Determination of the tacticity of polymethacrylates obtained from graft copolymers*

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^{13}C n.m.r. spectroscopy has been used to analyse copolymers of hydrophobic and hydrophilic polymethacrylates on starch. The analysis was carried out after releasing the grafted chains by hydrolysis. They were all syndiotactic as expected from a radical initiation method. Triad, tetrad, pentad or hexad signals were resolved.

(Keywords: polymethacrylates; tacticity; graft copolymers)

INTRODUCTION

In a previous paper[1] we reported the ^{13}C n.m.r. measurements of the stereoregularity of various polyacrylates. These polymers were obtained by acid hydrolysis of the graft copolymers formed on starch fractions. Using this technique we have obtained new information on these copolymers.

In this paper results are given for the stereoregularity of the following grafted polymethacrylates obtained by acid hydrolysis: poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly(hydroxyethyl methacrylate) (PHEMA) and poly(hydroxypropyl methacrylate) (PHPMA).

EXPERIMENTAL

Materials

The amylose (lineal starch fraction) was potato amylose V and the amylopectin (branched starch fraction) was potato amylopectin UG (both from AVEBE-Holland). All the monomers were supplied by Merck.

MMA, EMA and BMA were washed with dilute alkali, sodium chloride and water and distilled before use.

HEMA was carefully purified[2] to eliminate impurities. HPMA is mainly 2-HPMA but is usually supplied mixed with the 1-HPMA isomer. The impurities were removed by a procedure similar to that used for HEMA.

Polymerization

The reactions were carried out under nitrogen in a three-necked flask equipped with stirrer, and immersed in a constant temperature bath (30°C). The procedure was to disperse the starch fraction (2 g) in water (290 ml) and deoxygenate the stirred mixture by bubbling a slow stream of nitrogen for 30 min. Monomer (0.0469 mol) was added and after 5 min initiator solution (10 ml, 0.1 M solution of ceric ammonium nitrate in 1 N nitric acid) was added. The products were separated by filtration and washed. The amylose graft copolymers were then extracted with dilute alkali to remove any ungrafted amylose. However there was no ungrafted amylopectin (or $<5\%$) because of its high molecular weight, so in these cases alkali extraction was omitted. Afterwards, the sample was extracted with adequate solvent to remove the homopolymer produced.

To obtain acrylic chains free from carbohydrate, the graft copolymers were hydrolysed with perchloric acid (60%) after previous swelling in glacial acetic acid. Then, the acrylic polymer chains free from carbohydrate were precipitated by adding the solution in acetic acid to an ice–water system. However, this hydrolysis system was inadequate for the HEMA and HPMA graft copolymers[3], and so their hydrolysis was carried out in a 1 N HCl medium, by refluxing for 6 h. The acrylic polymer was recovered by filtration and then purified by a solution-precipitation method.

N.m.r. measurements

The ^{13}C n.m.r. spectra were measured with a Varian VXR 300 spectrometer operating at 75.4 MHz. The samples were examined as 15–20% (w/v) in a suitable solvent at 20°C using tetramethylsilane as internal reference. The conditions used were as follows: pulse width, 14 μs; acquisition time 1 s; delay time, 3 s; spectral width, 16000 Hz; 32 K data points for Fourier transform. The spectra were produced by using 20000–50000 transients.

The heteronuclear 2D experiment (HETCOR) and the DEPT pulse sequence were carried out using the standard sequences supplied by Varian.

For the PMMA, PEMA and PBMA, *d*-chloroform was used as solvent. For PHEMA *d*-pyridine was used and for PHPMA a *d*-dimethyl sulphoxide/*d*-chloroform solvent mixture was used to obtain the best resolution.

