

Vinylic Graft Copolymers of Cellulose. I. Effects of Monomer Concentrations and Crystallinity Index of Cellulosic Substrate on Grafting Vinyl Acetate onto Cotton*

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SYNOPSIS

Graft copolymerization of vinyl acetate (VA) and methyl acrylate (MA) on cotton cellulose was initiated by the Ce(IV) ion, and ungrafted vinylic polymer was separated from the graft copolymer by acetone extraction. The influence of the ratio aqueous initiator solution volume/monomeric volume (V_{aq}/V_{mon}), vinyl acetate volume/methyl acrylate volume (V_{VA}/V_{MA}), and the cellulose crystallinity index (CI) on the grafting reaction were studied. To modify the crystallinity of cellulose, native cotton was treated with NaOH in the concentrations 10, 15, and 20% (mercerized). The viscosimetric average molecular weight (M_v), the polymerization degree (PD), and the crystallinity index proposed by Nelson and O'Connor (CI) were determined for native and NaOH-treated cotton. The polymeric side chains grafted were separated from the cellulose backbone by acid hydrolysis in 72% H_2SO_4 . The viscosimetric average molecular weight (M_v) was determined, and the number of vinylic chains per cellulosic chain (graft frequency, GF) were calculated. The grafting percentage, %G, was higher for most amorphous cellulose and for a higher methyl acrylate percentage (%MA) in monomeric reaction mixtures (VA-MA). The V_{aq}/V_{mon} ratio that yields the highest %G was 70/30. The increase of the %G with the %MA in the VA-MA monomeric mixture seems to be due to both an increase in the length of vinylic grafted chains (as shown by its M_v) and the number of grafted chains (GF). The increase in the %G when the crystallinity index (CI) of the cellulosic substrate decreases seems to be due to an increase in the length of the vinylic grafted chains, but not to an increase in the number of grafted chains, since the M_v increases and GF decreases when the CI of cellulose decreases.

INTRODUCTION

The modification of cotton fibers by graft copolymerization techniques allows us to chemically change the cellulose chain by introducing polymeric chains that confer different structural characteristics to the initial material.

Among the redox systems, Ce(IV) ion offers many advantages. It produces a complex with cellulose, which decomposes to generate free radicals

onto the cellulosic backbone where grafting of vinylic monomers may occur.¹ Homopolymer formation is less significant than in other conventional radical initiator systems.

In this paper, we consider the effects of some reaction conditions on the grafting percentage (%G), the length of grafted chains (M_v), and the number of grafted chains per cellulose unit (GF).

EXPERIMENTAL

Materials

Hydrophilic cotton was purified by treatment with chloroform (18 h under reflux), ethanol (18 h under

* Dedicated to Professor Gonzalo Martín Guzmán on the occasion of his nomination as Emeritus Professor of the University of the Basque Country.

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reflux), and a 1% NaOH solution (10 h under reflux and nitrogen atmosphere),² called Cel. A in this paper.

After this purification process, mercerized cotton was prepared by treatment with NaOH solutions: 10, 15, and 20% (called here Cel. B, Cel. C, and Cel. D, respectively) at room temperature for 24 h, followed by washing and drying in a vacuum at 80°C.

Vinyl acetate and methyl acrylate (Merck for synthesis) were washed successively with a 10% NaOH solution and water, then dried with CaCl₂ and distilled under nitrogen at a reduced pressure before use. Cerium ammonium nitrate (Merck reagent grade) was used to prepare the initiator solution.

Graft Polymerization

The graft polymerization reaction was carried out as follows: a conditioned sample of cellulose (1.5 g) was immersed in cerium ammonium nitrate 0.01 N in a nitric acid solution pH 2.5. Three different volumes of this Ce(IV) solution were used: 80, 70, and 65 mL. After 20 min at 30°C, in a nitrogen atmosphere with mechanical stirring, the monomer mixture was added dropwise to the reaction mixture stirred in a nitrogen atmosphere at 30°C for 2.5 h. The total liquid volume (aqueous solution and monomeric mixture) was always 100 mL. The ratios of aqueous Ce(IV) solution volume/monomeric mixture volume, V_{aq}/V_{mon} , were: 80/20, 70/30, and 65/35. The monomeric mixture ratios of vinyl acetate volume/methyl acrylate volume, V_{VA}/V_{MA} , were 80/20, 85/15, 90/10, 95/5, and 100/0 (called here series 1, 2, 3, 4, and 5, respectively). After 2.5 h of reaction, the graft copolymer was filtered onto a sintered glass crucible and washed with water and acetone. The purification of the graft was performed by Soxhlet extraction with acetone.

