

# Stereoregularity of various polyacrylates obtained from graft copolymers onto starch\*

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$^{13}\text{C}$  nuclear magnetic resonance spectra of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA) and poly(butyl acrylate) (PBA), obtained from graft copolymers onto amylose or amylopectin, have been studied. The spectra of the polymers were recorded with a 75 MHz spectrometer and were analysed by triad, tetrad, pentad or hexad placements. All of them follow Bernoullian statistics, with an isotactic parameter of 0.51, 0.44 and 0.43 for PMA, PEA and PBA respectively. By comparison with other values found in the literature it can be asserted that the presence of the carbohydrate has no effect on the tacticity of the grafted polymer.

(Keywords: stereoregularity; polyacrylates; graft copolymers)

## INTRODUCTION

The  $^{13}\text{C}$  nucleus is of great interest in the study of polymer chains because it permits direct observation of the molecular skeleton, and because its range of chemical shifts is very large. It therefore gives the potential for seeing finer substructure than is possible in proton spectra<sup>1</sup>.

$^{13}\text{C}$  n.m.r. spectroscopy has been applied to the investigation of the stereochemical configurations of polymers in the last few years. Thus, Jonson *et al.*<sup>2</sup> have reported on the  $^{13}\text{C}$  n.m.r. spectra of several vinyl polymers. Peat and Reynolds<sup>3</sup> have reported on the  $^{13}\text{C}$  n.m.r. spectra of the stereoregular poly(methyl methacrylate). Matsuzaki *et al.*<sup>4,5</sup> have reported on the  $^1\text{H}$  n.m.r. spectra of polyacrylates and their deuterated polymers and determined their stereoregularity. These authors have also reported on the  $^{13}\text{C}$  n.m.r. spectra of some polyacrylates<sup>6</sup>.

In this paper we present the  $^{13}\text{C}$  n.m.r. spectra of polyacrylates obtained from the hydrolysis of their graft copolymers onto amylose and amylopectin. We have analysed the peaks by triad, tetrad, pentad or hexad placements.

## EXPERIMENTAL

### Materials

The amylose (linear starch fraction) was potato amylose V and the amylopectin (branched starch fraction) was potato amylopectin UG, both AVEBE-Holland production material.

Methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA), supplied by Merck, were purified by successive washing with dilute aqueous sodium bisulfite, water, sodium chloride saturated solution and water. After drying over sodium sulfate, they were distilled under suitable conditions.

### Polymerization

The monomers were polymerized in the presence of the starch fractions (amylose and amylopectin) by the ceric ion redox initiation method in a water dispersion at 30°C, under nitrogen. The results of these graft copolymerizations have been given elsewhere<sup>7</sup>. The grafting was carried out for various reaction times. Afterwards the reaction products were recovered by filtration and carefully washed and dried under vacuum until constant weight. The pure graft copolymer was obtained after removing the non-grafted acrylic polymer by extraction with Soxhlet equipment; the unreacted carbohydrate was removed by dissolving in dilute alkali solution.

The homopolyacrylates were separated from the carbohydrate by an acid hydrolysis process with perchloric acid, as described before<sup>7</sup>. Then, they were all purified by a solution/precipitation method.

### N.m.r. measurements

PMA was dissolved in d-acetone, PEA in d-chloroform, and PBA in d-benzene, to give them all a solution concentration of 0.1 g ml<sup>-1</sup>. N.m.r. measurements were carried out at temperatures of 20–25°C by means of a Varian-VXR 300 spectrometer operating at 75.4 MHz. Chemical shifts are quoted in ppm relative to tetramethylsilane (TMS) at 0 ppm. The spectral range was 16 588 Hz (200 ppm); in general, good spectra were produced by using 20 000–50 000 transients, a pulse width of 14  $\mu\text{s}$ , 1 s acquisition time and a delay time of 3 s, and 32 k data points for Fourier transform.

The carbon signal assignment was established in some cases by applying the DEPT pulse sequence.

