

Study of the Acid Hydrolysis of the Starch Graft Copolymers with Hydroxylic Methacrylates

M. GURRUCHAGA,* I. GOÑI, M. VALERO, and G. M. GUZMAN

Dpto. de Ciencia y Tecnología de Polímeros, Facultad de Química de San Sebastián, Universidad del País Vasco, Apdo. 1072, San Sebastián-20080, Spain

SYNOPSIS

The acid hydrolysis method is usually utilized to separate acrylic polymer chains grafted onto amylopectin (AMP). The hydrolysis with the HCl acid has been found to be appropriate when we grafted hydroxyethyl methacrylate (HEMA) and hydroxypropyl methacrylate (HPMA). Using the perchloric acid method, various secondary reactions appear falsifying the grafting yields. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

One of the most efficient methods for getting information about graft copolymers is the recovery of the grafted chains for analysis. In this way, it is possible to obtain important data such as: percent grafting, grafting mechanism, grafted chains microstructure, molecular weight, etc. Various methods have been applied in the hydrolysis of polymer backbones. The following methods have been utilized to recover vinyl side chains grafted onto starch: Acid hydrolysis with 1*N* hydrochloric acid,¹ enzymatic hydrolysis with α -amylasa,² periodate oxidation,³ or acid hydrolysis with perchloric acid.⁴ This last method, investigated by Dennenberg and Abbot,⁴ has been found to be rapid and effective for decomposition with removal of the starch moiety with little or no degradation of the grafted polymer. Thus, it has been widely used by many authors⁵ as well as by us.⁶

However, when hydrolyzing graft copolymers synthesized from hydroxylic methacrylates, we observed some details which reveal the existence of some secondary reactions during the hydrolysis, what led us to study the effect of the acid process on this kind of polymethacrylates.

EXPERIMENTAL

Materials

Amylopectin was a commercial product supplied by AVEBE Holland, and was used without further purification. 2-Hydroxyethyl methacrylate (HEMA) and 2-hydroxypropyl methacrylate (HPMA) (Merck) were purified carefully following a procedure described in the literature.⁷ The HPMA is a mixture of the isomers 1-HPMA and 2-HPMA, which are not separate after the purification.

Reagents

All the acids used were laboratory-grade chemicals: hydrochloric acid, acetic acid, and perchloric acid.

Analysis

The ¹³C-NMR spectra were registered at about 25°C with a Varian VXR-300 spectrometer, taking about 30,000 transients. The conditions of operation are as follows: a width pulse of 14 ms; 1 s acquisition time; time delay of 3 s; spectral width of 16,000 Hz with 32K data points for the Fourier transform.

Preparation of Graft Copolymers

The following graft copolymers were prepared: amylopectin-*g*-HEMA and amylopectin-*g*-HPMA.

* To whom correspondence should be addressed.

They were obtained by the following procedure: Amylopectin (2 g) was added to 290 cc of water and heated to 30°C under nitrogen. The monomer (0.0469 mol) was added to the dispersion after careful purification.⁸ Grafting sites were initiated on the amylopectin by the addition of 10 cc of a 0.1M of ceric ammonium nitrate solution in 1N nitric acid. This mixture was allowed to react for 4 h after the initiator addition and under a constant light source (40 W). The product was collected by filtration, washed several times in water, and vacuum-dried. The acrylic homopolymer was extracted in a Soxhlet apparatus using ethanol as solvent.

Hydrolysis of the Amylopectin and Side-Chain Recovery

Dennenberg and Abbott's Method. Amylopectin graft copolymer (2 g) was accurately weighed and added to 100 cc glacial acetic acid, which was heated to 90–100°C. The sample was stirred for 1 h to swell the grafted side chains. perchloric acid (60%) (2 cc) was added dropwise, and within 1–2 min the reaction was completed. The reaction mixture was immediately poured into ice water to precipitate the acrylic polymer side chains.

Brockway's Method. The samples were refluxed in 1N HCl for 6 h, and then the acrylic side chains were recovered by filtration.

RESULTS AND DISCUSSION

As mentioned before, we utilized the perchloric acid method to hydrolyze the obtained graft copolymers in order to separate the acrylic side chains. Afterwards, we checked the extent of the hydrolysis by characterizing the acrylic chains using the ¹³C-NMR spectroscopies.