*This paper is dedicated to the memory of Professor Martín Guzmán, sadly deceased 22 August 1991
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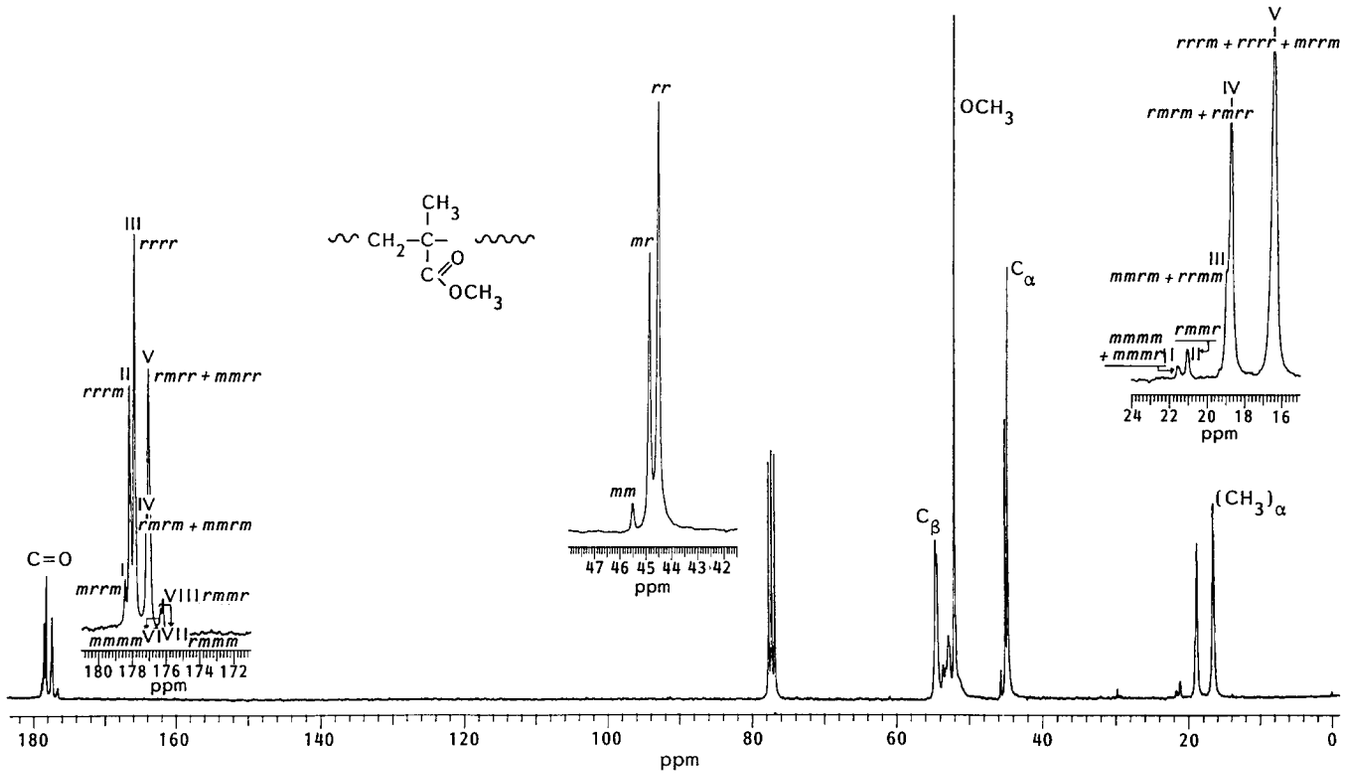

Figure 1 ^{13}C n.m.r. spectrum of PMMA in *d*-chloroform

Table 1 Assignments of the stereoregular sequence fractions of PMMA

Assignment		δ (ppm)	Experimental	Calculated ($P_m = 0.20_0$)
	mm	45.43	0.04_0	0.04_0
C_α	*mr*(*rm*)	44.79	0.33_3	0.32_0
	rr	44.44	0.63_2	0.64_0
	(I) *rmmm*(*mmmr*)*mmmm*	21.50	0.01_6	0.01_5
	(II)*rmmr*	20.98	0.02_1	0.02_6
$(CH_3)_\alpha$	(III) 2 × (*mmrm* + *rrmm*)	18.85	0.07_3	0.06_5
	(IV) 2 × (*rmrm* + *rmrr*)	18.63	0.24_8	0.25_5
	(V) *rr*	16.37	0.63_3	0.64_0
	(I) *mrrm*	178.35	0.02_7	0.02_6
	(II) *mrrr*(*rrrm*)	178.06	0.20_8	0.20_5
	(III) *rrrr*	177.77	0.41_8	0.41_0
C=O	(IV) 2 × (*mmrm* + *rrmm*)	177.07	0.07_2	0.06_5
	(V) 2 × (*rmrm* + *rmrr*)	176.92	0.24_8	0.25_6
	(VI) *mmmm*	176.30	0.00_2	0.00_2
	(VII) *rmmm*	176.24	0.00_9	0.01_3
	(VIII) *rmmr*	176.12	0.02_1	0.02_6

