

Synthesis of Graft Copolymers of Acrylic Monomers onto Amylose. II. Study of the Ceric Ion Behavior

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

Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química de San Sebastián, Apdo. 1072, San Sebastián-20080, Spain

SYNOPSIS

A study of the ceric ion consumption during graft polymerization of methyl acrylate (MA), ethyl acrylate (EA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) with amylose was carried out. Grafted acrylic polymers were isolated by the acid hydrolysis method. Weight-average and number-average molecular weights were determined by gel permeation chromatography (GPC). The number of grafted chains (mmol) ranged from 8.70×10^{-3} to 12.35×10^{-3} for acrylates and from 3.20×10^{-3} to 6.80×10^{-3} for methacrylates. These results were related to others obtained from the ceric ion consumption studies.

INTRODUCTION

A previous paper¹ reported evidence for grafting when polymerizations of MA, EA, EMA and BMA were initiated by ceric salt in dispersions of amylose. The effect of time on polymer composition was also studied.

In the present work, the gel permeation chromatography (GPC) technique was applied to obtain the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the acrylic polymer grafted chains. Using these values and those from the Ce(IV) determinations we can obtain relevant information about the structure of the copolymers, as reported previously with methyl methacrylate (MMA) and butyl acrylate (BA).^{2,3}

EXPERIMENTAL

The copolymerization reactions were carried out as described in other publications.^{1,4}

Determination of Total Ceric Ion Consumption

The concentration of total ceric ion in the reaction mixtures was determined volumetrically⁵ with ferrous sulfate; ferrous *o*-phenantroline (ferroin) was used as the indicator. An aliquot of this solution was removed at various intervals and the unreacted ceric ion was quenched in an excess of 0.0025*N* standard ferrous sulfate. The excess ferrous ion was then titrated with a 0.0025*N* standard ceric sulfate solution.

Gel Permeation Chromatography

The molecular weight distributions of the acrylic polymer grafted chains were obtained by GPC (Waters, model LC-150).

Four columns with microstyrogel of pore sizes 500, 10^4 , 10^5 , and 10^6 Å were used. The elution solvent was THF and the flow rate was maintained at 1 mL/min; 100 μL of a 0.05% acrylic polymer solution was injected.

The calibration of GPC was carried out with standard PS samples obtained from Waters Associates, with M_p of 1,800, 2,900, 4,000, 8,500, 50,000, 1×10^5 , 2.4×10^5 , 3.4×10^5 , 7.75×10^5 , 1.25×10^6 , 1.75×10^6 , 3×10^6 , and 2×10^7 .

The molecular weights, M_w and M_n , were calcu-

* To whom correspondence should be addressed.

Table I Mark-Houwink Constants in THF at 25°C for Various Monomers^{6,7}

Polymer	K (cm ³ /g)	a
PS	1.600 × 10 ⁴	0.706
PEMA	1.549 × 10 ⁴	0.679
PBMA	0.501 × 10 ⁴	0.758

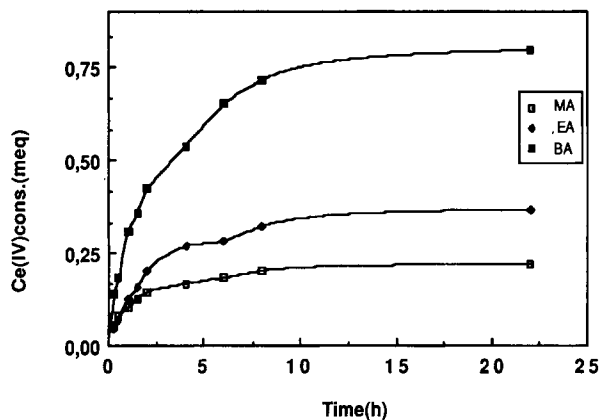
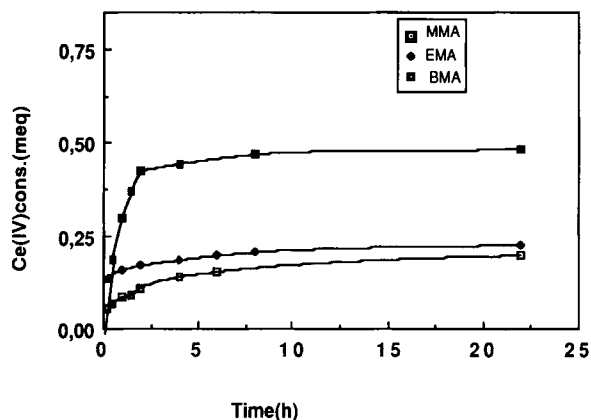
lated from GPC chromatograms and an analysis was made from the results of the universal calibration. The Mark-Houwink coefficients used for methacrylates are listed in Table I and for the acrylates we used the same coefficients as for PS.