Figures 1 and 2 show the ¹³C-NMR spectra of the PHEMA and PHPMA obtained after the perchloric hydrolysis. The peak or peaks (if the carbon is sensitive to tacticity) corresponding of each carbon of the structural unit are pointed out in the spectra. Although both spectra in Figures 1 and 2 show the absence of amylopectin, they show new bands (pointed out with arrows in figures) in addition to those characteristic of both polymethacrylates. This has led us to study about the secondary reactions that might occur, and in this way to investigate the viability of the acid hydrolysis methods to be used with the hydroxylic methacrylates. So we carried out the hydrolysis of these compounds by the Brockway's method.¹ From the spectroscopic anal-

ysis of the polymers obtained after this last hydrolysis method (Figs. 3 and 4), there is no evidence of secondary reactions, or at least ¹³C-NMR spectra do not show any additional band to those characteristic of both polymers. Changes in the solvents used to register the spectra have no significance in these cases. On the other hand, in addition to this difference on the spectra, the graft copolymerization yields calculated from both hydrolysis methods were quite different for both polymers (Table I), which indicates changes in the weight of the recovered chains.

In the view of these results, we thought that other reactions than hydrolysis might occur during the utilization of perchloric acid. Since the chemical shift of the carbonyl groups in the NMR spectra are ester chemical shifts, we think that during the hydrolysis process a new ester is produced. Thus, we hypothesize that the new ester can be produced by transesterification in either of three ways:

- (a) Intramolecular
- (b) Intermolecular with another polymer chain, or
- (c) Intermolecular with acetic acid solvent.

(a) and (b) The perchloric acid is a strong acid and also a very bad nucleophilus. Therefore, when we add it to these hydroxylic esters, a protonation of the oxygen atoms will be produced, and so a transesterification according to the mechanism in Figure 5 will occur. Since the reaction was carried out in an acetic acid medium, in order to produce the swelling of the copolymers, as the carbohydrate disappears, the acrylic chains will loose. Since they are in a gel state, the chains will have the necessary mobility to get their more relaxed structure. Thus, as we have said before, the above reaction can occur both in an intramolecular way producing cyclic structures [Fig. 6 (a)] and in an intermolecular way producing a crosslinking [Fig. 6 (b)]. Although this kind of reactions with hydroxylic esters is well known,⁹ it is not probable to expect any of the two proposed structures as responsible of the chemical shift for the C=O group as different as the observed by ¹³C-NMR spectroscopy. Furthermore, both structures could explain the additional bands between those of the O—CH₂ and the CH₂—OH of our polymers, but they could not explain the presence of a CH₃ band at 20 ppm. This led us to set up the third hypothesis.

(c) As mentioned, by the acid perchloric addition a protonation of the oxygen of the C=O of the methacrylic polyester occurs. Since we are working