In all cases the samples were prepared by dissolving ~100 mg ml^{-1} solvent.

RESULTS AND DISCUSSION

Stereoregularity of PMMA

Figure 1 shows a typical spectrum of PMMA in *d*-chloroform, together with the expansions of the carbonyl, α-methyl and quaternary carbons. The spectrum is similar to those of a radically obtained PMMA analysed by other authors[4,5]. The ratios of isotactic (*mm*) to heterotactic (*mr*, *rm*) to syndiotactic (*rr*) triads can be obtained either from the α-methyl signals or from the quaternary carbon signals. Their ratio is 4:33:63 as expected if the generation of configurational sequences follows Bernoullian triad statistics with a probability of *meso* placements P_m equal to 0.20; this value is similar to that of a radically obtained PMMA analysed by Pham *et al.* ($P_m = 0.22$)[6]. This same ratio is also reflected in the relative proportions of the three *rr* centred pentads obtained from the carbonyl signals, thus confirming the value of P_m. Therefore, this

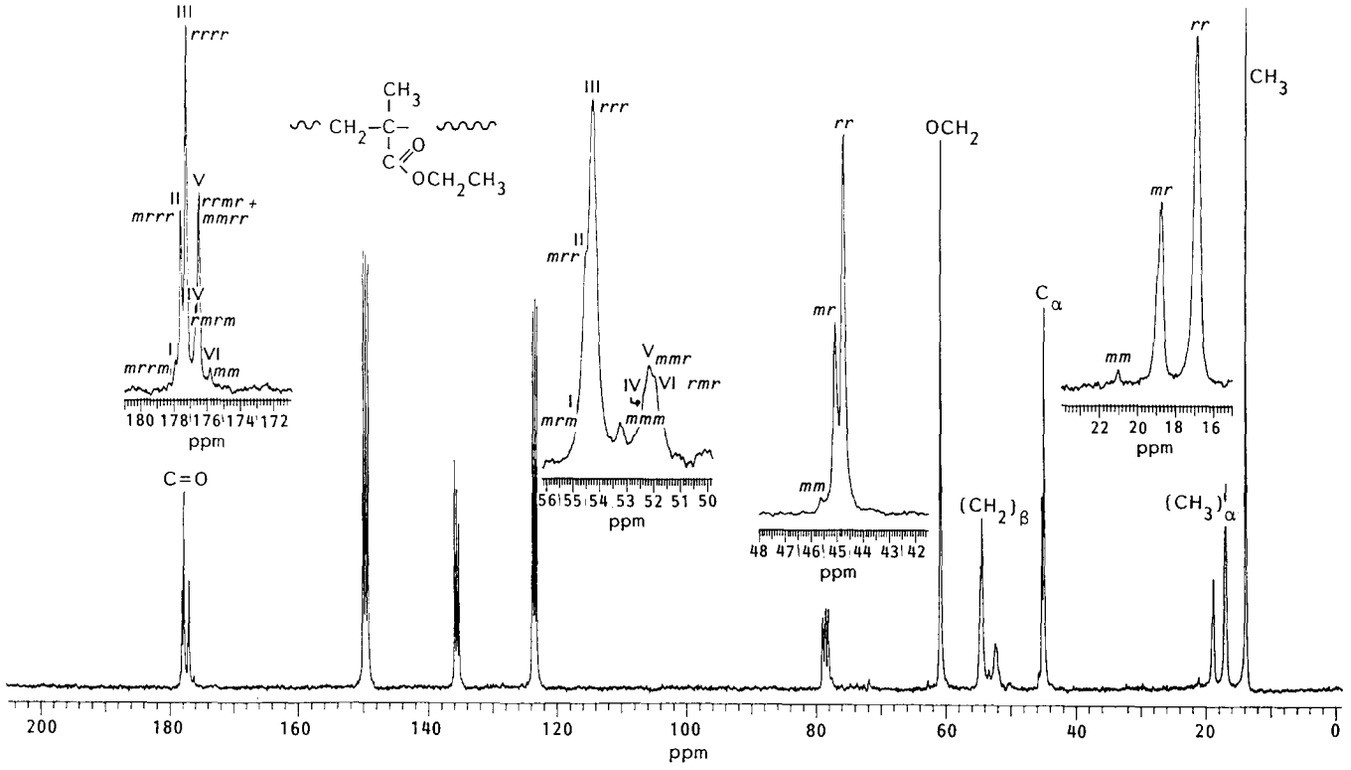

Figure 2 ^{13}C n.m.r. spectrum of PEMA in *d*-chloroform/*d*-pyridine

Table 2 Assignments of the stereoregular sequence fractions of PEMA

Assignment		δ (ppm)	Experimental	Calculated ($P_m = 0.19_0$)
	(I) *mm*	20.75	0.03_6	0.03_6
$(CH_3)_\alpha$	(II) *mr(rm)*	18.45	0.30_0	0.30_8
	(III) *rr*	16.57	0.66_3	0.65_6
	(I) *mm*	45.58	0.03_6	0.03_6
C_α	(II) *mr(rm)*	45.01	0.32_5	0.30_8