The percentage of graft %G was calculated as follows:

$$\%G = \frac{\text{dry wt of grafted sample} - \text{dry wt of original sample}}{\text{dry wt of original sample}} \times 100 \quad (1)$$

Copolymers of poly(vinyl acetate)-poly(methyl acrylate) PVA-PMA without cellulose were prepared in a similar way. The volumetric rate, V_{aq}/V_{mon} , was 70/30 and the monomeric mixture ratios were V_{VA}/V_{MA} : 80/20 and 90/10.

Acid Hydrolysis of Copolymers

Acid hydrolysis of graft copolymers was carried out as follows: Graft copolymer (1 g) was dispersed in 20 mL of 72% H₂SO₄ for 6 h at room temperature. Distilled water was then added until the H₂SO₄ concentration was 1 N and the mixture stirred at 140°C for 2 h. The hydrolyzed product was filtered and washed with distilled water until no acid reaction was reached.

Viscosity Measurements

An Ubbelohde viscosimeter was used for intrinsic viscosity, $[\eta]$, measurements. The Mark-Houwink equation was applied to calculate the viscosimetric average molecular weight.

A cadoxen [Cd(en)₃](OH)₂ solution with 5.7% of cadmium was prepared³ for the cellulose solutions. Mark-Houwink constants for the cellulose-cadoxen system at 25°C⁴ were used to calculate the viscosimetric average molecular weight (M_v) and the degree of polymerization (DP) of each cellulose sample.

The viscosimetric average molecular weight of hydrolyzed products was determined from acetone solutions at 25°C, using as Mark-Houwink constants $K \cdot 10^5 = 21.40$ and $a = 0.68$, corresponding to the acetone-poly(vinyl acetate) system at 25°C.⁴

The grafting frequency (GF) was calculated as follows:

$$\begin{aligned} GF &= \frac{\text{Number of vinylic chains}}{\text{Number of cellulosic chains}} \\ &= \frac{\text{Vinylic grafted chains wt}/M_v \text{ (PAV-PAM)}}{\text{Cellulose wt}/M_v \text{ (cellulose)}} \end{aligned} \quad (2)$$

IR Spectroscopy

Infrared (IR) spectra were obtained with a Beckman Accu Lab-6 spectrophotometer, using the potassium bromide pellet technique for cellulose, and its graft copolymer samples and films for hydrolyzed products were cast from acetone solutions.

To measure the crystallinity of cellulosic materials, the infrared ratio of absorbances proposed by Nelson and O'Connor was used as the crystallinity index (CI)⁵ at 1372 cm⁻¹ (C-H bending), which is most suitable for detecting the crystallinity and should not be affected by differences in the amount of water absorbed on cellulose, and 2900 cm⁻¹ (C-H stretching), which acts as internal standard:

Table I Crystallinity Index (CI), Intrinsic Viscosity ($[\eta]$) in Cadoxen Solution, Viscosimetric Average Molecular Weight (M_v), and Polymerization Degree (PD) for Native and Mercerized Cotton Cellulose with Different % NaOH Concentrations

	% NaOH in Mercerized	CI	$[\eta]$ (mL/g)	M_v	PD
Cel. A	—	0.68	770.03	340209	2088
Cel. B	10	0.58	749.03	279741	1722
Cel. C	15	0.53	717.68	267791	1650
Cel. D	20	0.49	705.04	263075	1621

$$a_{1372 \text{ cm}^{-1}}/a_{2900 \text{ cm}^{-1}} \quad (3)$$

The advantage of this ratio over others that have been used is that it can be applied to both celluloses I and II and therefore to samples containing a mixed lattice.

RESULTS AND DISCUSSION

The variables studied include crystallinity of cellulose, ratio $V_{\text{aq}}/V_{\text{mon}}$, and ratio $V_{\text{VA}}/V_{\text{MA}}$. The results obtained are given below with appropriate discussion.

Cellulose Characteristics

Table I shows the determined characteristics of different samples of cellulose: native and mercerized with NaOH solutions of different concentrations.

These results show that the NaOH treatment leads to a decrease in the crystallinity index (CI), calculated according to formula (3), which is in agreement with the general idea that native cellulose (cellulose-I) becomes cellulose-II, less crystalline, after NaOH treatment,^{6,7} with a decrease in hydrogen bonds.⁸⁻¹⁰ The cellulose polymerization degree, PD, also decreases because of the chain alkaline degradation.