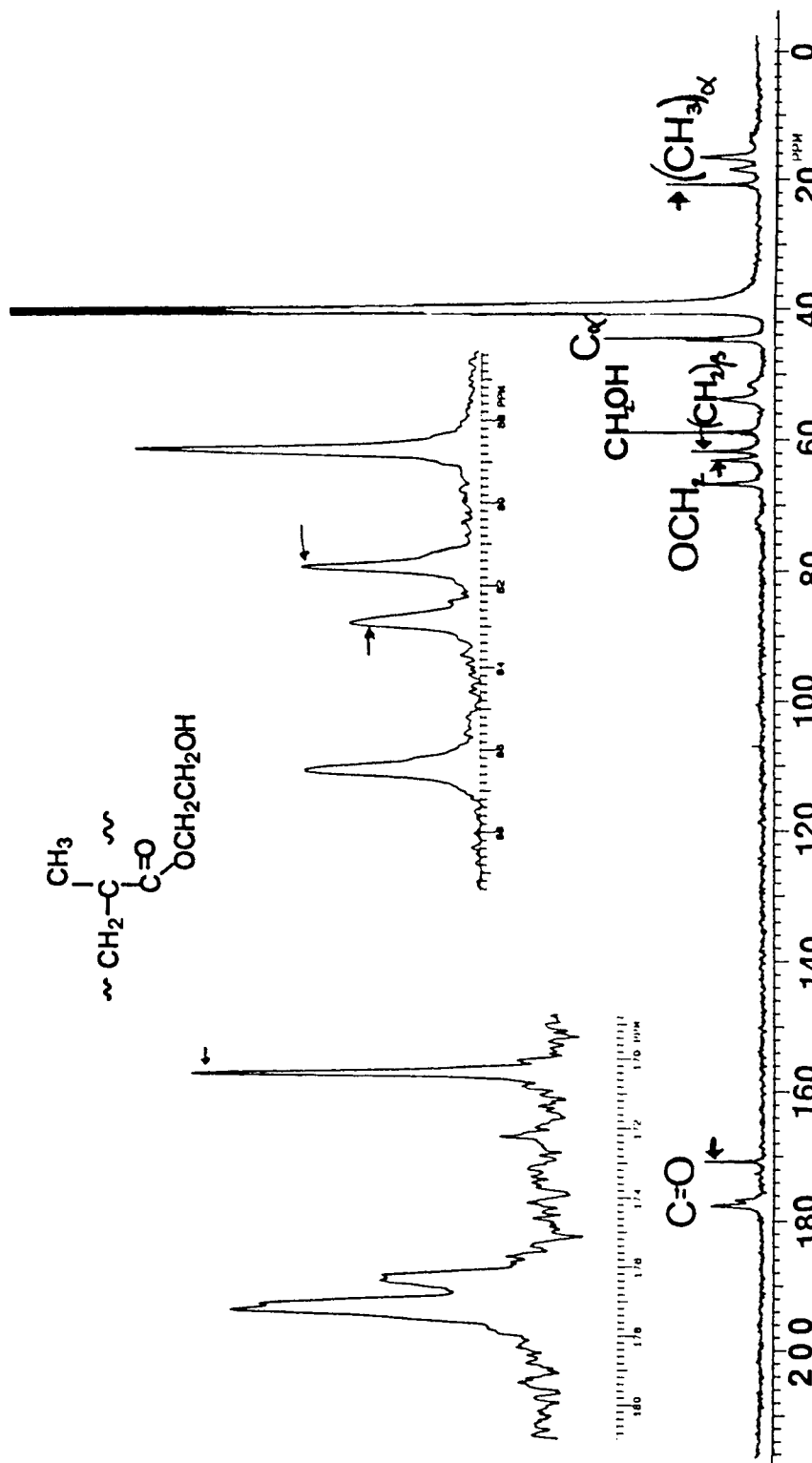


Figure 1 ^{13}C -NMR spectrum of poly(hydroxyethyl methacrylate) in d -DMSO obtained by hydrolysis with perchloric acid. The arrows point to the peaks appearing after the hydrolysis.