	(III) *rr*	44.65	0.64_5	0.65_6
	(I) *mrrm*	178.11	0.02_7	0.02_4
	(II) *mrrr(rrrm)*	177.79	0.21_2	0.20_2
C=O	(III) *rrrr*	177.47	0.41_4	0.42_8
	(IV) 2 × (*rmrm* + *mrmm*)	176.91	0.06_4	0.05_9
	(V) 2 × (*rrmr* + *mmrr*)	176.73	0.24_6	0.25_0
	(I) *mrm*	54.62	0.03_0	0.02_9
	(II) *mrr(rrm)*	54.42	0.24_3	0.24_9
β-CH_2	(III) *rrr*	54.11	0.53_4	0.53_1
	(IV) *mmm*	52.25	0.01_6	0.00_7
	(V) *mmr(rmm)*	52.03	0.06_9	0.05_8
	(VI) *rmr*	51.79	0.11_4	0.12_5

corroborates that the PMMA grafted chains are syndiotactic-rich, as observed by i.r. spectroscopy[7]. The triad and pentad fractions[6], obtained from the ^{13}C n.m.r. spectrum, are given in *Table 1*.

Stereoregularity of PEMA

Figure 2 shows the ^{13}C n.m.r. spectrum of PEMA in *d*-chloroform, together with the expansions of the signals of the quaternary, α-methyl, carbonyl and β-methylene carbons. As seen for PMMA, the ratio of the isotactic to heterotactic to syndiotactic triads can be obtained either from the signal of the α-methyl carbon or from that of the quaternary carbon. This ratio is 4:31:66, as deduced by applying Bernoullian statistics with a P_m value of 0.19. This value is similar to that of a radically obtained PEMA analysed by Pham *et al.* ($P_m = 0.20$)[6]. This parameter is confirmed from the ratio among the triads[6] and the pentads. The carbonyl pentads have been studied following the same assignments as for PMMA[8]. These results are summarized in *Table 2*.

