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Analysis of Graft Copolymers onto Starch by ^{13}C NMR Spectroscopy

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ABSTRACT: High-resolution ^{13}C NMR spectroscopy is a very useful technique for the identification of starch/acrylate grafted copolymers. The opportunity it provides for observing well-resolved spectra of swollen samples has made it possible for the first time to identify products as graft copolymers. In some cases the study of the stereoregularity of the grafted acrylic has also proved feasible.

Introduction

Since the early 1960s, ^{13}C nuclear magnetic resonance (^{13}C NMR) has provided stereochemical information on a large number of chemical compounds.[1] More recently, this technique has also been applied to the investigation of the stereochemical configurations of polymers.[2] A number of publications deal either with the estimation or with the measuring of the sequence distribution and the stereoregularity of block or random copolymers.[3,4] However, no work has been done on the identification of graft copolymers onto carbohydrates using ^{13}C NMR spectroscopy.

In other papers[5,6] we have dealt with the study by means of ^{13}C NMR spectroscopy of the stereoregularity of grafted acrylic branches obtained from the hydrolysis of various graft copolymers onto starch. However, that study involved the previous degradation of the grafted products.

Since high-resolution ^{13}C NMR has been proven to be a very useful technique for studying macromolecules and this has been enhanced by the possibility of obtaining the spectra not only from solutions but also from gels or solid samples, the purpose of this work has been to study, using this spectroscopic method, the whole graft copolymer swollen in a suitable solvent.

Experimental Section

Monomers. The grafted monomers were methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), hydroxyethyl methacrylate (HEMA), and hydroxypropyl methacrylate (HPMA), all supplied by Merck. Except the hydroxylic methacrylates, all were purified by successive washings with 1 N sodium hydroxide, water, a saturated solution of sodium bisulfite, a 20% solution of sodium chloride, and water. After drying over sodium sulfate, they were distilled under suitable conditions. The hydroxylic methacrylates were carefully purified and distilled, as described in the literature.[7]

Polymerization. All the graft copolymers were obtained in a water dispersion of the starch by initiation with a ceric ion at 30 °C.[8] All the reaction products were purified by extraction of the ungrafted carbohydrate and the homopolymer formed during the reaction.

NMR Measurements. All the graft copolymers' spectra were obtained after swelling the sample until a homogeneous gel was obtained. The solvent for the hydroxylic polymethacrylate graft copolymers was d-DMSO, while for the other copolymers a mixture d-DMSO/d-pyridine was used, to give in all cases a concentration of 100 mg/mL. TMS has been used as an internal reference.

NMR measurements were carried out at 20–25 °C, by using a VXR Varian 300 spectrometer taking about 30 000 transients. The relaxation times (T_1) for carbon nuclei were determined from the inversion/recovery curves.

Results and Discussion

Study of the Stereoregularity of the Acrylic Grafted Chains. Figure 1 shows the ^{13}C NMR spectrum of amylose-*g*-PMA. In this spectrum we can clearly distinguish the peaks corresponding to the carbon of the anhydroglucose unit (UAG)[9] and those of the polyacrylate. Chemical shifts are quoted in ppm relative to TMS at 0 ppm. Assignments are indicated on each peak; chemical shifts corresponding to the acrylic grafted chains are $\delta_{C=O}$ = 175.6 ppm, δ_{OCH} = 52.2 ppm, δ_{C_α} = 42 ppm, and δ_{C_β} = 35 ppm, and those pertaining to the amylose are δ_{C_1} = 100.4 ppm, δ_{C_4} = 79.1 ppm, δ_{C_3} = 73.6 ppm, δ_{C_2} = 72.3 ppm, δ_{C_5} = 71.9 ppm, and δ_{C_6} = 60.8 ppm. Thus we have not found significant differences in the chemical shifts of the peaks with respect to those of the pure polymers separately. However, when we analyzed the spectrum of the PMA[5] free chains, we observed that the C_α signal splits into two peaks, being sensitive to triads, and the C_β signal

† Professor Gonzalo Martin Guzmán died on August 22, 1991. This paper is dedicated to his memory.