RESULTS AND DISCUSSION

In the discussion we will also take into account the results from the systems PMMA-*g*-amylose^{1,2} and PBA-*g*-amylose³ obtained in previous experiments.

Study of Ceric Ion Consumption

As we explained in our previous reports,^{2,3} ceric ion can be consumed in both initiation and termination reactions. Figures 1 and 2 show that ceric ion consumption increases rapidly at the first stages of the reaction, and more slowly when reaction advances. This is in good agreement with the fact that the larger the ceric ion concentration in the reaction medium, the more rapidly the ceric ion is consumed.⁸ On the other hand, at the initial stages, the ceric ion can find many reaction sites, so the formation of active points is very rapid both in the amylose chains and in the monomer units. Furthermore, ox-

**Figure 1** Plots of the ceric ion consumption vs. time for various acrylates.**Figure 2** Plots of the ceric ion consumption vs. time for various methacrylates.

idative termination of the active sites in the growing polymeric chains can take place.

As the reaction time advances, the decrease of the slope could be due to a decrease of the initiation reaction on the carbohydrate, and could be explained by the following:

1. A diminution of the sites capable of being oxidized
2. Steric hindrance to the attack of the ceric ions on the amylose centers due to the grafted polymer already formed
3. An increase in the hydrophobic nature of the backbone as grafting takes place, which would inhibit the diffusion of the Ce(IV) ion, since we work in an aqueous medium.

By comparing the absolute values obtained with acrylates and methacrylates we observed that the ceric ion consumption is greater for acrylates than for methacrylates, and in each group the longer the alkyl group the larger is the ceric ion consumption. This last fact can be due to an increase in the steric hindrance which does not allow the entrance of more monomer to form new grafted chains. Thus, the radical formed by the Ce(IV) ion on the carbohydrate backbone will react with more Ce(IV), to be oxidized according to the reaction:



where S = starch. This termination reaction will be more probable than those of a typical radical polymerization process and will contribute to a higher ceric ion consumption.

Table II Average Molecular Weights for PMA [Poly(methyl acrylate)], PEA [Poly(ethyl acrylate)], and PBA [Poly(butyl acrylate)] Grafted at Various Reaction Times

Time (h)	PMA		PEA		PBA	
	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$
¼	2.132	306	501	163	—	—
½	—	—	—	—	828	167
1	1.890	305	454	163	1.400	233
1½	—	—	—	—	1.100	236
2	1.316	273	437	148	1.130	265
4	2.171	251	488	171	1.500	358
6	1.804	256	416	143	—	—
8	2.104	251	446	162	1.370	293
22	2.325	273	504	176	1.400	271

Molecular Weight Distribution

The molecular weights obtained for each reaction time are shown in Tables II and III. As it can be expected for a radical polymerization, M_n and M_w are practically constant in time.

Acrylic Grafted Chains

From the weights of the grafted polymer and its M_n , the total number of grafted chains (N_G) and the number of anhydroglucose units (AGU) per grafted chain (frequency) for each reaction were calculated² following the expressions:

$$N_G = \frac{\text{weight of acrylic grafted chains (g)}}{M_n} \quad \text{of the grafted chains}$$

$$\text{frequency} = \frac{\text{weight of grafted amylose (g)}/162}{N_G}$$

The values obtained for the four polymers used are listed in Tables IV, V, VI, and VII.

Figures 3 and 4 show that the number of grafted chains goes up with reaction time, and this number is larger for the acrylates. We also observed that the longer the alkyl group, the lower is the number of grafted chains.