## RESULTS AND DISCUSSION

### Stereoregularity of poly(methyl acrylate)

A typical  $^{13}\text{C}$  n.m.r. spectrum is shown in Figure 1, together with expansions of the  $\alpha$  and  $\beta$  carbon signals. All the spectra obtained for this polymer are those of

\* Dedicated to the memory of the late Dr G. M. Guzmán and Dr M. Valero

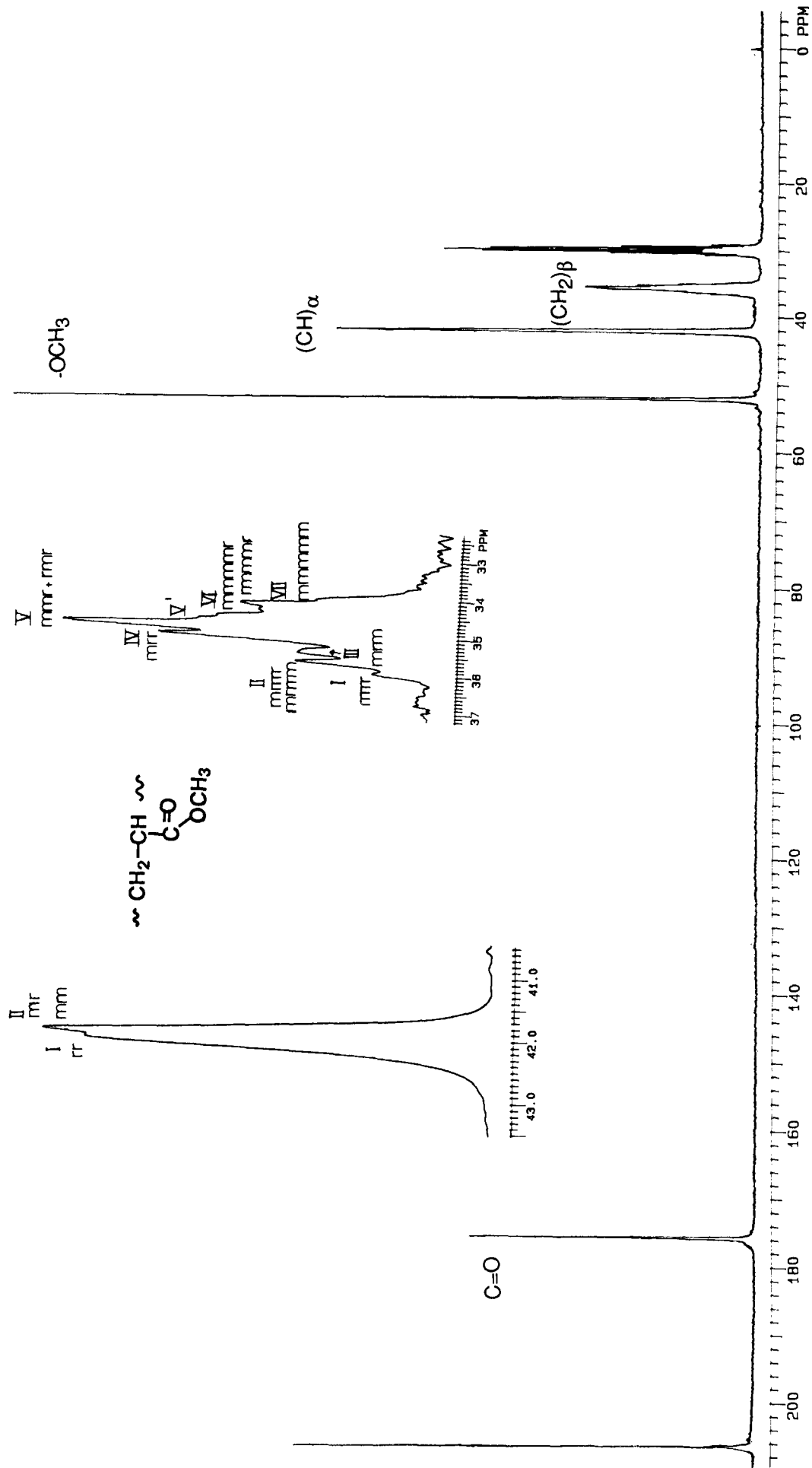


Figure 1  $^{13}\text{C}$  n.m.r. spectrum of the PMA grafted chains in d-acetone after hydrolysis of its graft copolymer onto amylose

conventional PMA polymerized by a radical mechanism. The ratio of isotactic (*mm*) to heterotactic (*mr* or *rm*) to syndiotactic (*rr*) triads can be obtained from  $C_\alpha$  signal. This ratio is about 26:50:24, that expected if the generation of configurational sequences follows Bernoullian statistics with a probability of *meso* placement ( $P_m$ ) equal to 0.51. This value is very close to that obtained by Matsuzaki *et al.*<sup>5</sup>, where  $P_m = 0.49$ , that is, the configuration is random and gives a stereostructure similar to those obtained with other radical polymerization methods<sup>5</sup>.