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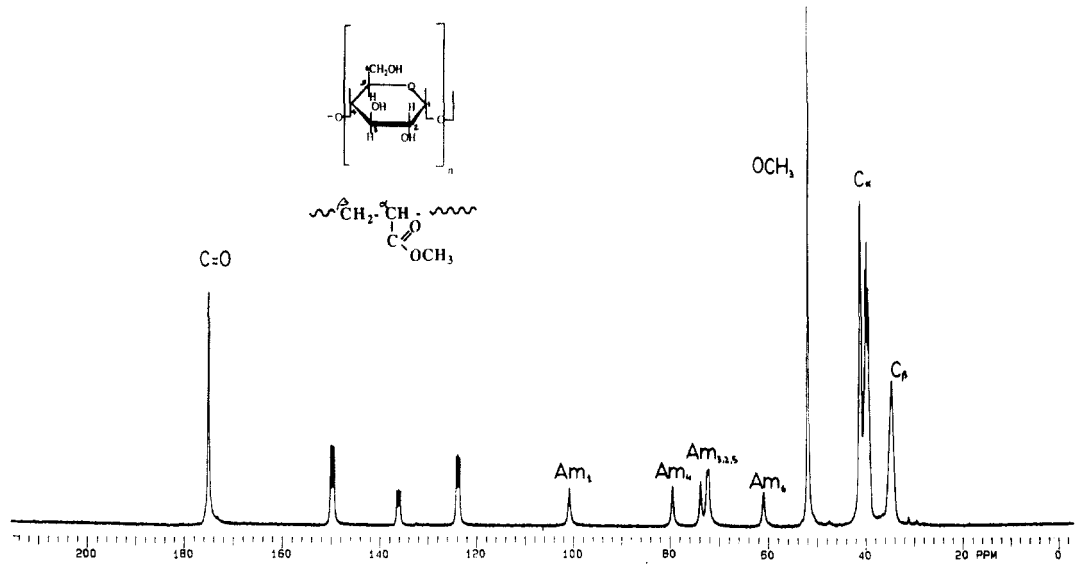

Figure 1. ^{13}C NMR spectrum of the graft copolymer PMA–amylose in d-DMSO/d-pyridine.

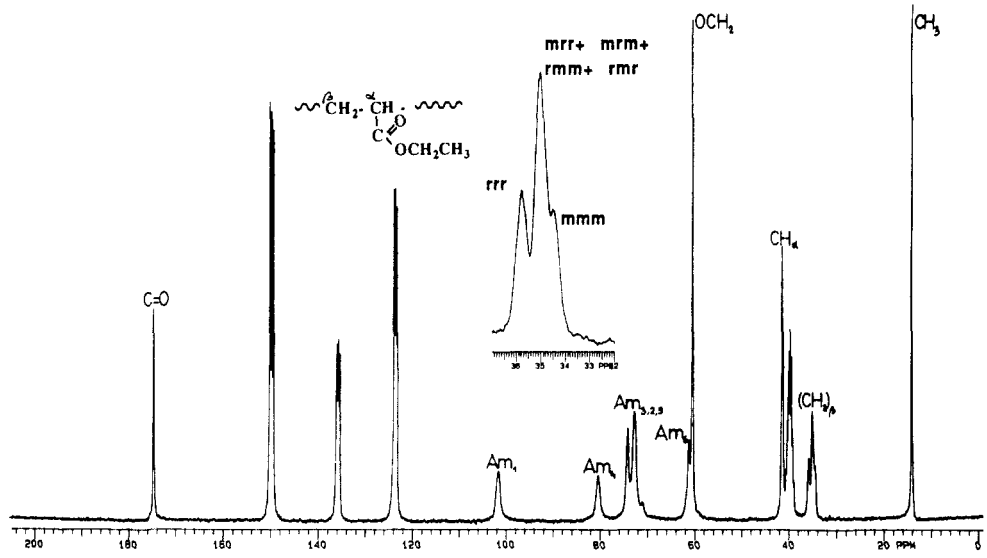

Figure 2. ^{13}C NMR spectrum of the graft copolymer PEA–amylopectin in d-DMSO/d-pyridine.