Stereoregularity of PBMA

Figure 3 shows the ^{13}C n.m.r. spectrum of PBMA[9]. Also shown are the expansions of the peaks of the

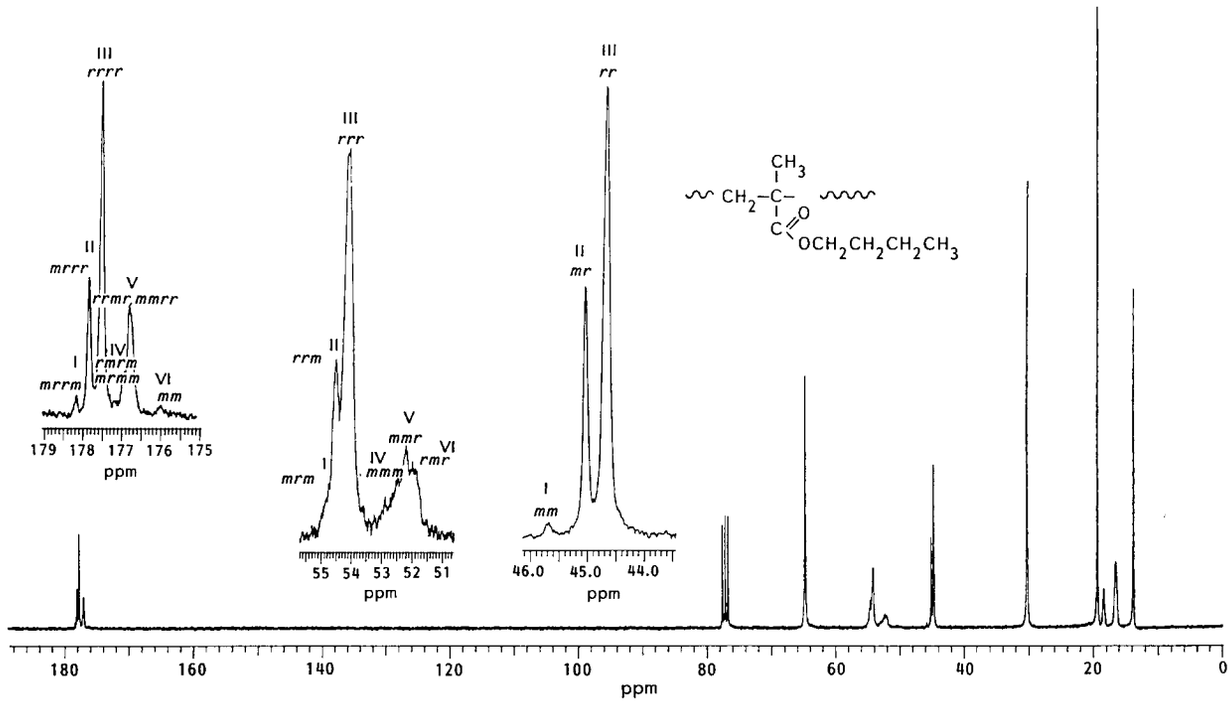

Figure 3 ^{13}C n.m.r. spectrum of PBMA in *d*-chloroform

Table 3 Assignments of the stereoregular sequence fractions of PBMA

Assignment		δ (ppm)	Experimental	Calculated ($P_m = 0.14_5$)
	(I) *mm*	45.68	0.02_1	0.02_1
C_α	(II) *mr(rm)*	45.03	0.25_3	0.24_8
	(II) *rr*	44.67	0.72_6	0.73_1
	(I) *mrrm*	178.17	0.01_4	0.01_5
	(II) *mrrr(rrrm)*	177.84	0.18_3	0.18_1
	(III) *rrrr*	177.51	0.54_9	0.53_4
C=O	(IV) 2 × (*rmrm* + *mrmm*)	177.20	0.03_0	0.03_6
	(V) 2 × (*rrmr* + *mmrr*)	176.79	0.20_1	0.21_2
	(VI) *mm*	176.00	0.02_3	0.02_1
	(I) *mrm*	55.22	0.02_1	0.01_8
	(II) *mrr(rrm)*	54.54	0.21_2	0.21_2
	(III) *rrr*	54.12	0.60_1	0.62_5
β-CH_2	(IV) *mmm*	52.89	0.00_7	0.00_3
	(V) *mmr(rmm)*	52.23	0.05_3	0.03_6
	(VI) *rmr*	52.03	0.10_7	0.10_6

quaternary, carbonyl and methylene carbons. In this case, the ratio for the different triads has been obtained from the quaternary carbon signal. This ratio is 2:25:73, as expected for Bernoullian statistics with $P_m = 0.14$, which is slightly different from that obtained by Pham *et al.* ($P_m = 0.17$)[6]. The same ratio can be observed from the analysis of the carbonyl and β-carbon peaks, as seen in *Table 3*.