The configurational triad and hexad fractions obtained from the <sup>13</sup>C n.m.r. spectrum are given in Table 1. Although in the literature only tetrad placements from the  $\beta$ -carbon signal are described<sup>6</sup>, the use of a high-frequency spectrometer has allowed us to study hexad placements from the  $\beta$ -carbon signal and triad placements from the  $\alpha$ -carbon signal. Thus, seven of the ten possible hexad peaks are resolved in the  $C_\beta$  spectrum. Assignments are based on triad probabilities on the assumption that the sample fits Bernoullian statistics. The *mmmmmm* signal of the methylene carbon appears at the uppermost field in the spectrum, which agrees with the study of Matsuzaki *et al.* from dimer model compounds<sup>6</sup>.

Stereoregularity of poly(ethyl acrylate)

Figure 2 shows the n.m.r. spectrum obtained for the PEA, together with expansions of the  $C_\alpha$ ,  $C_\beta$  and the branch methylene carbon signal. Assignments are based on the literature<sup>8</sup> and corroborated by a DEPT experiment.

We have not found any tacticity assignments for this polymer in the literature. The  $P_m$  value of this polymer was determined from the signal of the branch methylene which splits clearly into three peaks. So, we can say that the PEA obtained from the radical graft copolymerization onto amylose and amylopectin is an atactic polymer,  $P_m = 0.44$ .

The  $\beta$ -methylene resonance appears to be the most sensitive to stereochemical configuration. At least eight peaks can be distinguished, so the hexad sequences can be resolved and are listed in Table 2. These assignments are in good agreement with those attributed to the  $\beta$ -methylene of the PMA, and fit Bernoullian statistics.

Table 1 PMA triad and hexad fractions from the  $C_\alpha$  and  $C_\beta$ , respectively

PMA peak	Signal	$\delta$ (ppm)	Conf.	Exp.	Calc. ( $P_m = 0.50_7$ )
$C_\alpha$	(I)	42.08 <sub>9</sub>	<i>rr</i>	0.24 <sub>3</sub>	0.24 <sub>3</sub>
	(II)+(II')	41.93 <sub>2</sub>	$2 \times mr + mm$	0.74 <sub>3</sub>	0.75 <sub>7</sub>
$C_\beta$	(I)	36.01 <sub>4</sub>	<i>mrrrm</i>	0.03 <sub>0</sub>	0.03 <sub>1</sub>
	(II)	35.73 <sub>4</sub>	$2 \times mrrrr$ + <i>rrrrr</i>	0.08 <sub>3</sub>	0.08 <sub>9</sub>
	(III)	35.50 <sub>4</sub>	<i>mrm</i>	0.12 <sub>5</sub>	0.12 <sub>8</sub>
	(IV)	35.14 <sub>6</sub>	$2 \times mrrr$	0.24 <sub>6</sub>	0.24 <sub>8</sub>
	(V)+(V')	34.93 <sub>3</sub>	$2 \times mnr$ + <i>rmr</i>	0.37 <sub>3</sub>	0.38 <sub>0</sub>
	(VI)	34.27 <sub>5</sub>	$2 \times mmmmr$ + <i>rmmmr</i>	0.10 <sub>0</sub>	0.09 <sub>7</sub>
	(VII)	34.12 <sub>1</sub>	<i>mmmmmm</i>	0.04 <sub>3</sub>	0.03 <sub>3</sub>

Table 2 PEA triad and hexad fractions from the  $-OCH_2$  and  $C_\beta$ , respectively

