Regularity and stereoregularity of poly-*p*-isopropyl-α-methylstyrene

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Poly-*p*-isopropyl-α-methylstyrenes were prepared through anionic and cationic polymerizations at $-78°C$. The polymers were analysed by ^{13}C n.m.r. spectroscopy at 25, 87.5 and 100.62 MHz. The structure of the polymers was found to be regular. Metallation of a regular polymer can be followed with the help of u.v. spectroscopy but its extent is too small to be detected by n.m.r. spectroscopy. Polymer prepared at 50°C by radical polymerization is also found to be regular. All polymerizations obey Bernouillian statistics. The cationic polymer is predominantly syndiotactic. ^1H n.m.r. spectra at 250 and 360 MHz are re-examined and the results are in good agreement with those obtained with ^{13}C n.m.r. spectroscopy.

Keywords Poly-*p*-isopropyl-α-methylstyrene; nuclear magnetic resonance; stereoregularity; regularity; metallation

INTRODUCTION

The polymerization features of *p*-isopropyl-α-methylstyrene (IAMS) have been recently reported[1-6]. It has been shown[2] that polymers obtained at $-78°C$ through cationic polymerization, using Friedel–Crafts initiators, are mainly syndiotactic. The enthalpy and entropy of polymerization for this monomer have been determined in an equilibrium study of this anionic polymerization at various temperatures[5]. Irregularities in the polymer obtained under equilibrium conditions have been observed[6]. It has been suggested that such irregularities might be due to the methine proton abstraction of the isopropyl group, to metallation of the benzene ring[5] and to intramolecular chain transfer[2]. In order to obtain the most regular polymer possible and to avoid side reactions, polymerizations were carried out at $-78°C$ and the polymers analysed using ^1H and ^{13}C n.m.r. at high and low field strengths. Metallation of the regular polymer was attempted and the structure of the corresponding polymer re-examined.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) (Fisher Scientific ACS or OSI), methylene chloride (CH_2Cl_2), benzene, cyclohexane, $TiCl_4$ (PROLABO) and sodium were purified according to methods previously described[7,8].

All reagents were handled under high vacuum in all-glass apparatus equipped with suitable break-seals. The $TiCl_4$ solution was stored in breakable sealed phials.

N,N,N',N'-tetramethylethylenediamine (TMEDA) (Aldrich Chemical Co.) was twice fractionated on a spinning band column, dehydrated on H_2Ca and then on sodium mirrors.

p-Isopropyl-α-methylstyrene (Aldrich Chemical Co.) was carefully fractionated under reduced nitrogen pressure (V.P.C. purity >99.96%) and dehydrated on successive sodium mirrors.

Sec-butyllithium (FLUKA) was distilled under high vacuum and dissolved in anhydrous hexane. Ethylbromide (PROLABO) was kept for 2 days on K_2CO_3, two weeks on $CaBr_2$ and re-distilled under dry nitrogen immediately before use.

Polymerizations

Anionic and cationic polymerizations were performed using high vacuum techniques described elsewhere[7,8].

Anionic polymerizations. The polymerizations were initiated with carbanionic oligomers prepared '*in situ*' by the simultaneous condensation of THF and monomer vapours on a sodium mirror at $-78°C$, causing the monomer concentration in the condensed mixture to remain low. Prolonged contact of active oligomers with sodium was avoided. The active centre concentration was approximately 10^{-3} M. The polymerizations were carried out at $-78°C$ in THF for 5 h and terminated with methanol.

The number-average degree of polymerization ($\overline{DP}_n$) of anionic polymers varied from 26 (sample ANQ-E1) to 220 (sample ANQ-E2). Narrow molecular weight distributions (*MWD*) were observed ($I = \bar{M}_w$(g.p.c.)/$\bar{M}_n$(g.p.c.) $= 1.1$) which might indicate the absence of side reactions at that temperature.

Cationic polymerizations. The phial containing the catalyst solution (1.98×10^{-3} M $TiCl_4$ in CH_2Cl_2) was broken in the monomer solution (0.19 M in CH_2Cl_2) in the presence of a known amount of co-catalyst (water; 10^{-3} M) at $-78°C$. The polymerization was terminated after 5 min by adding methanol and complete conversion of the monomer was observed. A broad *MWD* was observed ($I = 6$) for the CTQ2 sample ($\bar{M}$ (osmotic) $=$ 32 500). A second sample (CTQ1, $\bar{M}_n = 10\,100$) was