As in the two preceding cases, the acrylic polymer obtained by means of a graft copolymerization initiated by Ce(IV) ion, is a typical syndiotactic polymer, as are those obtained by other radical initiation methods.

Stereoregularity of PHEMA

The spectrum of the PHEMA obtained from the hydrolysis of its graft copolymer onto amylopectin is shown in *Figure 4*. The assignment of the different peaks was made by using the HETCOR technique, and by comparison with the preceding polymethacrylates[10]. *Table 4* shows the assignments and calculations from applying Bernoullian statistics with a P_m value of 0.13.

By comparing PHEMA and PEMA it can be noticed that the difference between the values of their syndiotactic triads is higher than expected if only steric hindrance is taken into account. In the case of PHEMA, we think that the carbonyl group can closely approach the hydroxyl group of the adjacent unit forming a hydrogen bond interaction, and thereby increasing the tendency to form syndiotactic sequences.

Stereoregularity of PHPMA

Figure 5 shows the spectrum of the polymer obtained by first grafting a mixture of 1- and 2-HPMA onto

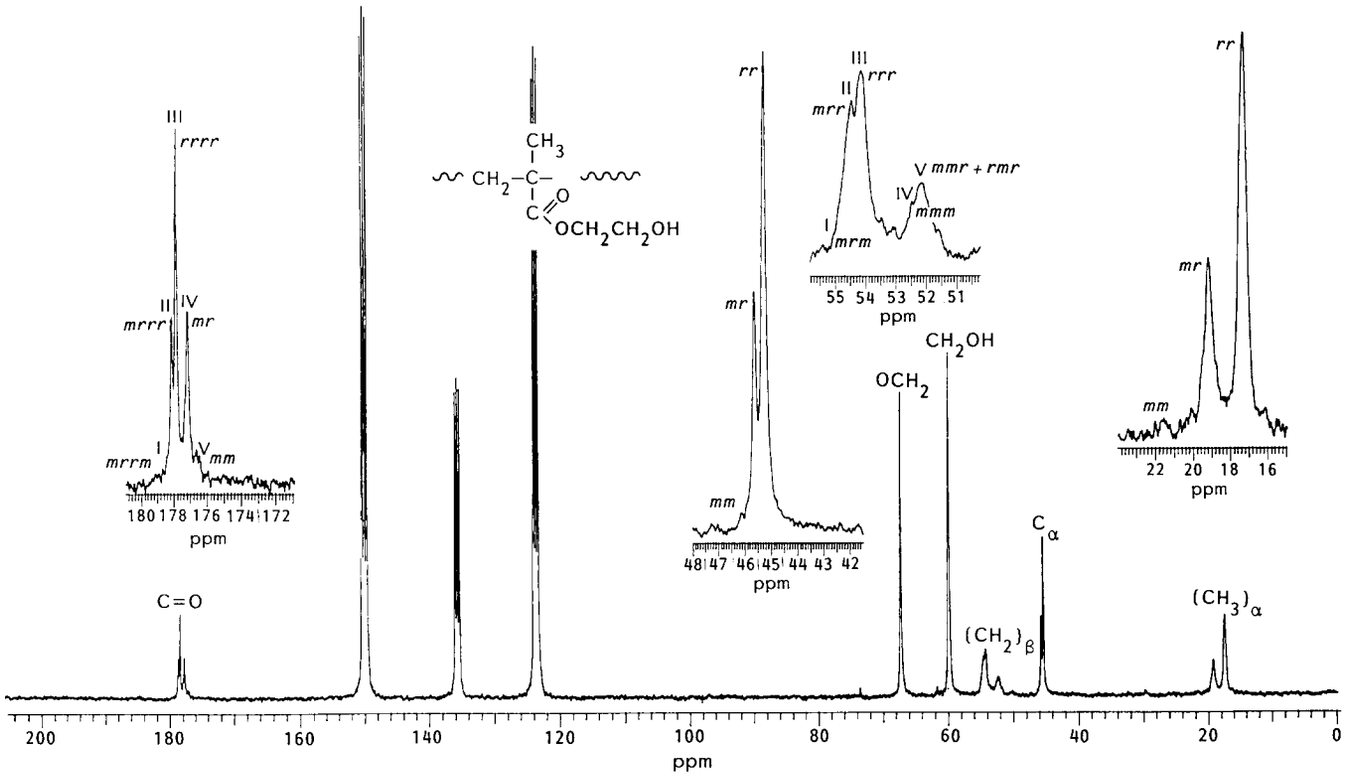

Figure 4 ^{13}C n.m.r. spectrum of PHEMA in *d*-pyridine

Table 4 Assignments of the stereoregular sequence fractions of PHEMA

Assignment		δ (ppm)	Experimental	Calculated ($P_m = 0.12_6$)
	mm	46.74	0.01_6	0.01_6
C_α	*mr*(*rm*)	46.23	0.22_0	0.22_0
	rr	45.84	0.76_4	0.76_4
	mm	20.74	0.01_7	0.01_6
$(CH_3)_\alpha$	*mr*(*rm*)	19.79	0.21_5	0.22_0