PEA peak	Signal	$\delta$ (ppm)	Conf.	Exp.	Calc. ( $P_m = 0.43_8$ )
$C_\beta$	(I)	36.09	<i>mrrrm</i>	0.04 <sub>8</sub>	0.03 <sub>4</sub>
	(II)	35.87	<i>mrrrr(rrrrm)</i>	0.08 <sub>8</sub>	0.08 <sub>7</sub>
	(III)	35.65	<i>rrrrr</i>	0.06 <sub>8</sub>	0.05 <sub>6</sub>
	(IV')	35.22	<i>mrm</i>	0.08 <sub>7</sub>	0.10 <sub>8</sub>
	(IV)	35.01	<i>mrr(rrm)</i>	0.24 <sub>9</sub>	0.27 <sub>7</sub>
	(V)	34.83	<i>mrm</i>	0.21 <sub>2</sub>	0.21 <sub>6</sub>
	(VI)	34.45	<i>mrm</i>	0.12 <sub>2</sub>	0.13 <sub>8</sub>
	(VII)	34.31	<i>mmmmr</i> ( <i>rmmmmm</i> ) + <i>rmmmr</i>	0.08 <sub>8</sub>	0.07 <sub>0</sub>
	(VIII)	34.08	<i>mmmmmm</i>	0.04 <sub>6</sub>	0.01 <sub>6</sub>
$-OCH_2$	(I)	59.97	<i>mm</i>	0.19 <sub>2</sub>	0.19 <sub>2</sub>
	(II)	60.32	<i>mr(rm)</i>	0.49 <sub>2</sub>	0.49 <sub>2</sub>
	(III)	60.25	<i>rr</i>	0.31 <sub>6</sub>	0.31 <sub>6</sub>
$-CH_2$		41.55	<i>mm</i>	0.19 <sub>2</sub>	0.19 <sub>2</sub>
		41.87	<i>mr(rm) + rr</i>	0.80 <sub>8</sub>	0.80 <sub>8</sub>

Table 3 PBA hexad fractions from  $C_\beta$

PBA peak	Signal	$\delta$ (ppm)	Conf.	Exp.	Calc. ( $P_m = 0.43_5$ )
$C_\beta$	(I)	37.55	<i>mrrrm</i>	0.03 <sub>9</sub>	0.03 <sub>4</sub>
	(II)	37.30	<i>mrrrr(rrrrm)</i>	0.09 <sub>3</sub>	0.08 <sub>9</sub>
	(III)	37.11	<i>rrrrr</i>	0.05 <sub>7</sub>	0.05 <sub>7</sub>
	(IV')	36.43	<i>mrr(rrm) + mrm</i>	0.36 <sub>8</sub>	0.38 <sub>5</sub>
	(V)	36.32	<i>mnr(rmm) + mnr</i>	0.34 <sub>8</sub>	0.35 <sub>3</sub>
	(VI)	35.90	<i>rmmmr</i>	0.03 <sub>4</sub>	0.02 <sub>6</sub>
	(VII)	35.79	<i>rmmmmm(rmmmr)</i>	0.04 <sub>8</sub>	0.04 <sub>0</sub>
	(VIII)	35.63	<i>mmmmmm</i>	0.01 <sub>3</sub>	0.01 <sub>6</sub>

Table 4 Probability of *meso* placement ( $P_m$ ) of various polyacrylates

Polymer	$P_m$
PMA	0.50 <sub>7</sub>
PEA	0.43 <sub>8</sub>
PBA	0.43 <sub>5</sub>

Stereoregularity of poly(butyl acrylate)

The <sup>13</sup>C n.m.r. spectrum of the PBA obtained by hydrolysing its graft copolymer on amylose, is reproduced in Figure 3. As in the two preceding cases, the signal of the carbonyl carbon is not affected by the stereoregularity of the polymer. The  $\beta$ -methylene carbon signal is split into peaks due to hexad placements; only splitting due to tetrad placements is described in the literature<sup>8</sup>. These resonances are divided into eight groups and are assigned as shown in the expansion of Figure 3. The calculated intensities for Bernoullian statistics are shown in Table 3, and almost coincide with the observed tacticities.

The obtained polymer is again a heterotactic polymer with an isotactic:heterotactic:syndiotactic triad ratio of 19:49:32. Thus, the  $P_m$  value is 0.43.

In Table 4 the  $P_m$  values of the three polyacrylates are listed.