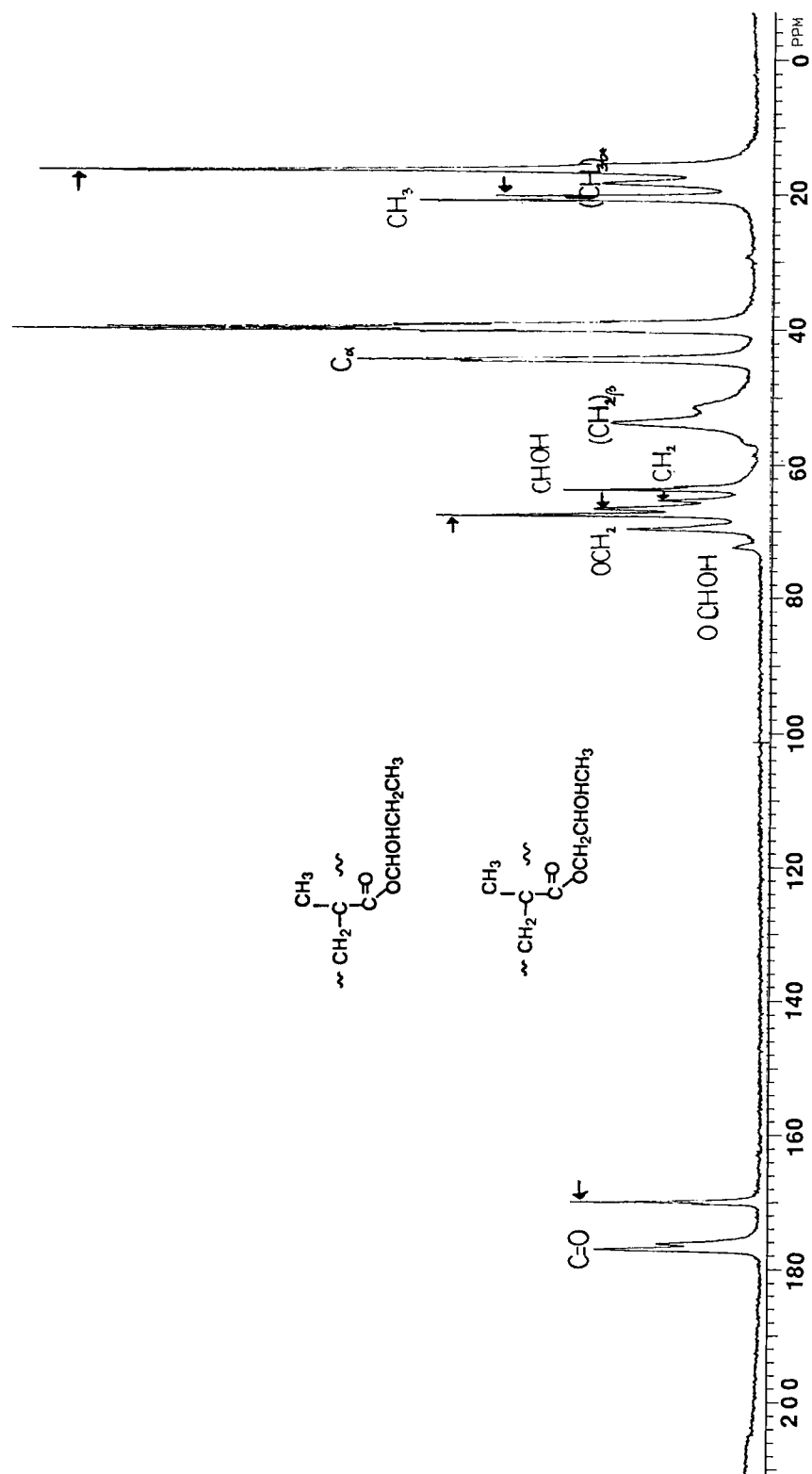


Figure 2 ^{13}C -NMR spectrum of poly(hydroxypropyl methacrylate) in d-DMSO obtained by hydrolysis with perchloric acid. The arrows point to the peaks appearing after the hydrolysis.