	rr	19.92	0.76_7	0.76_4
	I *mrm*	55.02	0.01_9	0.01_4
	II *mrr*(*rrm*)	54.50	0.19_7	0.19_2
β-CH_2	III *rrr*	54.11	0.64_3	0.66_8
	IV *mmm*	52.51	0.02_3	0.00_2
	V *mmr*(*rmm*) + *rmr*	52.12	0.11_8	0.12_4
	I *mrrm*	179.10	0.01_7	0.01_2
	II *rrrm*(*mrrr*)	178.82	0.16_6	0.16_8
C=O	III *rrrr*	178.54	0.57_7	0.58_4
	IV *mr*(*mr*)	177.87	0.20_9	0.22_0
	V *mm*	177.34	0.02_6	0.01_6

amylopectin, and later performing hydrolysis. The assignments were attributed to the peaks by applying HETCOR and DEPT techniques, and by comparing them with the other polymethacrylates as shown in *Table 5*.

The P_m value obtained for this polymer was 0.18. From this parameter a ratio of isotactic to heterotactic to syndiotactic triads of 3:30:67 was deduced.

If both hydroxylic polymers are compared, a big difference is noticed between the values of the syndiotactic triads ($rr_{PHEMA} = 0.76$ and $rr_{PHPMA} = 0.67$). In the case of PHPMA the influence of hydrogen bonds will be less than with PHEMA for two reasons: the existence of a mixture of isomers, 1- and 2-HPMA. As the chances are low that the 1-HPMA isomer unit will achieve a conformation that would allow hydrogen bonding, the total number of hydrogen bonds formed by PHPMA will be less than that formed by the PHEMA; the presence of the methyl group beside the carbon which has the hydroxyl group. This methyl group will produce steric hindrance to the formation of the hydrogen bond.

All the P_m values obtained for the five polymethacrylates described are listed in *Table 6*.