CONCLUSIONS

The polymers obtained from the graft copolymers onto starch, separated by an acid hydrolysis process, show

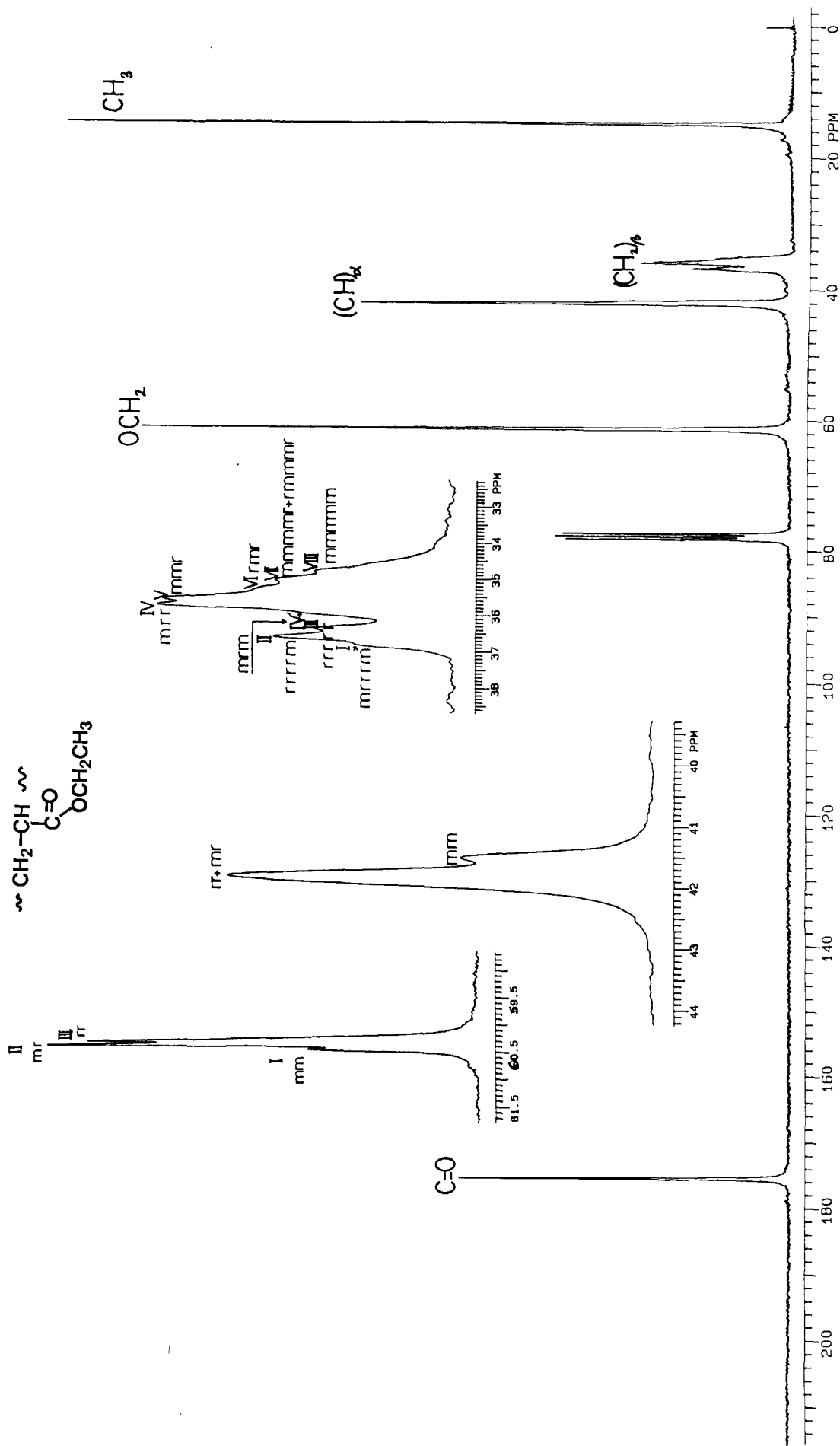


Figure 2  $^{13}\text{C}$  n.m.r. spectrum of the PEA grafted chains in d-chloroform after hydrolysis of its graft copolymer onto amylopectin