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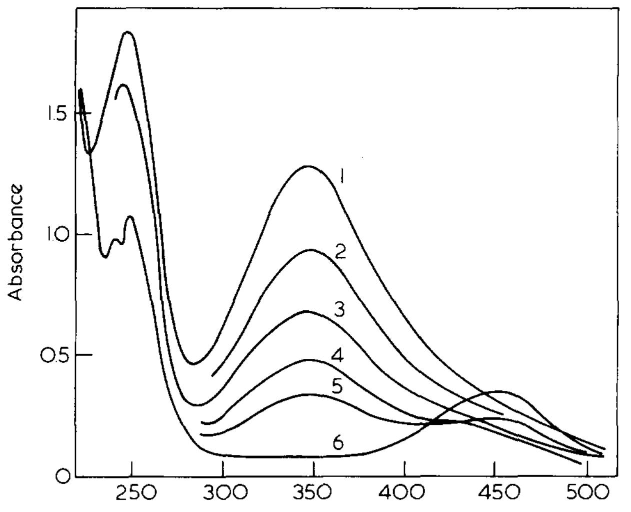


Figure 1 Stability of active centres at room temperature. Curve 1: Initial state. Curves 2, 3, 4, 5 and 6: after 1, 2, 5, 8 and 36 days respectively

prepared under nearly similar conditions using a larger amount of added water. In this case the yield was much lower but the *MWD* was very narrow ($I = 1.75$).

Radical polymerization. A sample was prepared through radical bulk polymerization in a sealed ampoule (6 ml/22 mg AIBN at 50°C for 4 days). Polymer (sample RAD, $\bar{M}_n = 11\,000$) with a broad *MWD* was obtained in a low yield (9%).

N.m.r. analysis

100 MHz ^{1}H and 25.15 MHz ^{13}C n.m.r. spectra were recorded at 25°C in $CDCl_3$ solutions (15% w/volume) with JEOL PS 100-FT and VARIAN XL-100 spectrometers. High field spectra were measured on CAMECA (250 MHz, 350 MHz) and BRUCKER (400 MHz, 360 MHz) instruments.

RESULTS AND DISCUSSION

Stability of anionic active centres of p*IAMS*

The living active centres observed at low temperature are slowly killed or transformed when the system is warmed to room temperature. At room temperature the u.v. spectrum of the initial carbanionic solution exhibits two main maxima at 347 and 250 nm. The 347 nm maximum only can be assigned to the carbanions as the monomer and the polymer chain absorb in the 213–292 nm and 210–270 nm ranges respectively. Upon ageing at room temperature the maxima decrease slowly while a new absorption band appears at 452 nm as shown in *Figure 1*.

As no isosbestic point is observed, this behaviour cannot be explained through the stoichiometric conversion of a single species as that for the spontaneous termination of polystyrylsodium[9].

However in the case of *p*IAMS it should be stressed that at room temperature the monomer is in equilibrium with the active chains. Thus, monomer, and units of active and terminated chains are present simultaneously in the medium and all absorb at the same wavelengths.

Either hydride abstraction leading to a double bond conjugated with the benzene ring, or a reaction of carbanions with the solvent, may be considered in order to explain this transformation as has been previously proposed for the case of poly-α-methylstyrylsodium[10,11].

This result may be related to the broad *MWD* observed[12] in the case of polymer samples which were submitted to polymerization–depolymerization runs as is usual in the course of equilibrium studies. However, this deactivation appears to be slow at room temperature and does not affect the thermodynamic values obtained from the equilibrium polymerization.

Metallation tests

In order to locate the site involved in the eventual side reactions, metallation of polymer chains of known microstructure was attempted. In the first test, a sample prepared at −78°C by anionic polymerization was brought together with sec-BuLi at 50°C in cyclohexane. The reaction was followed by u.v. spectroscopy and the very slow evolution of an absorption band with a maximum at about 340 nm was observed. The results are shown in *Figure 2*. The reaction was stopped by the addition of ethylbromide. A second experiment performed in benzene showed a maximum at 335 nm.

In both cases, the position of this new absorption peak does not allow any conclusion to be drawn about the nature of the metallation site as cumyl and benzyl derivatives absorb in the same range. The number of metallated sites was so low that irregularities could not be detected through n.m.r. studies on the resulting polymer.

Another experiment was performed in cyclohexane for 24 h at 45°C in the presence of TMEDA (sec-BuLi/TMEDA/styrene unit: 1/1/1). As previously observed, no metallation could be detected by n.m.r. In similar conditions with polystyrene models[13] and with cumene[14], it has been shown that metallation occured essentially on the *meta* and *para* positions of the benzene ring. Following this observation it might be assumed that in the case of poly-*p*-isopropyl-α-methylstyrene (PIAMS)