Here again, there are various reasons to explain this behavior for acrylates and methacrylates. For methacrylates, this is due to the different molecular weights for each polymer. Owing to the insolubility of the EMA and BMA in the reaction medium the molecular weights reached by PEMA [Poly(ethyl methacrylate)] and PBMA [Poly(butyl methacrylate)] as polymerization advances, are higher than those obtained with the MMA, which is soluble in the reaction conditions. The minor dispersibility of BMA in the medium compared with that of EMA, would be another reason for obtaining grafted polymers with increasing molecular weights as the size of the alkyl group of the methacrylic ester goes up. These physical variations on the way in which the reaction will take place, would be sufficiently important to give a very different R_p for each poly-

Table III Average Molecular Weights of Polymethacrylates Obtained at Various Reaction Times

Time (h)	PMMA		PEMA		PBMA	
	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
¼	1.043	391	2.210	793	2.239	1.012
½	—	—	—	—	2.650	1.071
¾	—	—	—	—	2.991	1.206
1	1.379	412	2.175	739	2.607	1.056
2	1.051	401	2.209	717	2.440	1.323
4	1.238	408	2.079	729	2.725	1.348
6	1.114	398	2.128	700	2.587	1.137
8	1.072	409	2.239	751	2.775	1.434
22	1.105	402	2.084	750	2.727	1.278

Table IV Number of Grafted Chains, Percent Grafted Monomer, and Percent Grafting (%G)² in the Copolymerization Reaction of PEMA at Various Reaction Times

Time (h)	$N_G \times 10^3$ (mmol)	%Pol _g	%G
¼	2.01	26	338
1	2.53	33	267
2	2.98	38	263
4	3.45	47	284
6	3.77	45	298
8	3.78	47	305
22	4.00	49	321

merization, and consequently different molecular weights. However, with the acrylates we found similar molecular weights for PMA and PBA, although those of the PEA are lower. So, the differences in the N_G of PMA and PEA with respect to those of PBA would be due to differences in the amount of grafted polymer. This amount decreases as the alkyl group of the ester becomes larger, so we could attribute this decrease to the steric hindrance produced by the larger molecules which will obstruct the entrance of new monomer molecules to add to the graft copolymer.

The plots of grafting frequency versus time are shown in Figures 5 and 6. We can observe that in practically all cases the frequency decreases with increasing reaction time. This agrees with the constancy in molecular weights and with the increasing N_G with time.

Some interesting conclusions can be drawn from these parameters. If we relate the ceric consumption to N_G we obtain the plots in Figures 7 and 8. In

Table V Number of Grafted Chains, Percent Grafted Monomer, and Percent Grafting (%G)² in the Copolymerization Reaction of PBMA at Various Reaction Times

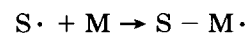
Time (h)	$N_G \times 10^3$ (mmol)	%Pol _g	%G
¼	0.41	6	84
½	0.92	17	134
¾	0.92	30	229
1	1.91	42	258
2	2.31	45	269
4	2.52	47	285
6	2.80	48	304
8	3.00	48	317
22	3.20	48	333

Table VI Number of Grafted Chains, Percent Grafted Monomer, and Percent Grafting (%G)² in the Copolymerization Reaction of PMA at Various Times

Time (h)	$N_G \times 10^3$ (mmol)	%Pol _g	%G
¼	8.50	35	149
1	9.95	46	208
2	10.5	49	236
4	10.6	53	248
6	12.0	55	250
8	12.5	57	236
22	12.4	60	214

Table VIII we also list this relationship at the longest reaction times.

We can observe that these values are higher for the methacrylates than for the corresponding acrylates, although the ceric ion consumption is lower for the methacrylates. If we analyze each group, we observe that as the size of alkyl group increases, the ceric ion consumption goes up for a minor N_G . The difference between acrylates and methacrylates can be explained because with acrylates the reaction

**Table VII** Number of Grafted Chains, Percent Grafted Monomer, and Percent Grafting (%G)² in the Copolymerization Reaction of PEA at Various Reaction Times

Time (h)	$N_G \times 10^3$ (mmol)	%Pol _g	%G
¼	8.57	31	366
1	9.53	36	282
2	10.1	42	267
4	10.9	46	261
6	11.3	47	237
8	11.6	48	208
22	12.4	49	193