Table I
Experimental and Calculated Tetrad Fractions from the β-Methylene of the Graft Copolymer Amylopectin–PEA

assignment		δ, ppm	exptl	calc $P_m = 0.43_8$
$CH_{2\beta}$	I: (rrr)	35.78	0.20_1	0.17_8
	II: (mrr)* + (rmm)* + (mrm) + (rmr)	35.04	0.70_9	0.73_8
	III: (mmm)	34.50	0.00_9	0.08_4

splits into at least seven peaks, showing hexads. But all the signals in Figure 1 are single peaks, and we cannot discern any sensitivity to the stereochemical configuration.

In Figure 2 we can see the spectrum corresponding to the amylopectin-*g*-PEA. Again, we can observe very clearly all the peaks corresponding to all the different carbons of the graft copolymer. Chemical shifts are the same as those of both polymers registered separately. Even though the ^{13}C NMR spectrum of the PEA free chains[5] allowed triad and hexad assignments, in its copolymer spectrum the C_α and the $-OCH_2$ carbon signals do not split and the C_β signal splitting is minor; from the C_B peak in the PEA spectrum hexad placements can be appreciated, and when this acrylic polymer is grafted, we can only discern tetrad placements. Since we know the assignments obtained in applying Bernoullian statistics to the PEA spectrum, we

Table II
Experimental and Calculated Triad Fractions from the Methine and Pentad Fractions from the Carbonyl of the Graft Copolymer Amylopectin–PMMA

assignment		δ, ppm	exptl	calc $P_m = 0.20_0$
C_α	(mm)	45.31	0.04_2	0.04_0
	(mr)*	44.73	0.31_8	0.32_0
	(rr)	44.42	0.64_0	0.64_0
C=O	(mrrm)	178.32	0.05_4	0.02_6
	(mrrr)*	177.85	0.18_8	0.20_5
	(rrrr)	177.58	0.40_9	0.41_0
	(mr)*	176.64	0.30_8	0.32_0
	(mm)	176.03	0.04_2	0.04_0

can take the value of the probability of having a meso placement ($P_m = [mm]^{1/2}$)[10] and use it to analyze the stereochemistry of our polymer. Taking into account the results summarized in Table I, we observe good agreement between the experimental and calculated results.

Figure 3 shows a not very well-resolved spectrum of the amylose-*g*-PBA copolymer. The resolution could not be improved because of the low solubility of this material which did not allow us to obtain a very homogeneous gel. Nevertheless, we can clearly identify the peaks corresponding either to the carbohydrate carbons or to the acrylic grafted polymer carbons. In spite of the fact that the

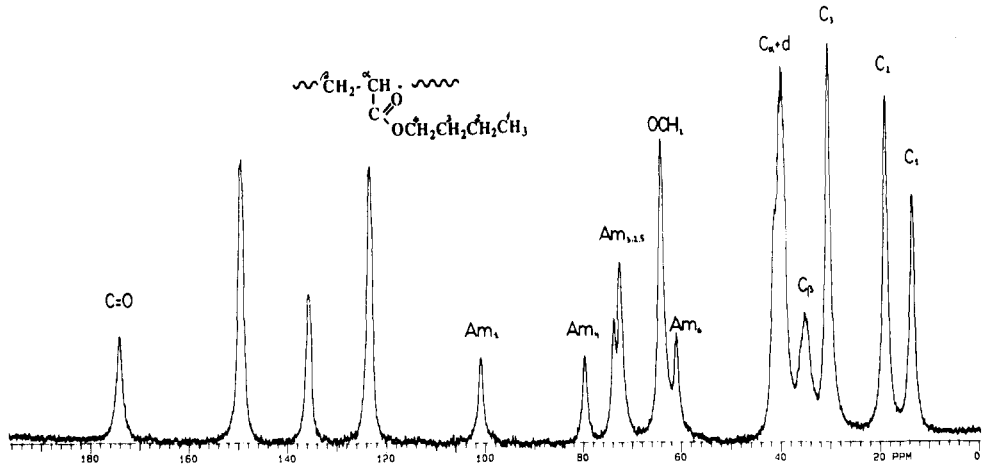

Figure 3. ^{13}C NMR spectrum of the graft copolymer PBA–amylose in d-DMSO/d-pyridine.