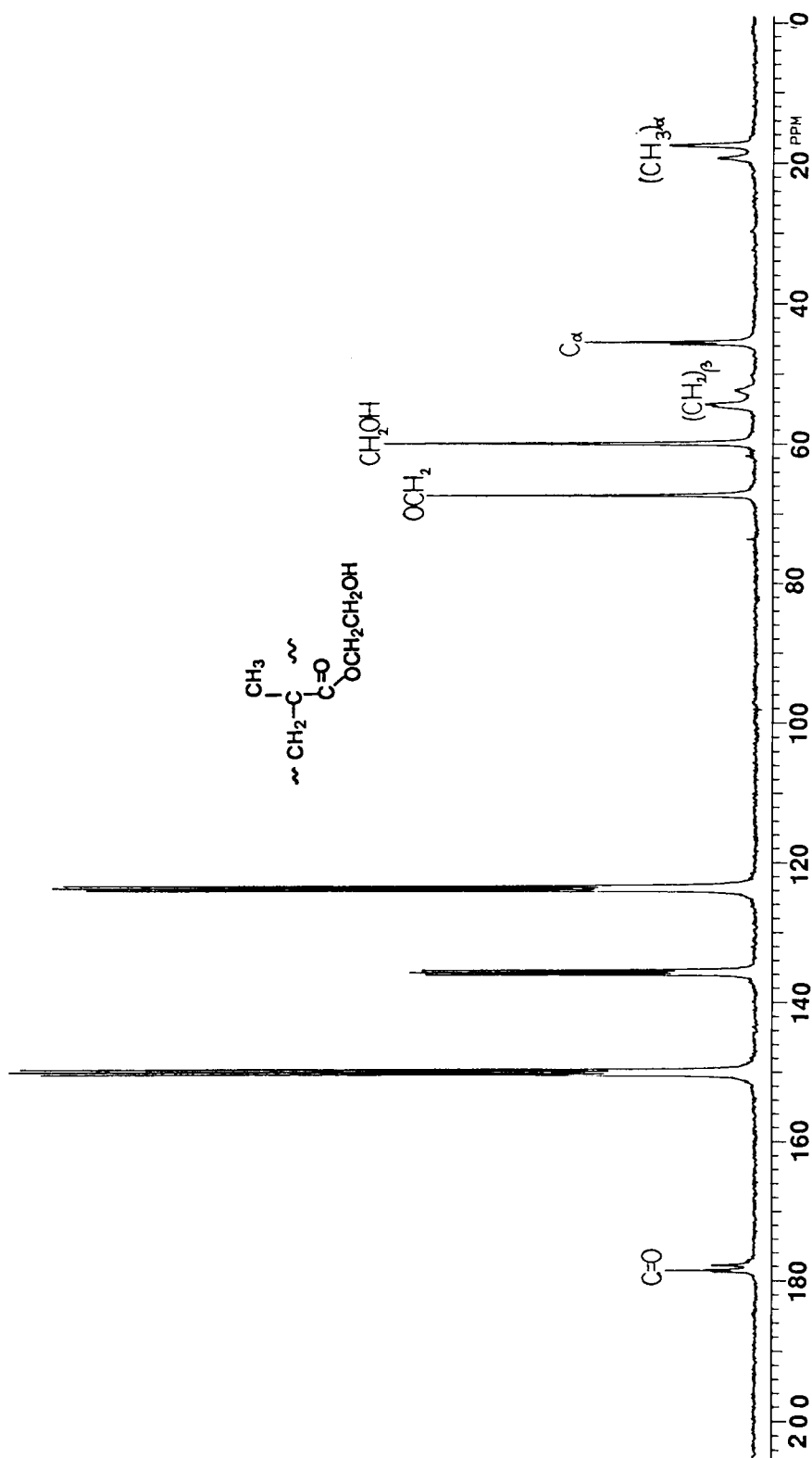


Figure 3 ¹³C-NMR spectrum of poly(hydroxyethyl methacrylate) in d-pyridine, obtained by hydrolysis with HCl, and corresponding to a standard syndiotactic PHEMA.

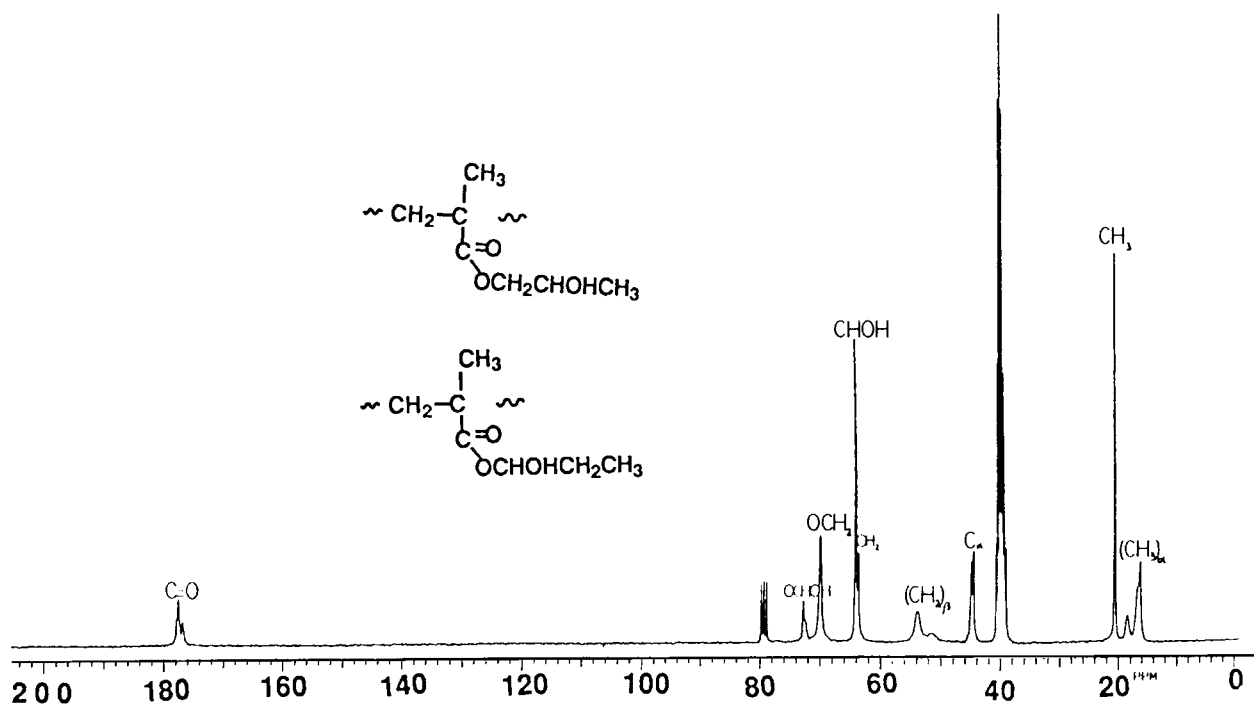
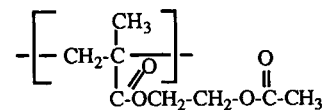