Table VIII Relation Between Ce(IV) Consumption and N_G for the Different Monomers

Monomer	Ce(IV) Consumption % (meq)	Ce(IV) Consumption/ N_G
MA	22	18
EA	37	30
BA	80	91
MMA	20	29
EMA	22	56
BMA	48	150

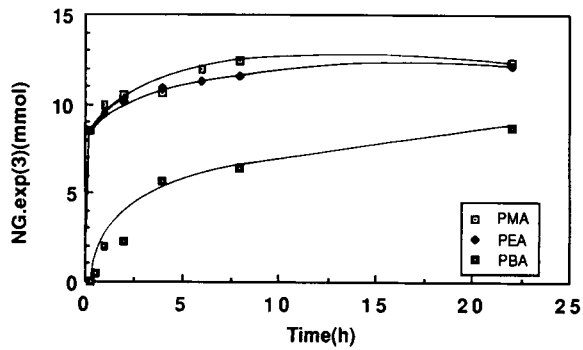


Figure 3 Number of grafted chains for various acrylates vs. time.

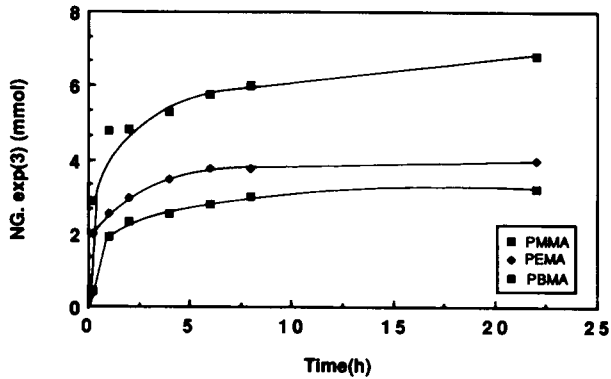


Figure 4 Number of grafted chains of various methacrylates vs. time.

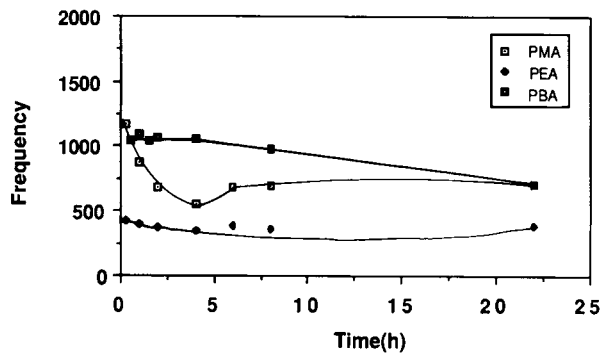


Figure 5 Data on grafting frequency obtained in the grafting of various acrylates at different reaction times.

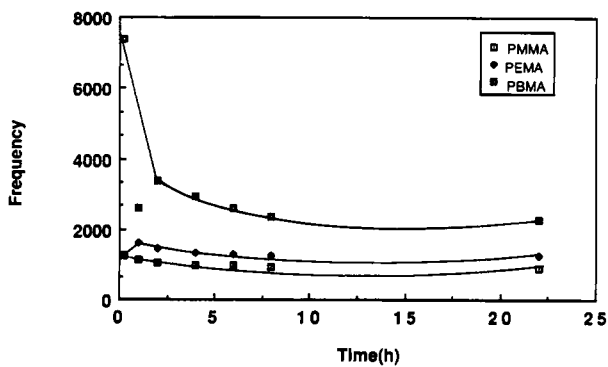


Figure 6 Data of grafting frequency obtained in the grafting of various methacrylates at different reaction times.

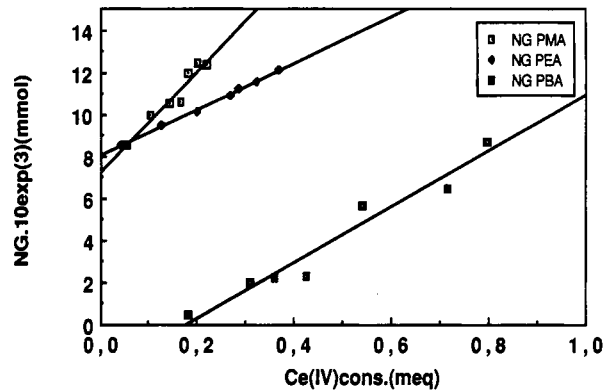


Figure 7 Relationship between the number of grafted chains and the ceric ion consumption for various acrylates.