Effect of Ratio of Initiator Ce(IV) Solution Volume/Monomeric Mixture Volume on Grafting Percentage

The highest percentage of grafting was achieved when the ratio $V_{\text{aq}}/V_{\text{mon}}$ was 70/30 for any ratio of $V_{\text{VA}}/V_{\text{MA}}$ (cellulose mercerized 15% NaOH, Cel. C), as shown in Table II.

It seems that for the ratio $V_{\text{aq}}/V_{\text{mon}} = 80/20$ the monomer quantity is too low to give a greater %G,

whereas for 65/35, homopolymer formation becomes the preferred process. Therefore, the %G decreases.

Effect of Cellulose Crystallinity and % Methyl Acrylate in Monomeric Mixture on Grafting Percentage

Figure 1 shows the effect of the methyl acrylate percentage on the monomeric mixture (VA-MA) and that of the crystallinity index of cellulosic material on the percentage of graft yield.

The percentage of grafting is observed to increase significantly as the MA percentage increases in the monomeric mixture. This shows the higher reactivity of MA over that of VA. The %G also increases when the crystallinity of the cellulosic substrate decreases.

Analysis of the Hydrolyzed Grafted Vinyllic Chains

Graft copolymers were treated with 72% H_2SO_4 to eliminate cellulosic backbone and to obtain grafted

Table II Percentage of Grafting (% G) of Cellulose Copolymers for Different Volumetric Ratios: Aqueous Initiator Solution/Monomeric Mixture ($V_{\text{aq}}/V_{\text{mon}}$); and for Different Volumetric Ratios: Vinyl Acetate/Methyl Acrylate ($V_{\text{VA}}/V_{\text{MA}}$)

$V_{\text{aq}}/V_{\text{mon}}$	$V_{\text{VA}}/V_{\text{MA}}$	%G
80/20	80/20	43
	85/15	39
	90/10	6
70/30	80/20	170
	85/15	73
	90/10	33
65/35	80/20	31
	85/15	27
	90/10	3

The cellulosic substrate was cellulose mercerized 15%, NaOH, Cel.C.

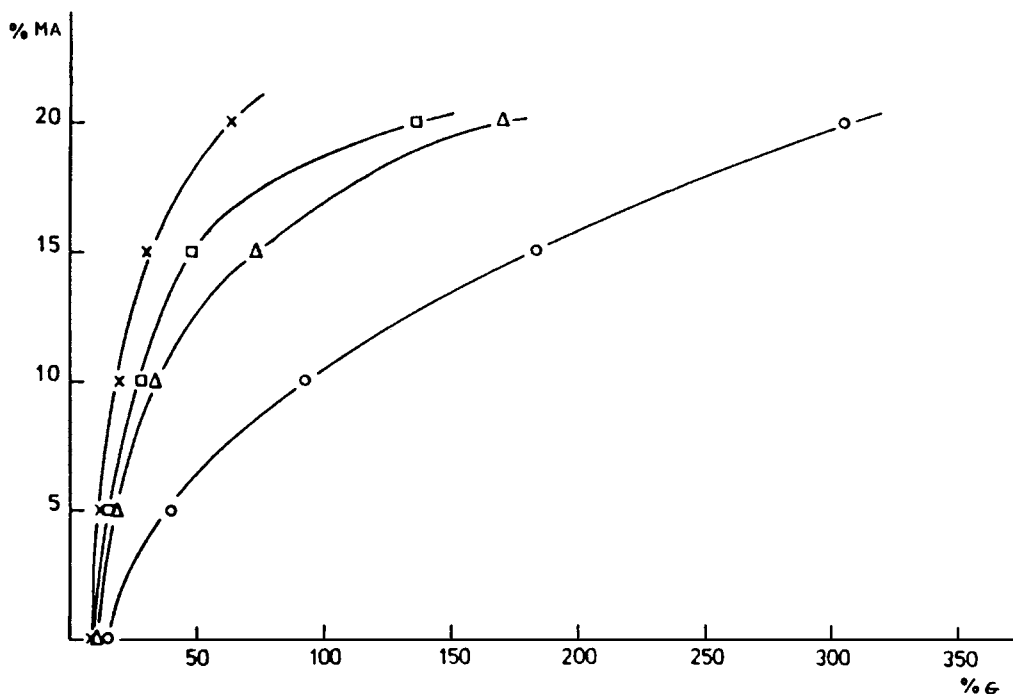


Figure 1 Grafting percentage of cellulose copolymers, for different methyl acrylate percentages in monomeric mixture (VA-MA) and for different cellulosic substrates. (x) Native cellulose (Cel. A); (□) mercerized 10% NaOH (Cel. B); (Δ) mercerized 15% NaOH (Cel. C); (○) mercerized 20% NaOH (Cel. D).