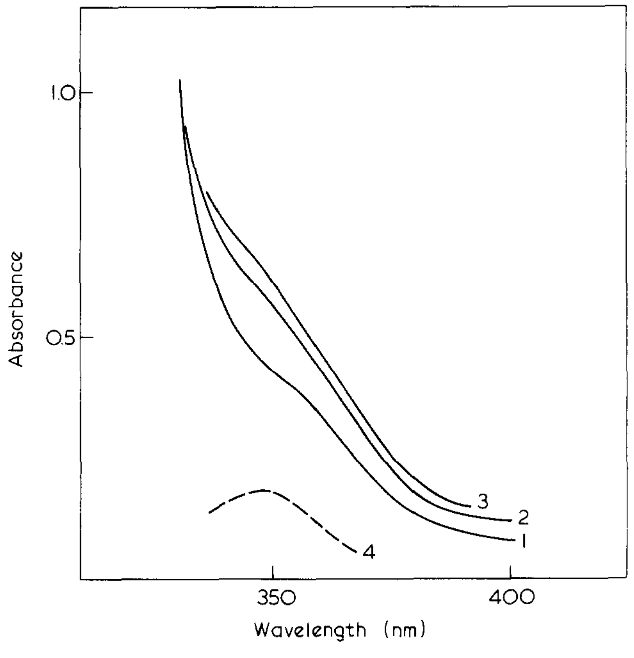


Figure 2 Metallation test with sec-BuLi in cyclohexane. Curve 1: Initial state. Curves 2 and 3: after 2 and 13 days respectively. Curve 4: difference between 3 and 1

such a reaction is substantially limited by steric hindrance.

In conclusion, the only experimental observation in support of metallation of PIAMS is the very weak absorption at 340 nm; this would indicate the presence of cumyl type carbanions. However, their concentration was too low to allow detectable irregularities in the polymer chain.

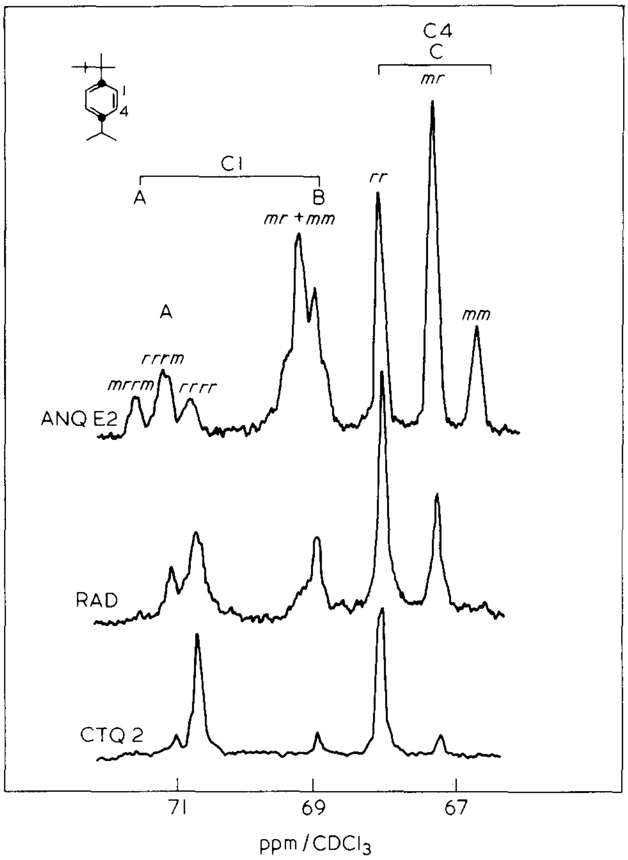
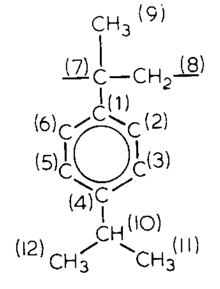


Figure 3 25 MHz ^{13}C n.m.r. spectra of quaternary aromatic carbons of PIAMS

^{13}C *n.m.r. analysis of PIAMS*

^{13}C n.m.r. spectra[15,16] of poly-α-methylstyrene (PAMS) are used for comparison for the analysis of PIAMS spectra. Carbon atoms of the polymer unit are numbered as follows:



Aromatic carbons. From the ^{13}C n.m.r. spectra of PAMS, peaks of the aromatic carbons in the 25 MHz ^{13}C n.m.r. spectra are found in the 47–50 ppm and 66–72 ppm/$CDCl_3$ ranges. Peaks of the quaternary carbons C1 and C4 are shown in *Figure 3* and the results are listed in *Table 1*.

This portion of the spectra is divided into three groups of peaks. From the areas under each group of peaks and measurements of the relaxation times shown in *Table 1*, it can be readily concluded that groups A and B are associated with one carbon atom and group C with the other carbon atom. Since the C–1 carbon atom is more sensitive to the tacticity of the chain than the C–4 carbon, the A and B groups ought to be associated with the C–1 carbon, and in turn the C–4 carbon atom being sensitive only to triad effects. Assuming a predominantly syndiotactic structure for the cationic sample[2], the C–4 peak at 68 ppm and the C–1 peak at 70.6 ppm are assigned to the *rr* triad and *rrrr* pentad respectively. The A

Table 1 25 MHz ^{13}C n.m.r. spectra: chemical shifts and relaxation time T_1 of aromatic carbons