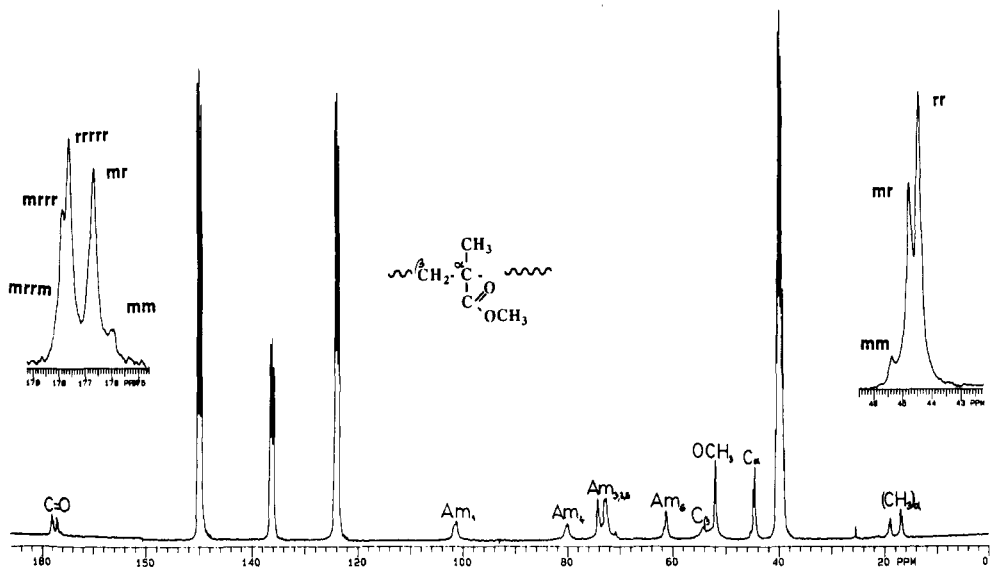

Figure 4. ^{13}C NMR spectrum of the graft copolymer PMMA–amylopectin in d-DMSO/d-pyridine.

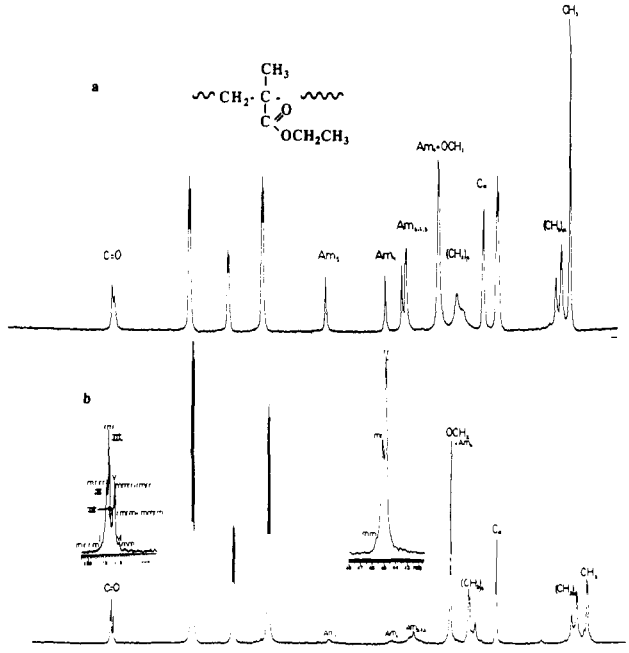

Figure 5. ^{13}C NMR spectra of the graft copolymers PEMA–amylose: (a) PEMA-*g*-amylose in d-DMSO/d-pyridine, (b) PEMA-*g*-amylose in d-pyridine.

pure PBA[5] spectrum allows hexad placement assignments, from the spectrum of the graft copolymer it is not possible to make any study of the tacticity of the grafted chains.