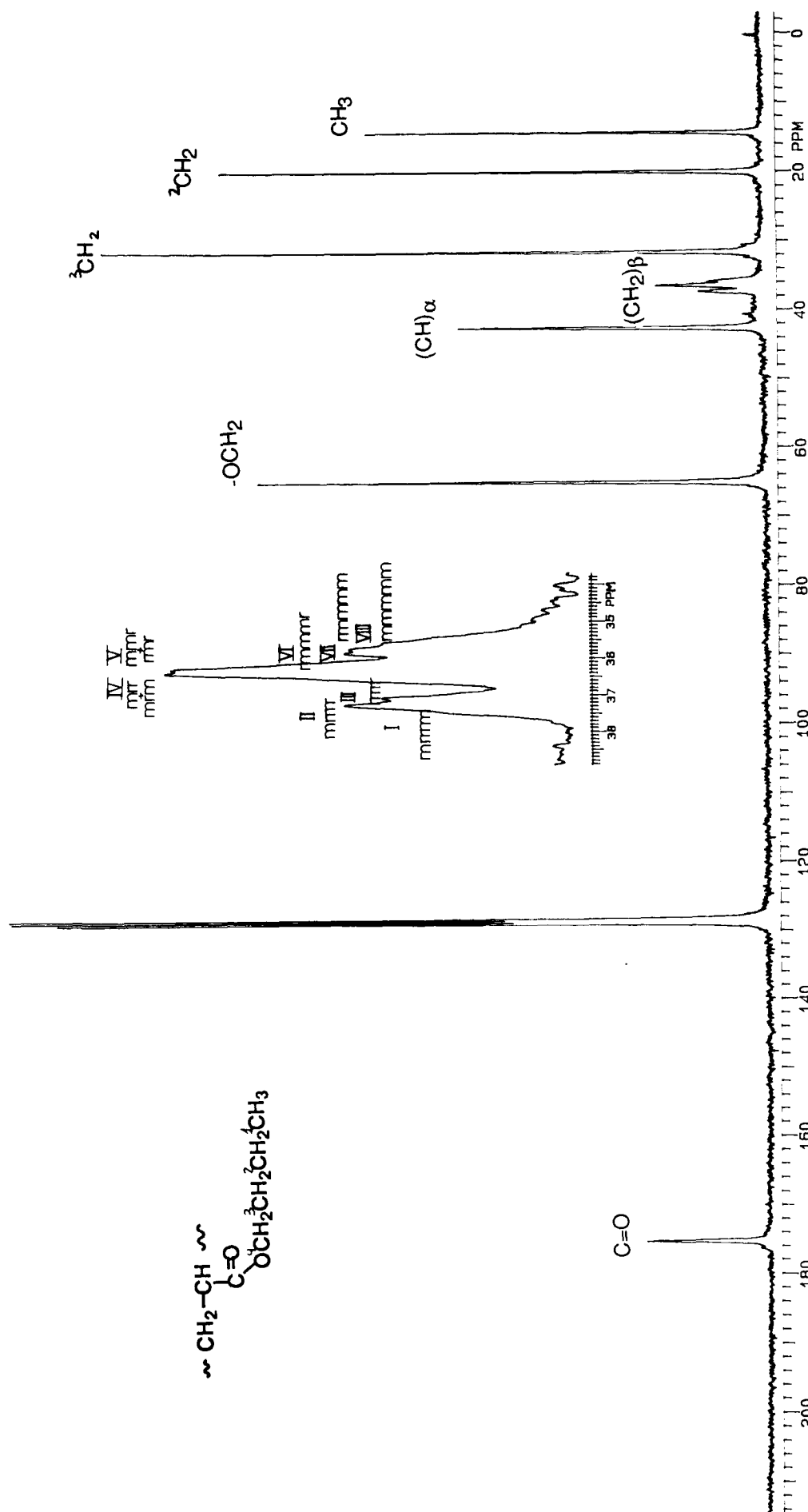


Figure 3  $^{13}\text{C}$  n.m.r. spectrum of the PBA grafted chains in d-benzene after hydrolysis of its graft copolymer onto amylose

very well resolved  $^{13}\text{C}$  n.m.r. spectra. The high sensitivity of the spectrometer utilized has permitted the resolution of a higher number of tactic sequences than found in the literature. From these spectra, it can be concluded that they are all heterotactic random polymers with a slight bias towards syndiotacticity in the PEA and PBA cases. We can also observe that the isotacticity decreases slowly as the alkyl size of the acrylic ester increases.

On the other hand, the three polymers analysed show typical spectra of polyacrylates synthesized by a radical initiation method, therefore it can be concluded from the n.m.r. spectra that the propagation steps in this polymerization process are of a conventional radical type, and are uninfluenced, from the steric point of view, either by the nature of the polymerization medium or by the presence of the initiator and of the carbohydrate. In addition, the spectra of the grafted chains obtained at different reaction times are identical, which means that as the grafting advances and the number of grafted chains increases, the steric hindrance produced does not affect the tacticity of the growing chain.

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