	C–1					C–4			C–2, C–3, C–5, C–6		
δ (ppm/$CDCl_3$)	71.4	71.0	70.6	69.2	69	68.0	67.2	66.7	49.4	48.1	47.5
T_1* (s)											
Anionic		0.66		0.75		0.88	0.90	0.88	0.06		0.06
Cationic			0.66		0.59					0.06	
N.O.E.			2.0				1.9			2.0	

* T_1 determined at 25°C for 15% w/vol solutions in $CDCl_3$ (inversion recovery)

Table 2 Relative abundance of triads*

	Anionic			Cationic			Radical		
Triads	C–4	C–7	α–CH_3	C–4	C–7	α–CH_3	C–4	C–7	α–CH_3
mm	0.21	0.23	0.22	–	–	0.005	0.05	0.06	0.05
mr	0.48	0.47	0.49	0.13	0.14	0.13	0.35	0.39	0.33
rr	0.31	0.30	0.28	0.87	0.86	0.865	0.60	0.55	0.62
4 is/h^2		1.08			1.02			0.98	
P_m		0.46			0.07			0.23	

* Determined on ^{13}C n.m.r. patterns for C–4, C–7 and on ^{1}H n.m.r. patterns for α–CH_3

group may then be assigned to the syndiotactic pentads and the **B** group to the overlapping hetero- and isotactic triads *mr* and *rr*.

From the measured areas of the C-group peaks (the C–4 carbon) the relative abundance of the triads is found for three samples and the results together with the values of the ratio $4is/h^2$ are reported in *Table 2*. For each sample, the polymerization process seems to obey Bernouillian statistics with a value of $4is/h^2$ close to 1. From the values obtained for the C–4 triads, values of the probability parameter P_m listed in *Table 2* are computed and then used for the computation of the expected pentad intensities of the C–1 carbon. The results are shown in *Table 3* where a good agreement between the observed and the computed values is found.

Table 3 25 MHz ^{13}C n.m.r. spectra: microtacticity of the C–1 carbon of PIAMS

	Anionic		Cationic		Radical	
n-ads	calc.	obs.	calc.	obs.	calc.	obs.
(*mmmm*) (*mmmr*) (*rmmr*) (*mmrm*) (*rmrm*) (*mmrr*) (*rmrr*)	0.69	0.689	0.124	0.10	0.395	0.377
(*mrrm*)	0.061	0.072	0.003	ϵ	0.029	0.025
(*mrrr*)	0.151	0.156	0.106	0.11	0.209	0.186
(*rrrr*)	0.094	0.089	0.764	0.77	0.365	0.407

At high field strengths (87.5 or 100 MHz—^{13}C) C–2, C–3, C–5, C–6 signals exhibit triad effects. Spectra for cationic and anionic samples are shown in *Figure 4*. Assuming the cationic sample is mainly syndiotactic, assignment of the peaks is first determined for that sample and then applied to the anionic sample. The relative abundance of the triads corresponds to the height of the sticks shown in *Figure 4*. These results are in good agreement with those given in *Table 2* for the C–4 carbon.

The ^{13}C n.m.r. results for the aromatic carbons lead us to the conclusion that all three polymerization processes

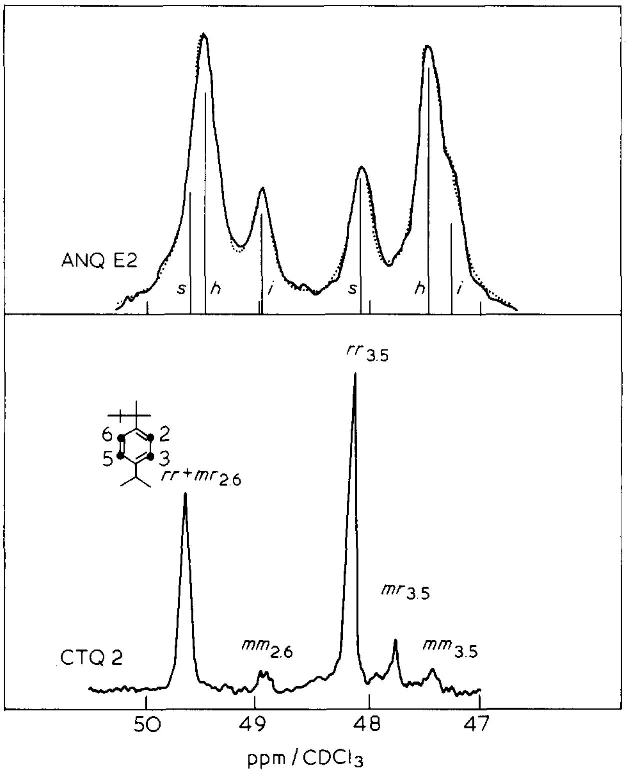


Figure 4 High field ^{13}C n.m.r. spectra of *ortho* and *meta* aromatic carbons of PIAMS (ANQE2: 87.5 MHz; CTQ2: 100.62 MHz). (——) Experimental spectrum; (· · · ·) computed spectrum; (||) sticks correspond to the relative abundance