Table III
Experimental and Calculated Triad Fractions from the Methine and Pentad Fractions from the Carbonyl of the Graft Copolymer Amylopectin–PEMA

assignment		δ, ppm	exptl	calc $P_m = 0.19_0$
C_α	(mm)	46.28	0.03_9	0.03_6
	(mr)*	45.78	0.33_7	0.30_8
	(rr)	45.49	0.62_4	0.65_6
C=O	I: (mrrm)	178.81	0.03_4	0.02_4
	II: (mrrr)*	178.24	0.20_1	0.20_2
	III: (rrrr)	177.94	0.42_1	0.42_8
	IV: (rmrm)* + (mrmm)*	177.37	0.08_0	0.05_9
	V + V′: (rrmr) + (mmrr)*	177.21	0.22_4	0.25_1
	VI: (mm)	176.53	0.04_1	0.03_6

Figure 4 shows the spectrum of the graft copolymer of PMMA onto amylopectin in which we can observe the peaks corresponding to all the different carbons of the macromolecule. In this case, as we see from the pure grafted PMMA,[6] the C_α signal splits into a triplet due to the presence of isotactic, heterotactic, and syndiotactic triads, from which we can deduce that $P_m = 0.20$. Thus, we obtain the results shown in Table II. The resolution of this spectrum is good enough to make a serious study of the grafted chain tacticity; however, we observe that it is not possible to distinguish the pentads centered in mm and mr from the carbonyl carbon as we did from the PMMA free chains.

In Figure 5 we observe two different ^{13}C NMR spectra for amylose-*g*-PEMA. Figure 5a shows the graft copolymer

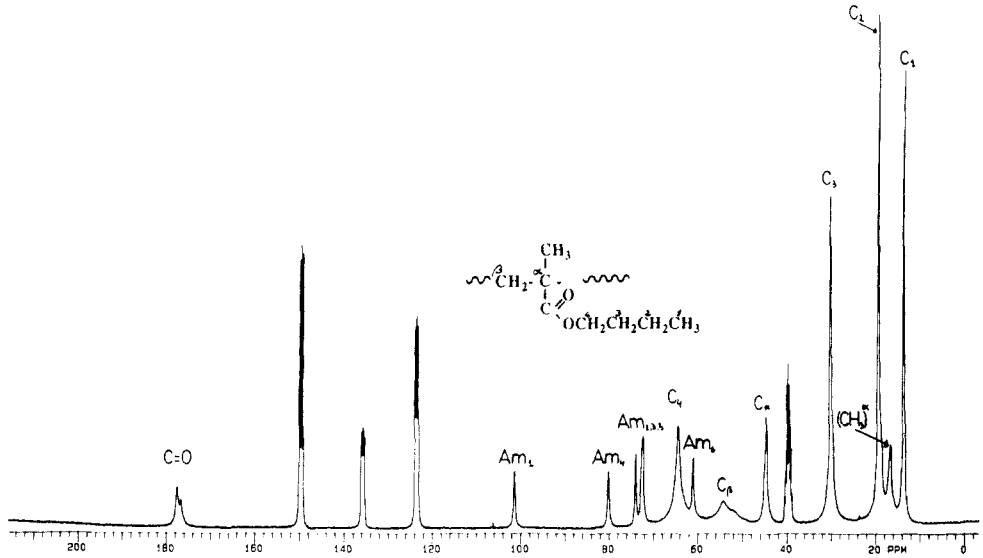

Figure 6. ^{13}C NMR spectrum of the graft copolymer PBMA–amylose in d-DMSO/d-pyridine.

