mm*	0.04
	161.11	0.36	45.23	0.34	18.87	0.35	*mr*	0.33
	161.01	0.61	44.97	0.63	16.97	0.62	*rr*	0.63
MEA2	161.25	0.97	45.67	0.95	22.19	0.97	*mm*	0.97
	161.11	0.03	45.19	0.04	19.00	0.03	*mr*	0.03
	161.01	<0.01	44.93	0.01	17.00	<0.01	*rr*	<0.01

[a] Assuming Bernoullian statistics ($P_m = 0.21$ and 0.98 for samples MER1 and MEA2, respectively)
[b] Relative experimental intensity

pentad (C_9) stereosequences, closely corresponds to that of *mm* and *mmmm* placements, respectively. Only minor signals attributable to different stereosequences are observed (*Tables 2* and *3*), thus substantiating a highly isotactic polymer structure.

The backbone methylene signal is characterized by a not too sharp singlet at 51.8 ppm, flanked by a very small one at about 53.5 ppm (*Figure 9*), in agreement with the dyad assignment.

In the C_9 signal (*Figure 8*) the peaks corresponding to *mmmr* and *mmrm* pentads are definitely larger than those of *mmrr* and *mrrm* pentads, ruling out, as expected, the occurrence of an enantiomorphic-type polymerization mechanism[15]. The unfavourable signal-to-noise ratio, however, does not allow us to ascertain if the polymer stereochemistry obeys either Markovian or Bernoullian statistics. A P_m value of about 0.98 has been evaluated according to the latter model. Number average sequence lengths for meso and racemic placements are 65 and 1, respectively.

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

Sample	Chemical shift (ppm)	Assignment	Intensity Calculated[a]	Found
MER1	177.96	*mrrm*	0.03	0.04
	177.57	*rrrm*	0.21	0.20
	177.36	*rrrr*	0.39	0.39
	177.0	*mmrm*	0.01	0.01
	176.81	*mmrr*	0.06	0.06
	176.65	*rmrr + rmrm*	0.26	0.26
	176.3	*mmmm*	<0.01	0
	176.1	*mmmr*	0.01	0.01
	175.98	*rmmr*	0.03	0.03
MEA2	177.9	*mrrm*	0.01	0.01
	177.0	*mmrm*	0.04	0.04
	176.81	*mmrr*	0.01	0.01
	176.27	*mmmm*	0.89	0.88
	176.11	*mmmr*	0.05	0.06

[a] Assuming Bernoullian statistics ($P_m = 0.21$ and 0.98 for samples MER1 and MEA2, respectively)

To gain information about molecular mobility, ^{13}C n.m.r. T_1 data and NOEF have been measured at 50.3 MHz, in $CDCl_3$ solution at room temperature, of both poly(MEAB) samples and IEAB samples, for comparison (*Table 4*).

Apart from the quaternary carbon signals, the NOEFs

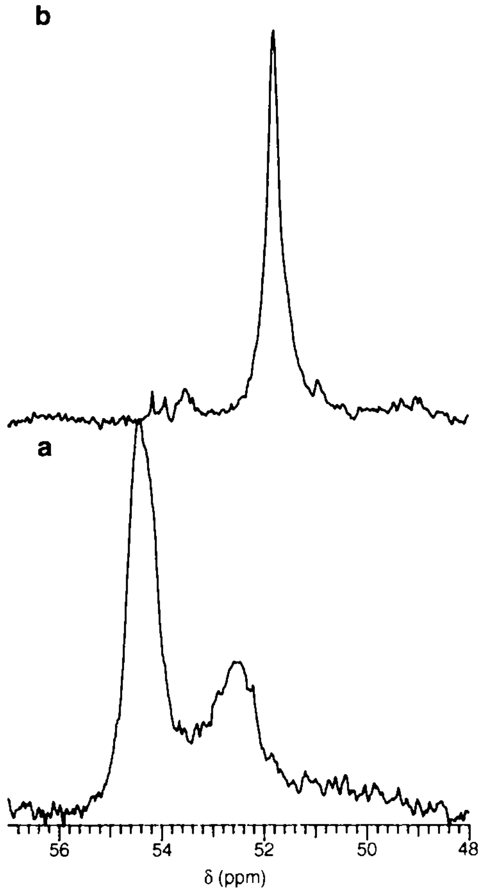


Figure 9 Main chain methylene signals of (a) radical and (b) anionic poly(MEAB) in the proton decoupled ^{13}C n.m.r. spectrum, in $CDCl_3$ at 50 C