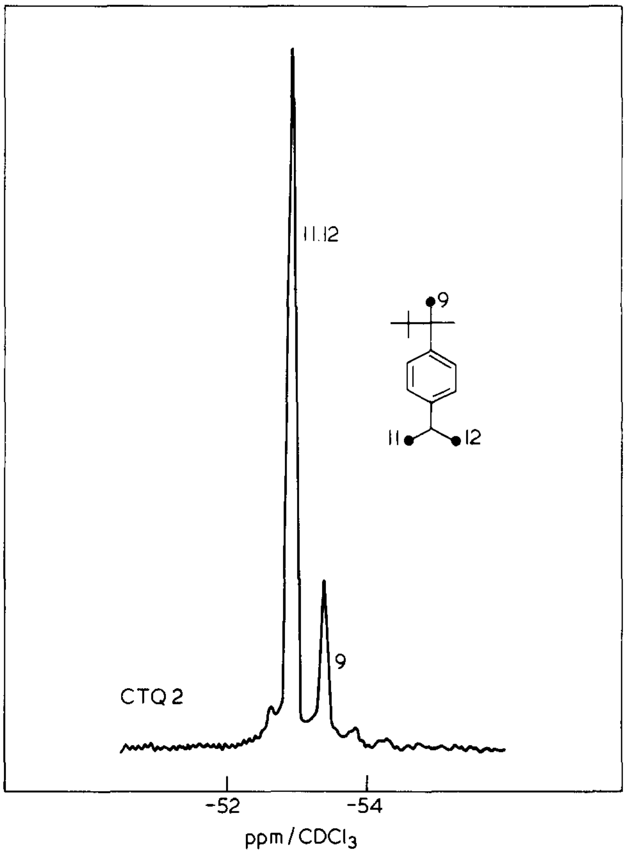


Figure 5 100 MHz ^{13}C n.m.r. spectra of α-methyl and (isopropyl)-methyl carbons of syndiotactic PIAMS

Table 4 25 MHz ^{13}C n.m.r. spectra: chemical shifts and relaxation time T_1 of aliphatic carbons

	C_{11}, C_{12}	C_9	C_{10}	C_7		C_8
δ (ppm/CDCl$_3$)	−52.8	−53.6	−43.6	−34.0	−34.2	−16.4
T_1* (s)						
Anionic	0.35		0.20		0.36	0.02
Cationic	0.35		0.20	0.43		0.02
N.O.E.	3.0		1.9	2.0		1.9

* T_1 determined at 25°C for 15% w/vol solutions in CDCl$_3$ (inversion recovery)