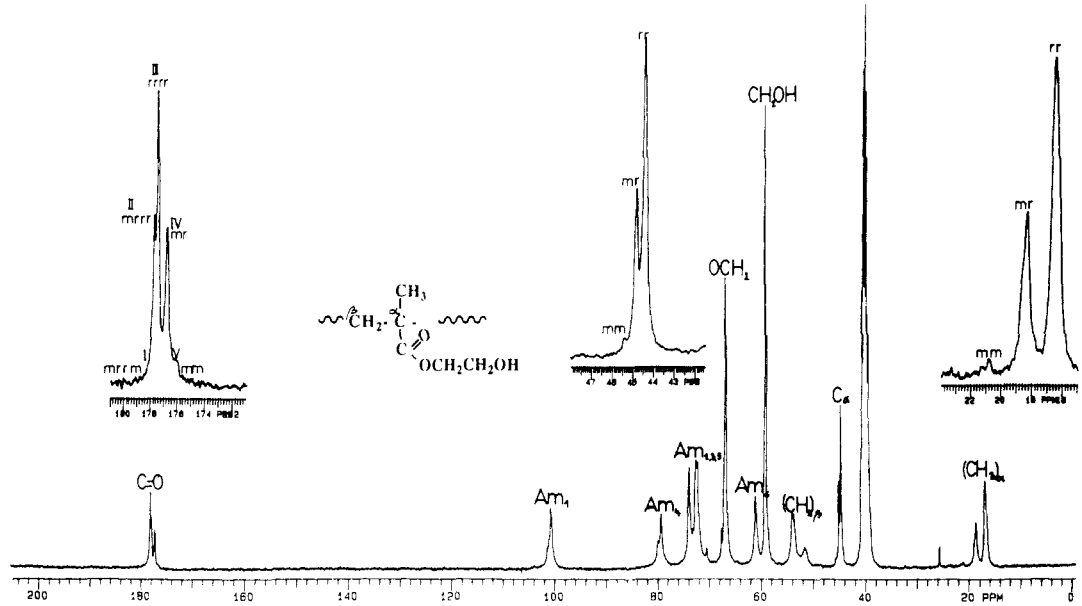

Figure 7. ^{13}C NMR spectrum of the graft copolymer PHEMA–amylopectin in d-DMSO.

Table IV
Experimental and Calculated Triad Fractions from the α-Methyl and Methine and Pentad Fractions from the Carbonyl of the Graft Copolymer Amylopectin–PHEMA

assignment		δ, ppm	exptl	calc $P_m = 0.12_6$
$CH_{3\alpha}$	(mm)	19.27	0.01_4	0.01_6
	(mr)*	18.31	0.22_2	0.22_0
	(rr)	16.49	0.76_4	0.76_4
C_α	(mm)	45.40	0.01_4	0.01_6
	(mr)*	44.84	0.23_2	0.22_0
	(rr)	44.43	0.75_3	0.76_4
C=O	I: (mrrm)	178.27	0.02_3	0.01_2
	II: (mrrr)*	177.75	0.17_2	0.16_8
	III: (rrrr)	177.50	0.57_2	0.58_4
	IV: (mr)*	176.79	0.21_7	0.22_0
	V: (mm)	176.20	0.01_6	0.01_6

onto amylose swollen with pyridine/DMSO. This spectrum is good enough to identify the carbons of our compound, but it is not possible to discern the splitting of the signals arising from tacticity as was possible for PEMA chains obtained after hydrolyzing the graft copolymer,[6] except for that coming from the $(CH_3)_\alpha$. In the PEMA free chain spectrum the signals sensitive to tacticity are carbonyl to pentads, quaternary and α-methyl

Table V
Experimental and Calculated Triad Fractions from the Methine and Pentad Fractions from the Carbonyl of the Graft Copolymer Amylopectin–PHPMA

assignment		δ, ppm	exptl	calcd $P_m = 0.18_2$
C_α	(mm)	45.42	0.03_4	0.03_3
	(mr)*	44.79	0.28_2	0.29_8
	(rr)	44.44	0.68_4	0.66_9
C=O	I: (mrrm)	178.01	0.05_2	0.02_2
	II: (mrrr)*	177.49	0.18_9	0.19_9
	III: (rrrr)	177.23	0.44_2	0.44_8
	IV: (mr)*	176.54	0.28_9	0.29_8
	V: (mm)	175.92	0.02_8	0.03_3

group carbons to triads, and β-carbon to tetrads.

It is interesting to observe the important role of the solvent in the resolution of these spectra. In the ^{13}C NMR spectrum of PEMA-*g*-amylose swollen in pyridine, shown in Figure 5b, the stereoregularity of the acrylic polymer is reflected as clearly as in the spectrum of the pure PEMA, although the signals of the UAG carbons are weak. However, this is a good spectrum to study stereoregularity effects. In this case we have again taken into account the P_m value deduced from the PEMA spectrum to make the assignments; this value was equal to 0.19. The