vinyl chains. Under these conditions, the degradation of copolymers of poly(vinyl acetate)-poly(methyl acrylate) without cellulose was very low, while ungrafted cellulose was carbonized. The vinyl graft copolymers of cellulose showed three different behaviors after this acid treatment: Hydrolyzed products from higher grafting percentage copolymers were swollen in acetone, but did not dissolve at all, which may be due to some cellulosic residues that have not been eliminated by the hydrolysis. These cellulosic residues are shown in their IR spectra (Fig. 2, sample HCD1) in the 1200–1000 cm^{-1} region. It seems that the grafted vinyl chains have protected the cellulose backbone against hydrolysis. Hydrolyzed products from moderate %G copolymers were soluble in acetone, and no cellulosic residues were observed in their IR spectra. Lower %G copolymers were nearly destroyed after acid hydrolysis.

Effect of Methyl Acrylate Percentage on Vinyl Grafted Chains M_v and GF

The increase in %G of cellulosic copolymers can be explained in two ways: an increase in the length of

the vinyl grafted chains, and an increase in the number of grafted chains.

Figure 3(a) and (b) shows how M_v and GF defined in eq. (2) increases with the methyl acrylate percentage in the monomeric mixture.

The increase in the M_v of vinyl chains with the %MA [Fig. 3(a)] indicates that the growth of the grafted chains on cellulose is favored by the presence of MA, probably due to its greater reactivity. It has also been shown that the increase in the M_v with the %MA tends to be stronger when the amorphous character of the cellulosic substrate of copolymer increases, as will be discussed below.

The increase in the GF of cellulosic vinyl copolymers with the %MA in the monomeric mixture [Fig. 3(b)] indicates that the number of cellulose-vinyl chain bonds increases with the ratio of this monomer in the mixture VA/MA.

From these results, it may be assumed that the increase in the graft percentage of cellulosic copolymer with the %MA is due to both an increase in the vinyl chain length and to an increase in the number of the cellulose-vinyl chain bonds. This shows that the higher reactivity of MA versus VA is shown in both reactions: the growing vinyl chains and the grafting on cellulose.