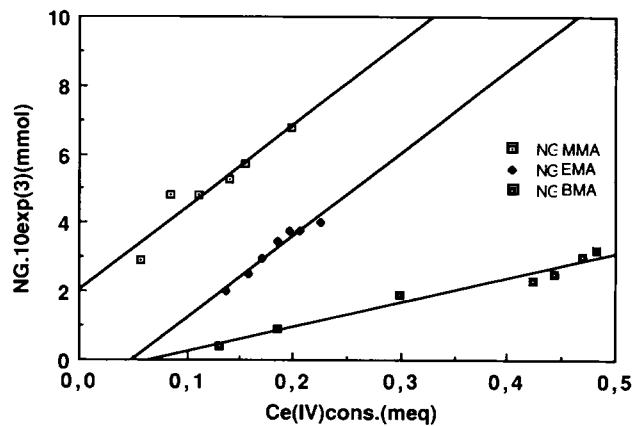


Figure 8 Relationship between the number of grafted chains and the ceric ion consumption for various methacrylates.

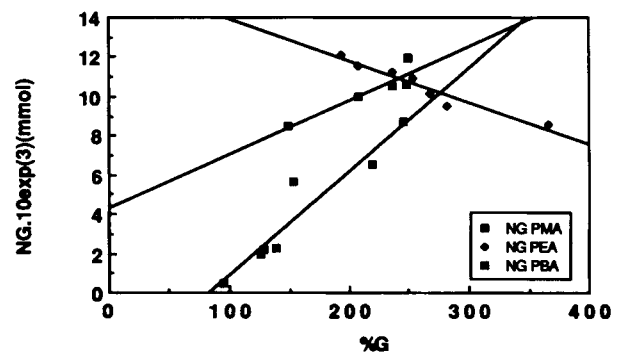


Figure 9 Number of grafted chains vs. percent grafting (%G) for various acrylates.

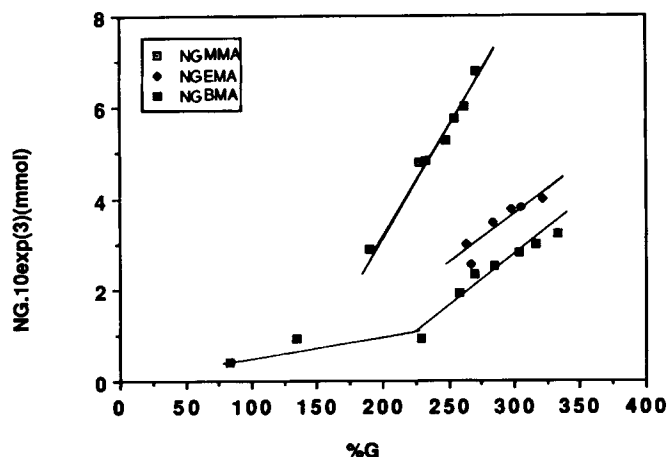


Figure 10 Relationship between N_G and the %G for various methacrylates.

is preferential to the reaction



so that the monomer is grafted more quickly than homopolymer is formed.⁹ This is in good agreement with the fact that the acrylates have a %GE higher than the methacrylates.

The decrease in N_G and the increase in the ceric ion consumption as size of the alkyl group gets larger, can be explained by the following: as the size of alkyl group increases the steric hindrance increases too, and so the monomer entrance to start new grafted chains will be more difficult than the entrance of ceric ions to oxidize the radical sites on the carbohydrate. This agrees with the diminution of %GE when the size of the alkyl group increases.

If we relate N_G and %G,¹ we obtain the plots shown in Figures 9 and 10. In all cases we obtain a linear relationship, and thus the increase in %G could be due to an increase in N_G and not to an increase in molecular weight.

We can observe an exception in this behavior, with PEA. In this case the slope goes down. This may be due not to a decrease in the %G with reaction time, caused by an increase of the amount of grafted amylose and not by a lesser N_G .

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