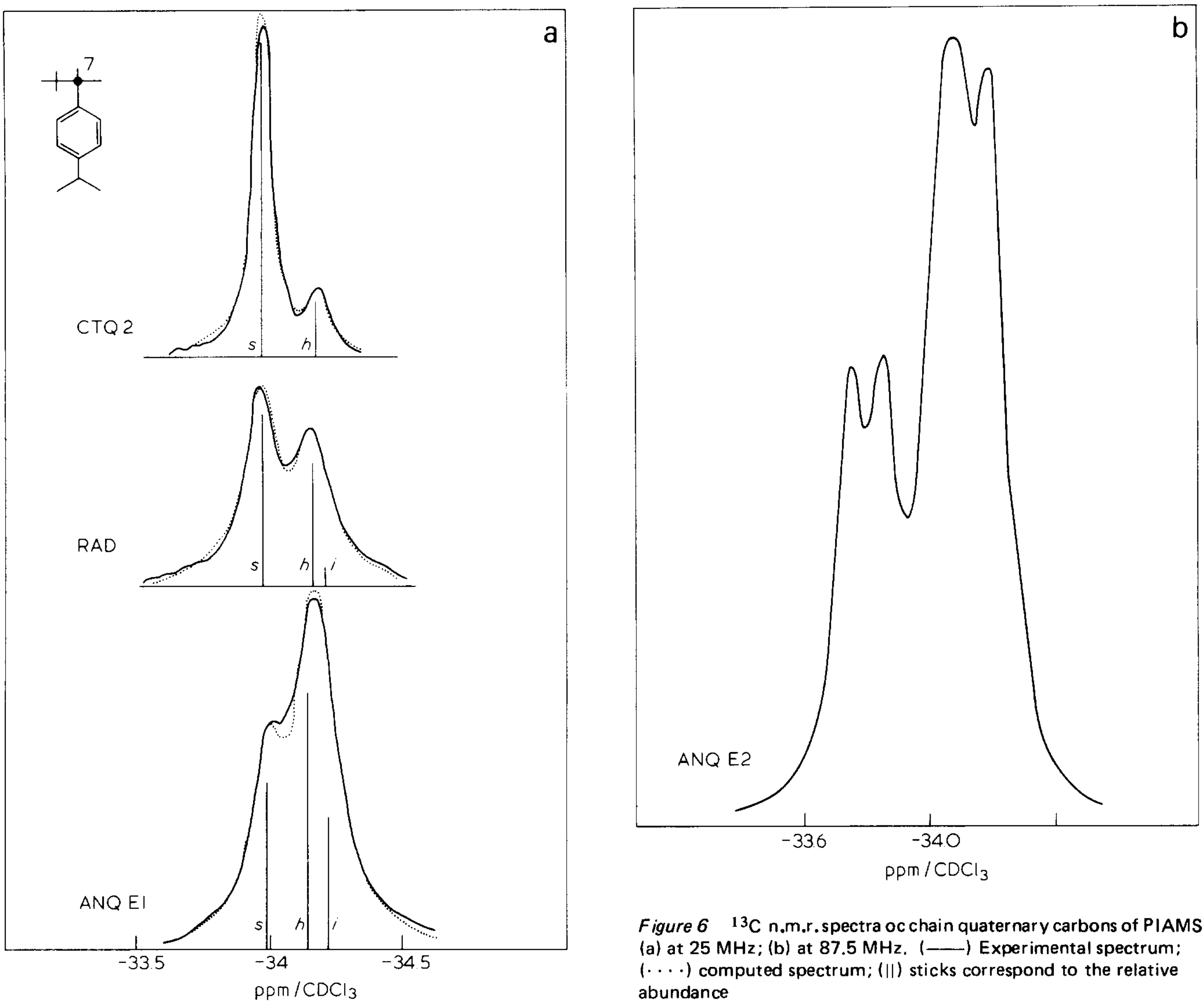


Figure 6 ^{13}C n.m.r. spectra oc chain quaternary carbons of PIAMS. (a) at 25 MHz; (b) at 87.5 MHz. (——) Experimental spectrum; (····) computed spectrum; (||) sticks correspond to the relative abundance

appear to be Bernouillian. This is rather surprising in the case of the cationic polymerization although a similar conclusion has been reached in the case of PAMS[17]. This would mean that propagation occurs mainly through free ions for both anionic and cationic systems under the present polymerization conditions.

Aliphatic carbon atoms. The chemical shifts and the relaxation parameters for the different aliphatic carbon atoms are listed in *Table 4*. Assignments were performed using partial decoupled spectra.

Isopropyl and α-methyl carbons. At 25 MHz the signals for the C–11 and C–12 carbons of the isopropyl group and those of the α-methyl carbon (C–9) overlap. However, at 100 MHz a clear separation is obtained for the syndiotactic sample as can be seen from *Figure 5*. From the relative abundance, the resonances at −52.8 and −53.6 are readily assigned to the C–11 and C–12 carbons and the C–9 carbon respectively. In the case of anionic and radical polymers, the resonance of the α methyl carbon is enlarged by stereosensitivity effects and overlaps the isopropyl methyl signals which therefore, does not allow any resolution even at high field strengths.

Chain quaternary carbon. Figure 6a shows that the quaternary C–7 carbon exhibits triad effects at 25 MHz. Starting with the cationic sample, the peaks are analysed in terms of the *rr*, *mr* and *mm* triads and the results are in good agreement with the data in *Table 2*. From *Figure 6b* it can be seen that at higher field strength a pentad effect, as reported for PAMS[18], is observed.

Chain methylene carbon. Peaks assigned to chain methylene carbons C–8 from comparison with PAMS spectra are shown in *Figure 7*. Assignment is relatively simple with the cationic sample which is predominantly syndiotactic but this is not the case with the anionic and radical polymers.

High field ^{1}H n.m.r. analysis of PIAMS

Once assignments have been made for the various carbons of the polymer chain through ^{13}C n.m.r. analysis the relative abundances of these carbons can be computed and it is found that they coincide with a regular structure in all cases. Branching sites either on the benzene ring or the isopropyl methine carbon are not detected. This may result either from the lack of sensitivity of the ^{13}C n.m.r. techniques, or from the screening of the eventual branch signals by other carbons, i.e. quaternary aromatic or chain carbons. The good agreement of the distributions obtained from the C–1, C–4, C–7 patterns with Bernouillian statistics does not support an eventual overlapping of signals due to irregularities and