Figure 4 ^{13}C -NMR spectrum of poly(hydroxypropyl methacrylate) in d-DMSO/d-chloroform, obtained by hydrolysis with HCl, and corresponding to a standard syndiotactic PHEMA.

in an acetic acid medium, this protonation could happen also in the $\text{C}=\text{O}$ of this acid. So, following an analogous mechanism, an esterification of the OH group of the hydroxylic methacrylate with the acetic acid will take place obtaining the correspondent acetate, as shown in Figure 7. Thus, a new compound would be obtained with some of its structural units represented by the formula



This new carbonyl introduced in the molecule will have a higher mobility than the preceding one and it will give a single band. Thus, the presence of the new bands at 170 and 20 ppm will be explained.

Table I Grafting Yields Obtained for Two Hydroxylic Methacrylate Graft Copolymers Using the Perchloric Acid Hydrolysis and HCl Hydrolysis Method

Parameter	AMP- <i>g</i> -PHEMA		AMP- <i>g</i> -PHPMA	
	HCl Hydrolysis	HClO ₄ Hydrolysis	HCl Hydrolysis	HClO ₄ Hydrolysis
% Grafting ^a	129	151	129	200
% Pol _g ^b	39.2	41.8	36.5	41.2
% CT ^c	50.4	55.0	90.7	99.9

^a % Grafting = (weight of grafted acrylic chains/weight of grafted starch) × 100.

^b % Grafted polymer = (weight of grafted acrylic chains/weight of used monomer) × 100.

^c % Total conversion = (weight of grafted and ungrafted acrylic chains/weight of used monomer) × 100.

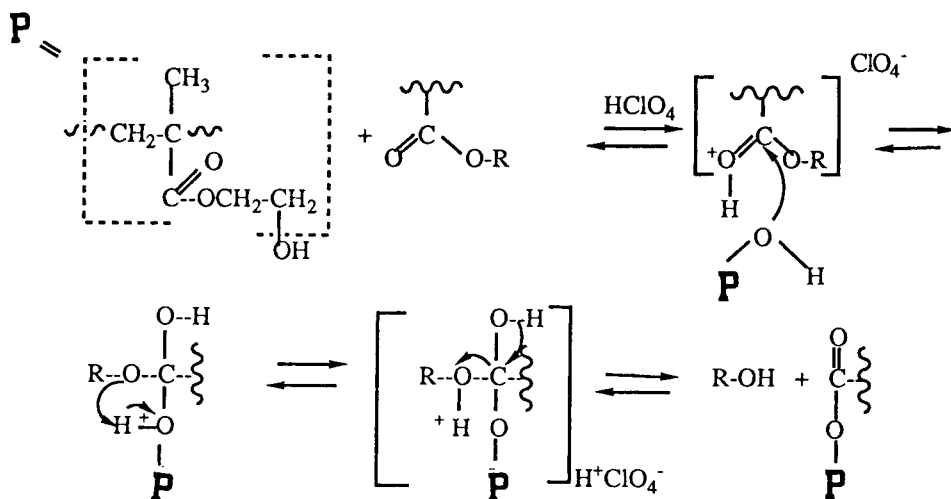


Figure 5 Transesterification of the hydroxylic monomers during the amylopectin hydrolysis with perchloric acid.