Table 4 ^{13}C n.m.r. spin-lattice relaxation times (T_1), NOEFs and correlation times (τ) for IEAB and poly(MEAB)s in $CDCl_3$ solution at 50.3 MHz

	IEAB			Sample MER1			Sample MEA2		
Carbon atom	T_1[a] (s)	NOEF[a]	τ (10^{-10} s)	T_1[a] (s)	NOEF[a]	τ (10^{-10} s)	T_1[a] (s)	NOEF[a]	τ (10^{-10} s)
C_1	>21	0.85		2.3	0.51		2.3	0.67	
C_2	2.6	1.98	0.18	0.22	1.24	2.2	0.23	1.35	2.1
C_3	2.6	1.88	0.18	0.23	1.33	2.1	0.24	1.47	2.0
C_4	>18	0.71		2.5	0.22		2.8	0.48	
C_5	>21	0.62		3.2	0.21		3.7	0.35	
C_6	3.2	1.81	0.15	0.46	1.46	1.0	0.49	1.67	1.0
C_7	3.1	1.98	0.15	0.45	1.28	1.1	0.48	1.45	1.0
C_8	0.97	1.90	0.49	0.19	1.12	2.7	0.17	1.28	3.0
C_9	>8	0.66		1.9	0.26	-	1.5	0.28	
C_{10}	>10	1.66	–	1.1	0.37		1.0	0.51	
C_{11}	4.4	1.96	0.04	0.10	0.59	2.5	0.07	0.55	3.8
C_{12}	4.4	1.96	0.04	0.06	1.23	2.8	0.06	1.67	2.8
C_{13}	1.6	1.86	0.15	0.08	1.04	3.2	0.09	1.00	2.8
C_{14}	1.6	1.96	0.15	0.09	1.05	2.8	0.10	1.26	2.5

[a] ±10%

observed for IEAB 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 suggests that the dipolar relaxation mechanism is quite inefficient for these carbon atoms.

Correlation times have been evaluated from the corresponding T_1, under the assumption that only directly bonded hydrogens contribute to the relaxation process[16]. The values reported in *Table 4* are consistent with a fast, almost isotropic tumbling of the IEAB molecule, with a preferred rotation around the long axis, as suggested[17] by the rather large τ of C_8. The significantly smaller values of the methyl groups can be attributed to their fast internal rotation[18].

The τ values (*Table 4*) evaluated from the ^{13}C T_1 data of poly(MEAB) carbons do not agree with an isotropic overall tumbling model with a single correlation time and differ significantly from the corresponding τ values evaluated from the observed NOEFs, suggesting that in this case a distribution of correlation times has to be considered[19]. The reported data, however, are indicative of a significantly reduced mobility of polymer side chains, as compared with the low molecular weight model compound. As expected, the correlation times of the different carbons suggest that segmental mobility increases in going from the main chain to the side chain and that only the phenyl ring most removed from the polymer backbone maintains some rotational freedom about the side chain long axis.

No significant difference is observed in the ^{13}C n.m.r. dynamic parameters of the two samples of poly(MEAB), in contrast to reports for other poly(methacrylates)[20-22]. This result seems to suggest that in the present case the overall molecular motion is more influenced by the large side chains than by the main chain stereochemistry, in partial accord with the reported dependence of segmental mobility on the bulkiness of the ester group[21].

The reported data seem to imply a significant effect of main chain configuration on polymer conformation in solution, whereas the influence, if any, on the mobility of azobenzene groups is rather limited. Accordingly polymer tacticity is expected to have a greater effect on the chiroptical properties, which depend on macromolecular conformation, than on the photochromic behaviour, which involves a partial rearrangement of the side chains, consequent to the *trans–cis* isomerization of the azo group. This point will be more thoroughly investigated in two forthcoming papers[8,9].

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