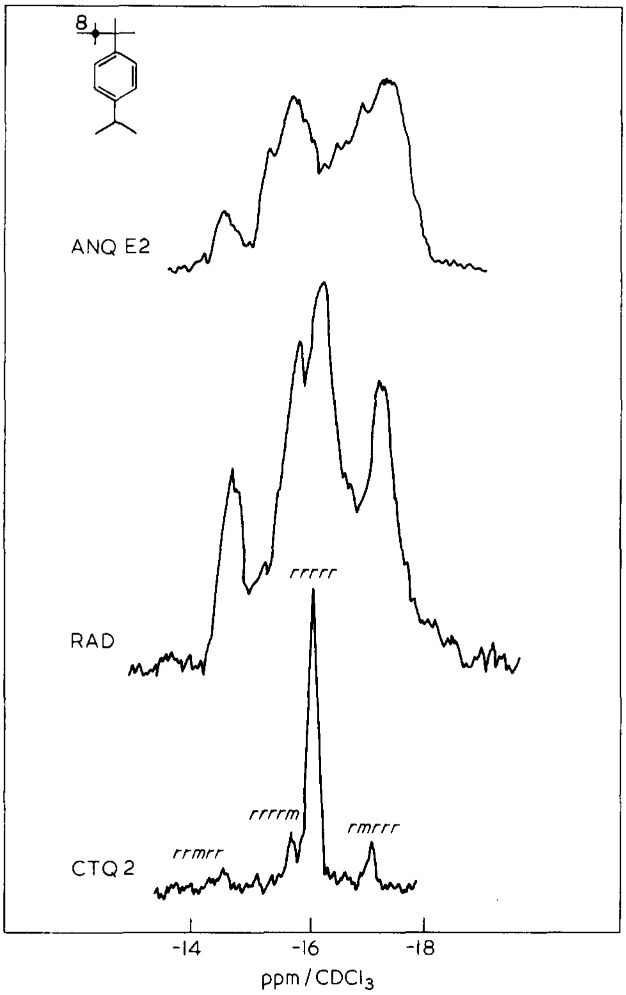


Figure 7 High field strength ^{13}C spectra of chain methylene carbons of PIAMS (ANQE2: 87.5 MHz; CTQ2: 100.62 MHz; RAD: 100.62 MHz)

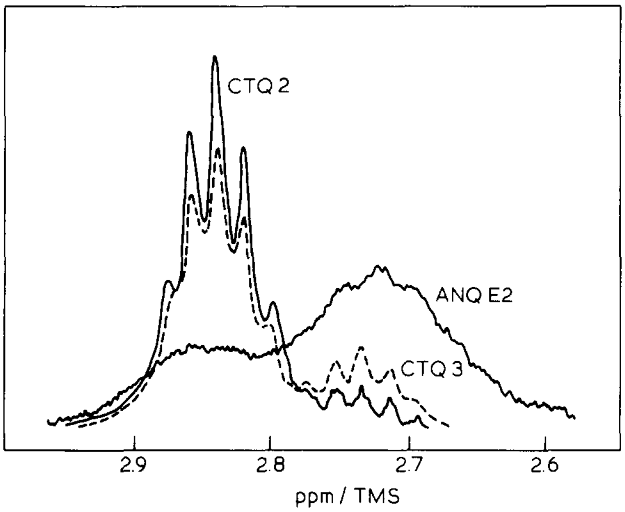


Figure 8 ^{1}H spectra of isopropyl methine protons of PIAMS (at 360 MHz for syndiotactic sample; at 250 MHz for anionic sample)

stereoregularity effects. These results do not coincide with the observed 220 MHz proton n.m.r. spectra of PIAMS reported previously[6] where irregularities in the chain were detected. Consequently proton n.m.r. spectra of PIAMS at high field were re-examined.

Isopropyl methine protons. Spectra for the syndiotactic samples measured at 360 MHz are shown in *Figure 8*. Two well resolved heptets are observed corresponding to the *rr* and *rm* triads at 2.83 and 2.73 respectively. In the case of the anionic polymer, at 250 MHz overlapping of the *rr* multiplet at 2.83 ppm with the *mr* and *mm* multiplets at 2.70 ppm leads to a very broad pattern. The tacticity roughly estimated from these spectra is close to the tacticity determined by ^{13}3 n.m.r. The resonance pattern for the isopropyl methine proton in the 2.6 to 2.9 ppm range shown in *Figure 8* differs to a considerable extent from the pattern previously reported[4] for the same range.

Isopropyl methyl protons. Isopropyl methyl protons are sensitive to triad effects as can be seen from *Figure 9*. Comparison of the spectra at 350 MHz for cationic, radical and anionic samples, starting with the cationic one, leads to *rr*, *mr* and *mm* assignments. The corresponding calculated tacticity is in good agreement with the tacticity as deduced from the pattern of the α–CH_3 protons. The low field shoulders in the 1.26 to 1.29 ppm range may be attributable to a tail of chain CH_2 protons as observed for PAMS[18]. Here again the pattern shown in *Figure 9* differs from the pattern reported previously[4] for the same protons.

Aromatic protons. The *ortho* and *meta* protons of the benzene ring are not magnetically equivalent and their spectrum is of an A_2B_2 type[19]. *rr*, *mr* and *mm* doublets for each of the *ortho* and *meta* protons may appear. This is particularly true in the case of the cationic polymer which is mainly syndiotactic and for which a good resolution, and hence a precise assignment, could be expected.