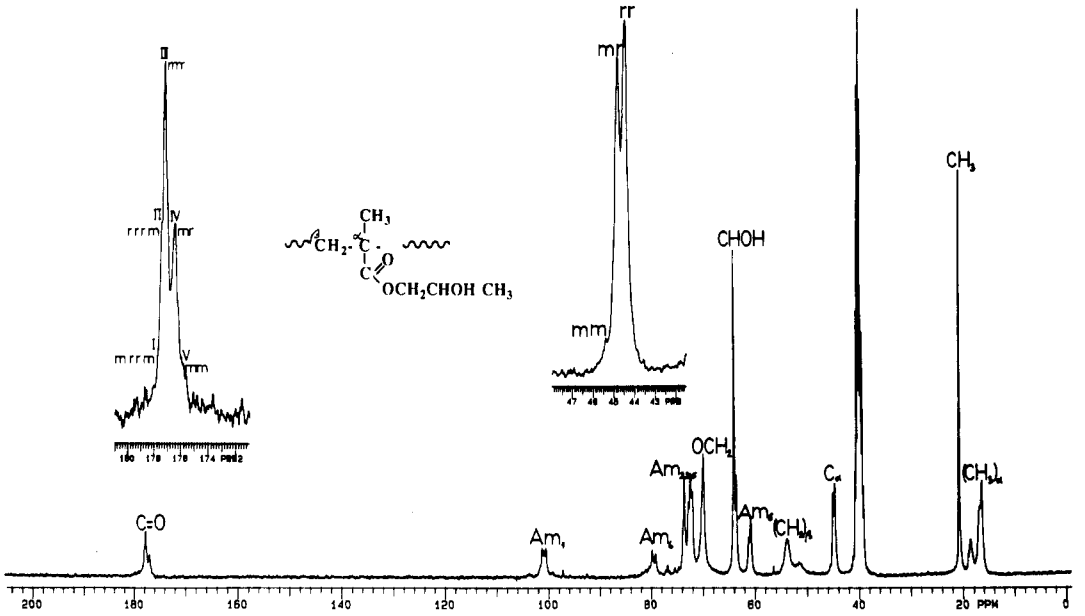

Figure 8. ^{13}C NMR spectrum of the graft copolymer PHPMA–amylopectin in d-DMSO.

Table VI
Spin–Lattice Relaxation Times (T_1) for the Different Carbons of Various Polymers

polymer	carbon	T_1, s
amylopectin	Am_1	0.226
	Am_2	0.241
	Am_3	0.252
	Am_4	0.230
	Am_5	0.252
	Am_6	0.120
PMMA	–C=O	1.569–2.751
	$-CH_{2\beta}$	0.0883
	$-OCH_3$	0.615
	$-C_\alpha$	1.225
	$-(CH_3)_\alpha$	0.0758
PEA	–C=O	2.289
	$-OCH_2$	0.625
	$-CH_\alpha$	0.200
	$-CH_{2\beta}$	0.114
	$-CH_3$	1.475
PHPMA	–C=O	2.779–3.069
	–OCHOH[a]	0.401
	$-CH_2$[a]	0.232
	–CHOH	0.2675
	$-OCH_2$	1.433
	$-CH_{2\beta}$	0.185
	$-C_\alpha$	2.147
	$-CH_3$	0.404
	$-(CH_3)_\alpha$	0.188

[a] Pertaining to the isomer 1-hydroxypropyl polymethacrylate.

sequence distribution has been estimated from the triad data, assuming Bernoullian statistics, and the results are shown in Table III.

From Figure 6 we can extract similar conclusions. The spectrum quality is good enough to identify all of the different carbon peaks of the graft copolymer PBMA–amylose, but it is not resolved enough to make possible the study of the stereoregularity of the grafted chains, as we did from the free chain spectrum,[6] where C_α, C_β, and C=O split into triad, tetrad, and pentad placements, respectively.