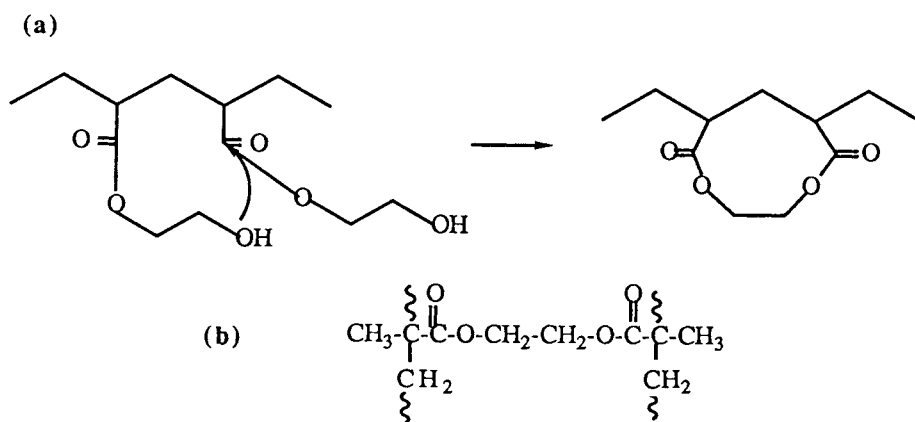


Figure 6 New molecular structures obtained after the perchloric acid hydrolysis process.

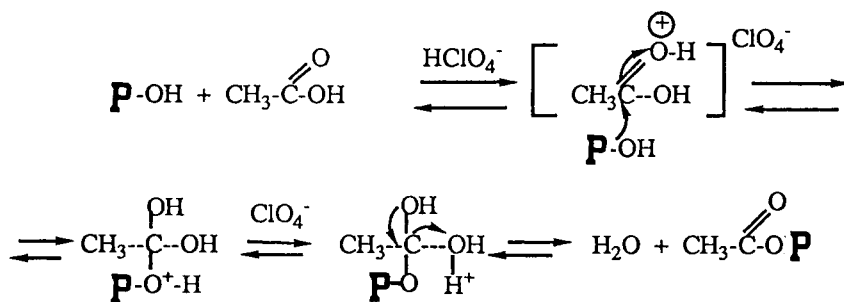


Figure 7 Esterification of the acetic acid during the hydrolysis of the amylopectin with perchloric acid.