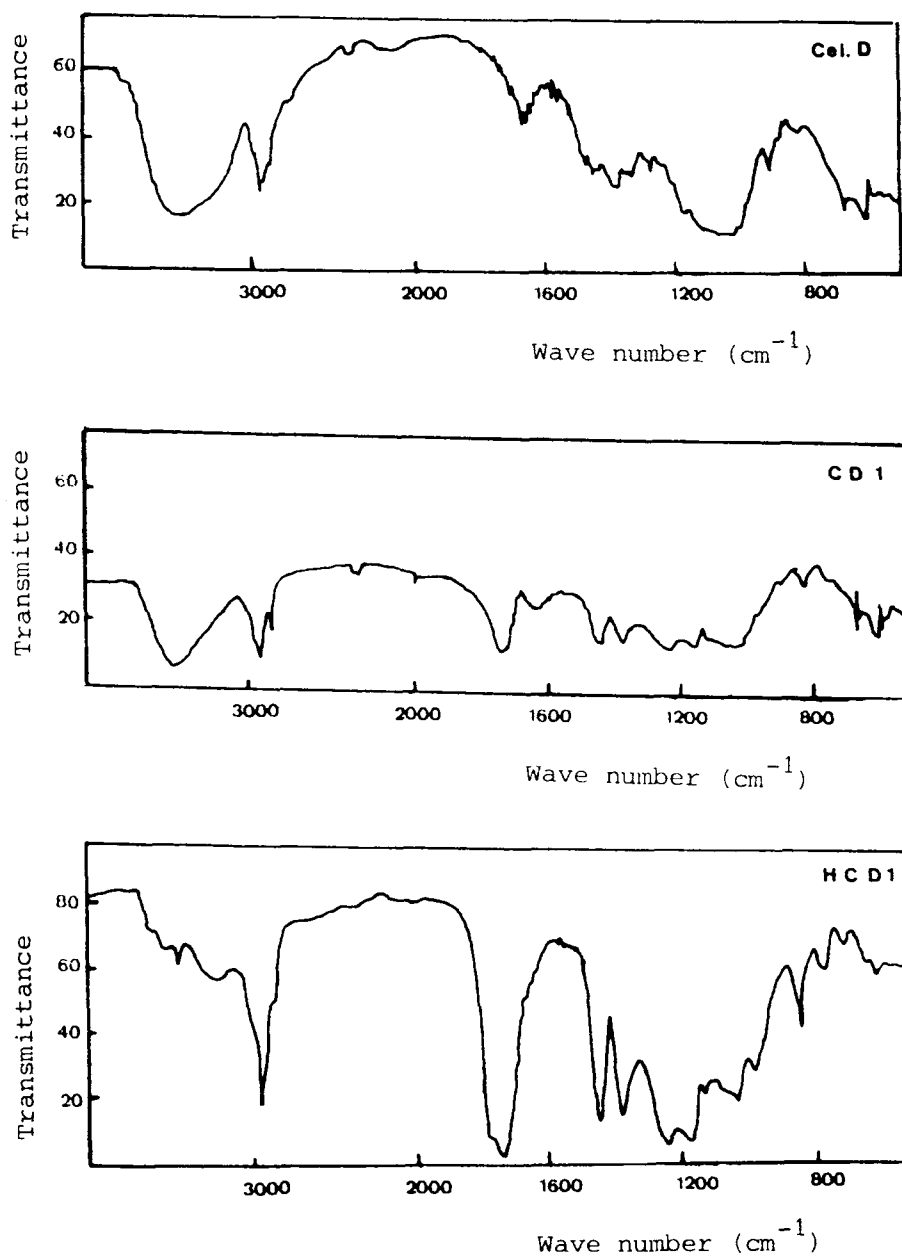


Figure 2 Infrared spectrum of cellulose mercerized 20% NaOH (Cel. D); one of their vinyl copolymers, CD1: 170%G and vinyl grafted chain after H_2SO_4 treatment, HCD1.

Effect of Cellulose Crystallinity on Vinyl Grafted Chains M_v and GF

It is assumed that grafting on cellulose occurs exclusively in the accessible regions of cellulose,¹¹ which are less ordered and less crystalline, and therefore diffusion and grafting of a monomer is restricted to these regions.¹²

Figure 4 shows the relationship between the crystallinity index (CI) of the cellulosic substrate and

the M_v of the vinyl chains grafted on it [Fig. 4(a)] and the number of vinyl chains per cellulose unit (GF) [Fig. 4(b)]. It is seen that the M_v , and therefore the length of the vinyl chains, increases as the crystallinity index decreases [Fig. 4(a)]. It may be thought that the growth of the vinyl chains is favored by the amorphous character of the cellulosic substrate.

The increase of GF with the crystallinity index of the cellulosic substrate for any ratio V_{VA}/V_{MA}

[Fig. 4(b)] indicates that the number of vinylic chains grafted on cellulose is higher for a higher crystallinity index.

Although the grafting percentage is higher in most amorphous celluloses (CI lower) as shown in Figure 1, the data shown in Figures 4(a) and (b) seem to indicate that in most amorphous cellulosic substrates (and for any ratio of V_{VA}/V_{MA} used) the growing vinylic chain reaction predominates over the grafting on the cellulose reaction, since the M_v increases and the GF decreases. Therefore, the higher %G in less crystalline samples is due to the