In *Figure 10*, two well resolved doublets at 6.97 and 6.95 ppm for the *rr* triad and at 6.69 and 6.67 ppm for the *mr* triad ($J = 7.9$ Hz) are observed for the syndiotactic polymer. In the case of the anionic sample where all types

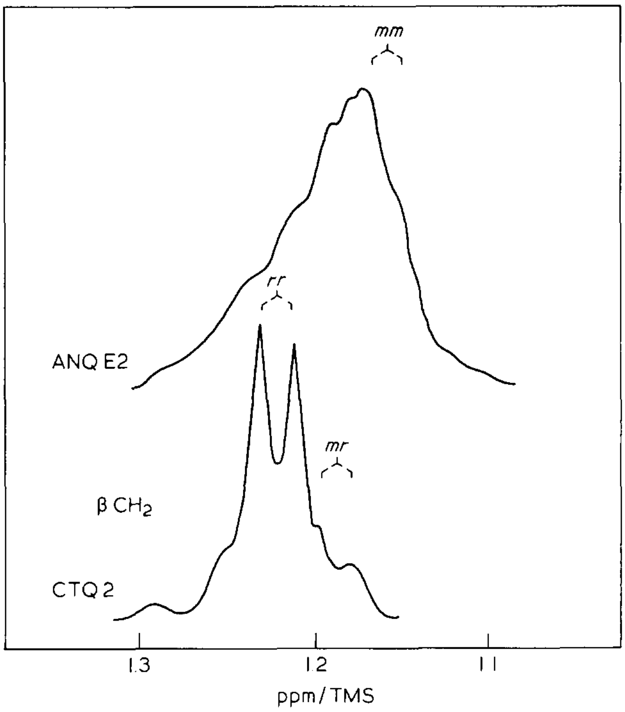


Figure 9 350 MHz ^{1}H spectra of isopropyl methyl protons of PIAMS for cationic and anionic samples

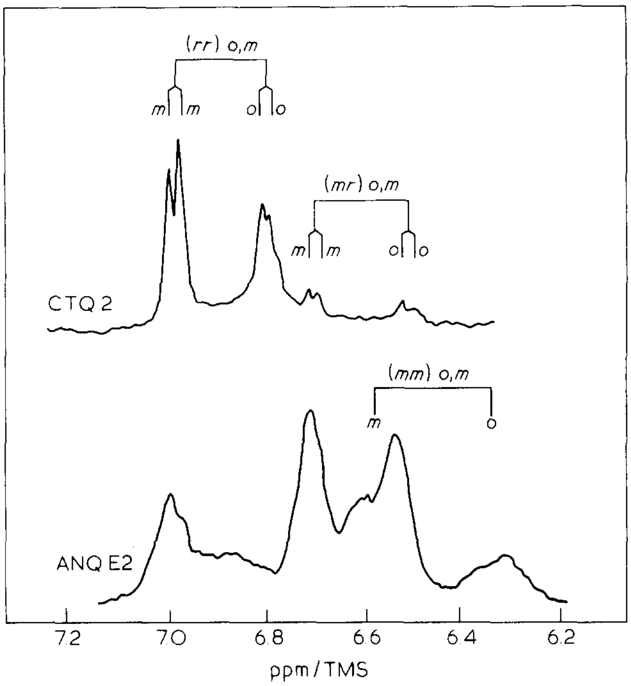


Figure 10 350 MHz ^{1}H spectra of aromatic protons of PIAMS for cationic and anionic samples

Table 5 Proton–proton ratios obtained from ^{1}H n.m.r. spectra of PIAMS

Ratio	Regular	Anionic followed by metallation	Cationic
H_B^*/CH	4	4.00	4.06
$H_B/\Sigma Al.H^{**}$	0.363	0.364	0.371

* H_B = aromatic protons
** ΣAl.H = all aliphatic protons except isopropylic CH

of stereosequences are present, peaks of the *ortho* protons are broader which might be due to a pentad splitting of this resonance. Thus, the chemical shifts of the isotactic sequences are centred around 6.6 and 6.3 ppm. The present assignments are different from the assignments previously reported[4].

From the measured areas under the peaks, the relative abundances of various protons are estimated and examples are given in *Table 5*. These results confirm values found from ^{13}C n.m.r. spectra. All analysed polymers, including PIAMS where metallation was attempted, are found to have a regular structure.

CONCLUSION

From ^{13}C and ^{1}H n.m.r. measurements at high field strengths reported above, it was found that PIAMS prepared through anionic or cationic polymerization at −78°C had a regular structure. Attempted metallation of a regular polymer with BuLi was not conclusive as only slight effects in u.v. spectra were observed. A polymer sample prepared by radical polymerization at 50°C also appeared to be regular. Anionic, cationic and radical polymerizations yielded polymers with various tacticities. ^{13}C n.m.r. spectroscopy appeared to be the most accurate method in analysing the stereoregularity of the polymers. However, owing to the multiplicity of peaks, spin–lattice relaxation times were required for some assignments. Regular polymers were used to re-examine assignments of ^{1}H n.m.r. spectra at high field strength.

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