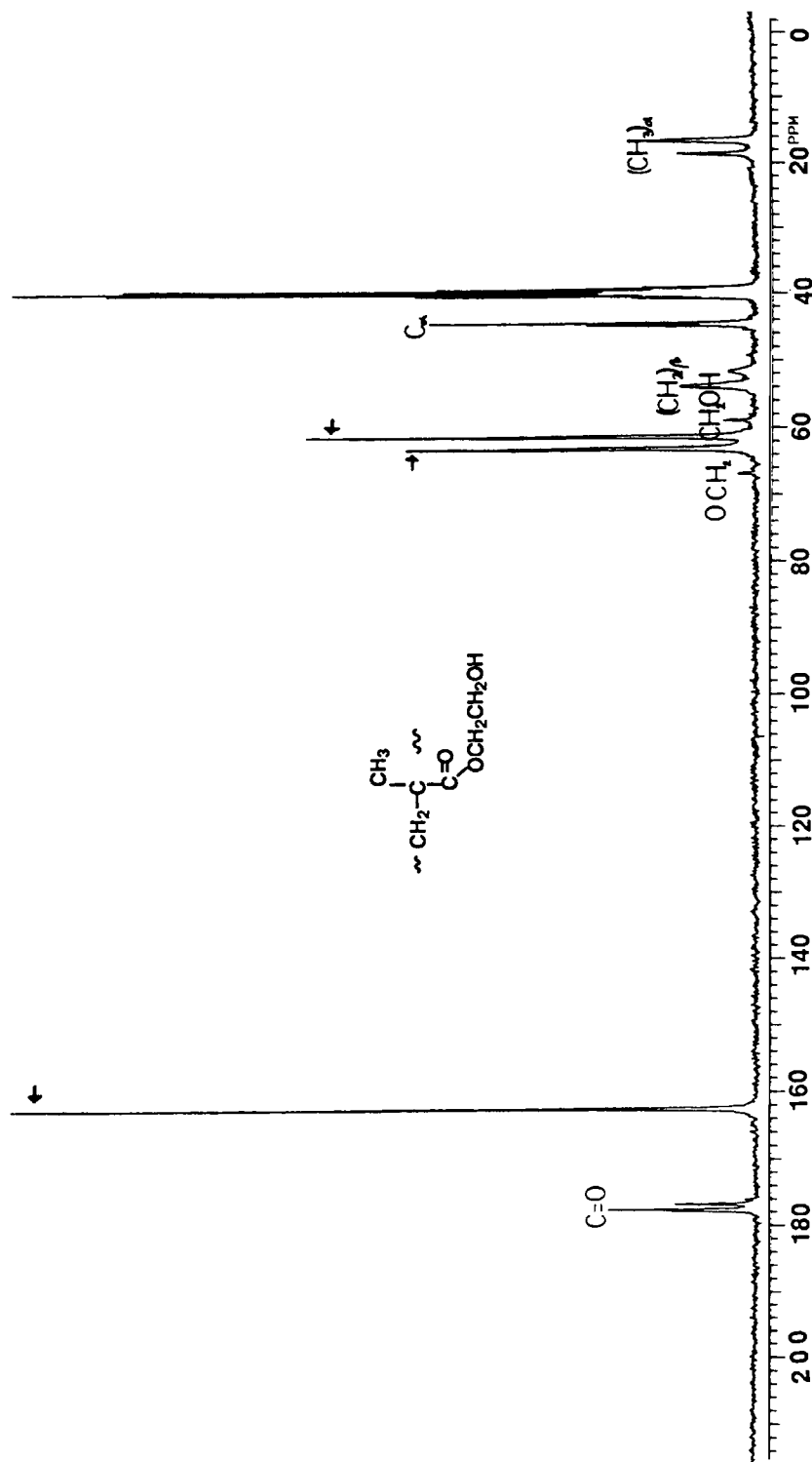


Figure 8 ^{13}C -NMR spectrum of poly(hydroxyethyl methacrylate) obtained by hydrolysis with perchloric acid in a formic acid medium. The arrows point to the peaks appearing after the hydrolysis.

To check this last hypothesis, we carried out the hydrolysis in a formic acid medium. If this hypothesis were true, the absorption band at 20 ppm due to the methyl group of the acetic acid would disappear, but not the others. The NMR spectrum so obtained shows the new bands above mentioned, and it does not show that due to the methyl group, as we see in Figure 8. In this way, we corroborate the last hypothesis.

As the three hypothesis are based on quite the same organic process, all of them should occur. Furthermore, the presence of the new bands between those of the OCH_2 and the CH_2OH carbons will be explained by both processes. In all of them, a change in the molecular weight of the grafted polymer will occur, and consequently this hydrolysis procedure will not be suitable for calculating the grafting yields of our copolymers. However, if the hydrolysis is carried out in 1N HCl, no variation on the grafted chains is observed, although it is also an acid hydrolysis process. Thus, this method is suitable for hydrolyzing the graft copolymers formed between starch and hydroxylic acrylates.

This research has been supported by grants from: Diputación Foral de Guipuzcoa, Universidad del País Vasco

(203.215-E168/90), and Comisión Interministerial de Ciencia y Tecnología (CICYT): MAT 90-0912.

REFERENCES

1. C. E. Brockway, *J. Polym. Sci., A-1*, **2**, 3721-3731 (1964).
2. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **10**, 929 (1966).
3. L. A. Gugliemelli, G. L. Mayer, and C. R. Russell, *U.S. Pat.*, **3**, 132,181 (1964).
4. R. J. Dennenberg and T. P. Abbott, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 693-696 (1976).
5. T. P. Abbott and C. James, *J. Appl. Polym. Sci.*, **26**, 207 (1981).
6. I. Goñi, M. Gurruchaga, M. Valero, and G. M. Guzman, *J. Polym. Sci., A-1*, **21**, 2573-2580 (1983).
7. B. D. Ratner and I. F. Miller, *J. Polym. Sci., A-1*, **10**, 2425 (1972).
8. I. Pinchuk, E. C. Eckstein, and M. R. Van Der Mark, *J. Appl. Polym. Sci.*, **29**, 1749-1760 (1984).
9. J. March, *Advanced Organic Chemistry: Reactions, Mechanism and Structure*, McGraw-Hill, New York, 1977, p. 366.

Received November 14, 1991

Accepted April 26, 1992