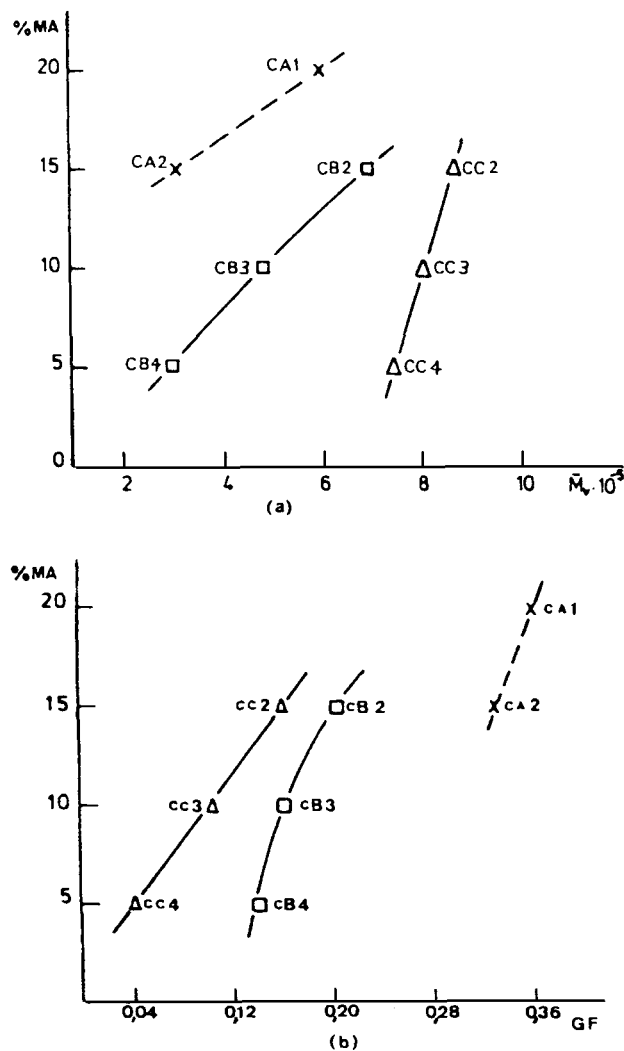


Figure 3 Relationship between methyl acrylate percentage, %MA, in monomeric mixture for different cellulosic substrates. (x) Native cellulose, Cel. A; (□) mercerized 10% NaOH, Cel. B; (Δ) mercerized 15% NaOH, Cel. C; (a) viscosimetric average molecular weight, M_v , of grafted vinylic chains; (b) grafting frequency, GF.

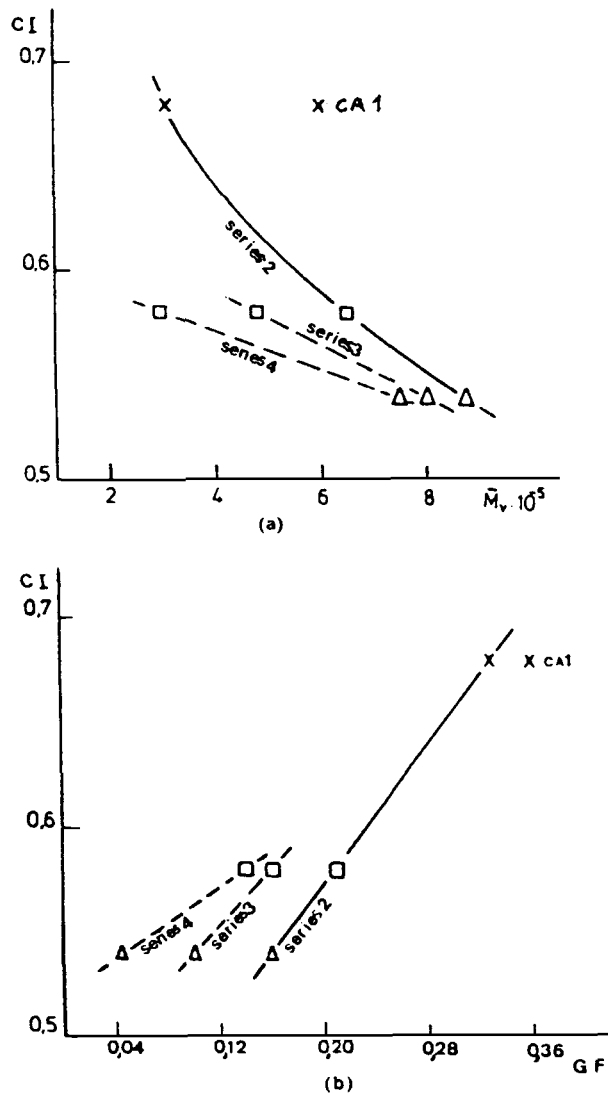


Figure 4 Relationship between the crystallinity index (CI) of cellulosic substrate for different ratios V_{VA}/V_{MA} (series 1: $V_{VA}/V_{MA} = 80/20$ with only one point: CA1; series 2: $V_{VA}/V_{MA} = 85/15$; series 3: $V_{VA}/V_{MA} = 90/10$; series 4: $V_{VA}/V_{MA} = 95/5$); (a) viscosimetric average molecular weight (M_v) of grafted vinylic chains; (b) grafting frequency (GF).

growth of the grafted chains and not to a higher number of vinylic grafted chains.

The authors thank the CICYT for the research grant that supported this work (Project no. 0395/85). They also wish to express their appreciation to Mrs. Mercedes Leal for her collaboration in the viscosimetric measurements.

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Received December 27, 1989

Accepted October 12, 1990