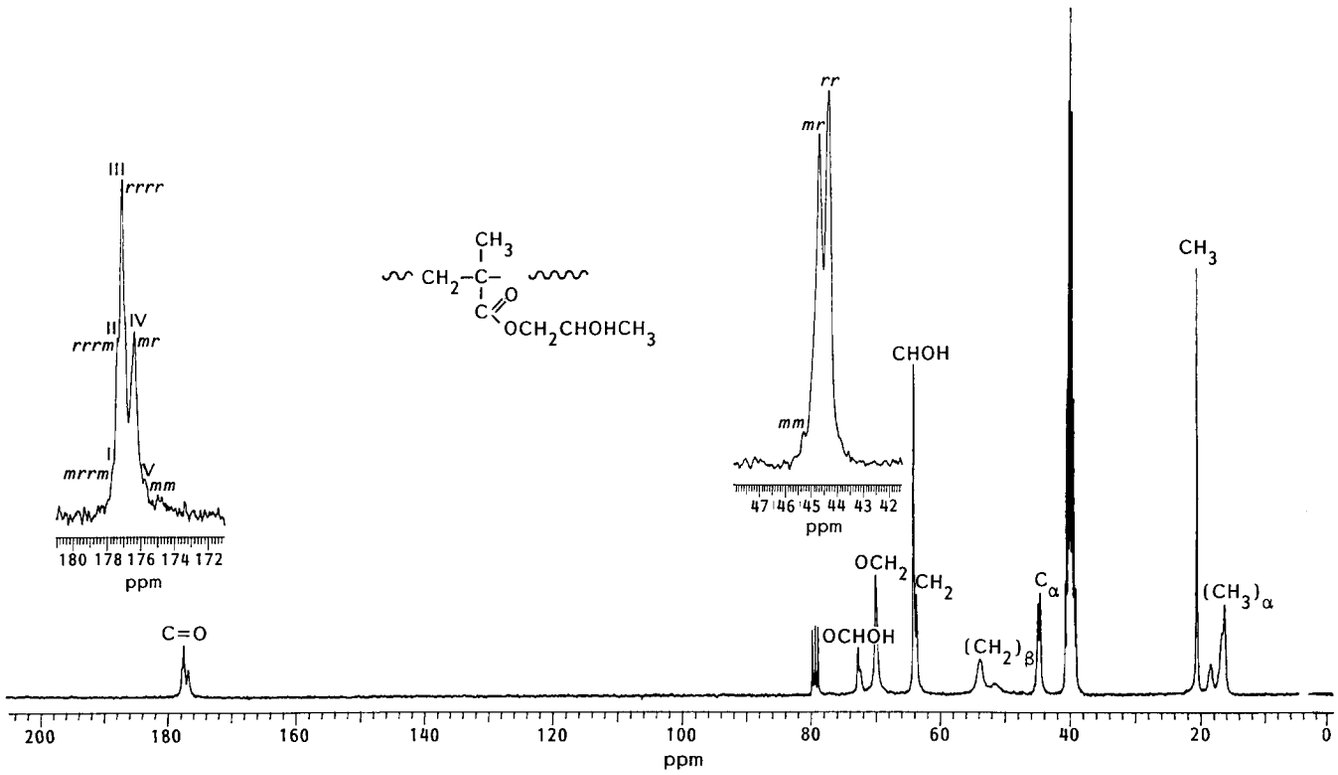

Figure 5 ^{13}C n.m.r. spectrum of PHPMA in *d*-dimethyl sulphoxide/*d*-chloroform

Table 5 Assignments of the stereoregular sequence fractions of PHPMA

Assignment		δ (ppm)	Experimental	Calculated ($P_m=0.18_2$)
	mm	45.30	0.03_3	0.03_3
C_α	*mr*(*rm*)	44.70	0.30_2	0.29_8
	rr	44.35	0.66_5	0.66_9
	I *mrrm*	177.62	0.05_1	0.02_2
	II *rrrm*(*mrrr*)	177.34	0.20_3	0.19_9
C=O	III *rrrr*	177.08	0.43_4	0.44_8
	IV *mr*(*rm*)	176.36	0.27_8	0.29_8
	V *mm*	175.76	0.03_4	0.03_3

Table 6 Compilation of the probability of *meso* placements (P_m) obtained for each polymethacrylate

Polymer	P_m
PMMA	0.20_0
PEMA	0.19_0
PBMA	0.14_5
PHEMA	0.12_6
PHPMA	0.18_2

CONCLUSIONS

From this and a previous study[1] we can conclude that ^{13}C n.m.r. spectroscopy is a valuable technique which allows routine analysis of the tacticity of acrylic and methacrylic grafted polymers.

All the polymers showed a probability of *meso* placements quite similar to those described in the literature. Thus, it can be said that the presence of the carbohydrate and the reaction medium do not affect the radical polymerization process from a stereochemical point of view.

All the polymers were syndiotactic, and this syndiotacticity increased slightly as the alkyl group of the methacrylic ester increased. This means that steric hindrance is an important factor affecting stereoregularity.

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