Figures 7 and 8 show the PHEMA and PHPMA graft copolymer spectra, respectively. In both cases, we obtain excellent resolution, as good as that obtained from the acrylic polymers without grafting.[6] The most probable reason for this improvement in resolution with respect to that obtained with all the other graft copolymers analyzed

Table VII
Percent Grafting (% G) of Various Graft Copolymers onto Starch Calculated by Means of ^{13}C NMR Spectroscopy or from a Hydrolytic Method

graft copolymer	% G_H	% G_{NMR}
amylose–PMMA	255	258
amylose–PMMA	187	187
amylose–PEMA	234	236
amylose–PBMA	118	121
amylose–PMA	250	257
amylose–PEA	272	276
amylose–PEA	217	222
amylose–PBA	158	159
amylopectin–PEMA	100	110
amylopectin–PHEMA	138	138
amylopectin–PHEMA	100	100
amylopectin–PHPMA	149	145
amylomaize–PMMA	160	164
amylomaize–PEMA	234	236

in this paper is the very homogeneous gels formed by this kind of graft copolymer. Thus, because of the high resolution of these spectra, the probabilities of meso placement (P_m) can be deduced either from the relative areas of the α-CH_3 or the C_α resonances of the spectra of the graft copolymers or from applying the P_m obtained from the spectra of the pure acrylic polymers obtained after the hydrolysis. In such a way, we obtain the assignments in Tables IV and V, using the Bernoullian statistics.

Calculation of the Percent Grafting. As is known, one of the characteristics of NMR spectroscopy is the proportionality between the signal intensity and the concentration of each carbon type. Depending upon the carbon type (primary, secondary, ...) and on its chemical bonds, that is, depending on the carbon surrounding or lattice, the time needed to achieve equilibrium in the magnetic field will be different. So, to establish any comparison among the different peaks, the relaxation times must be taken into account. If a train of radio-frequency pulses is so closely spaced that full relaxation does not occur between pulses, maximum intensities will not be realized; instead, the signal intensities will be proportional to the extent of relaxation, which may not be the same throughout the spectrum. For a 90° pulse (as in our case), the pulse spacings must be 5 times the spin–lattice relaxation time (T_1) to ensure 99% relaxation.[11] The spin–

lattice relaxation time (T_1) defines the rate of the equilibration process.

In order to calculate percent grafting (% G = ratio between the weights of the acrylic grafted polymer and the grafted carbohydrate) directly without the previous degradation of the product, we measured the T_1 of the carbons of our copolymer as we can see in Table VI.

In view of these values and taking into account that we used a delay between pulses of 3.0 s, signals adequate for quantitative study are as follows: starch, all peaks; polyacrylates, $-OCH_2$, CH_α, and $(CH_2)_\beta$; polymethacrylates, $(CH_2)_\beta$ and $(CH_3)_\alpha$.

Thus, from the relative areas of the C_4 of the UAG and of one suitable peak of the acrylic polymer, and taking into account that from the NMR spectra we extract molar ratios instead of weight ratios, Table VII was deduced by using the formula

$$\% \text{ G} = \frac{\text{weight of acrylic grafted chains (g)}}{\text{weight of grafted carbohydrate}} \times 100$$

The agreement between the results obtained from both methods confirms the validity of this spectroscopy technique to carry out this quantitative study.

Conclusions

The improved resolution and sensitivity of ^{13}C NMR spectroscopy has made it possible to identify for the first time the graft copolymers onto starch without being degraded first. It has also made it possible to know the stereoregularity of the acrylic grafted chains, although this technique is not useful in all cases because a very homogeneous gel is necessary to obtain a highly resolved spectrum.

The spectra do not improve when time and temperature increase.

On the basis of the percent grafting results obtained from the ^{13}C NMR spectra, it becames important to notice the great usefulness of this spectroscopic technique to determine the graft copolymer composition.

Acknowledgment. We thank the Diputacion Foral de Guipúzcoa, Universidad del Pais Vasco (203.215-E168/90), and CICYT (MAT90-0912) for the facilities granted to have this work performed.

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Registry No. Starch-*g*-PMA (graft copolymer), 110911-64-3; starch-*g*-PEA (graft copolymer), 119969-41-4; starch-*g*-PBA (graft copolymer), 110911-65-4; starch-*g*-PMMA (graft copolymer), 110911-66-5; starch-*g*-PEMA (graft copolymer), 140853-19-6; starch-*g*-PBMA (graft copolymer), 140853-20-9; starch-*g*-PHEMA (graft copolymer), 111611-13-3; starch-*g*-PHPMA (graft copolymer), 140853-21-0.