Synthesis of graft copolymers of hydrophobic and hydrophilic methacrylates onto amylopectin

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Mixtures of hydrophilic and hydrophobic methacrylates were grafted onto amylopectin, using the ceric ion redox initiation system. The pairs hydroxyethyl methacrylate (HEMA)/methyl methacrylate (MMA), hydroxypropyl methacrylate (HPMA)/MMA, HEMA/ethyl methacrylate (EMA) and HPMA/EMA were grafted at different concentrations of the monomer feed. In all cases, a major formation of ungrafted acrylic polymer can be observed when the hydrophilic monomer used is HPMA. High yields were obtained with all the mixtures at certain concentrations of the monomer feed.

(Keywords: copolymers; amylopectin; methacrylates)

INTRODUCTION

Graft copolymerization is an important method for increasing the biocompatibility of materials for use in medicine and surgery. Such biomaterials are of great significance in the fabrication or coating of devices and prostheses. An important factor in achieving this biocompatibility is the relation between the hydrophilic and hydrophobic groups in the macromolecule.

The current work is a continuation of an earlier study[1] on grafting copolymerization of hydrophilic and hydrophobic monomer mixtures onto amylopectin using ceric ammonium nitrate as initiator, with the aim of obtaining new biocompatible materials. We report here the graft copolymerization onto amylopectin of the mixtures hydroxyethyl methacrylate (HEMA)/methyl methacrylate (MMA), HEMA/ethyl methacrylate (EMA), hydroxypropyl methacrylate (HPMA)/MMA and HPMA/EMA. The variation of characteristic grafting yields for the different feed compositions are studied.

EXPERIMENTAL

Materials

The amylopectin used was a commercial product (Amylopectin-UG, Avebe, Holland). The hydrophilic methacrylates (Merck) were purified as described previously[2]. The hydrophobic methacrylates (Merck) were purified by washing and distilling under suitable conditions. Other reagent grade chemicals were obtained from various suppliers.

Methods

The graft copolymers were obtained by the method described previously[1]. The monomer feed compositions studied ranged from hydrophobic/hydrophilic = 0/100 to hydrophobic/hydrophilic = 100/0.

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RESULTS AND DISCUSSION

The parameters studied were: per cent grafting efficiency (%GE); per cent grafting (%G); per cent grafted polymer ($\%Pol_g$); and per cent total conversion (%CT). The results obtained for the four mixtures studied are shown in *Tables 1–4*. The term homopolymer will be used in the following to refer to the ungrafted acrylic polymer.

Table 1 Grafting yields of the copolymerization of HEMA/MMA onto amylopectin

HEMA/MMA (%)	Solid (g)	%GE	%G	$\%Pol_g$	%CT
100/0	4.31	86.1	129	39.2	50.4
90/10	4.90	85.0	140	46.0	59.8
80/20	6.00	84.6	187	63.4	81.1
70/30	5.32	85.8	153	54.2	69.0
60/40	4.35	74.6	68.3	25.7	47.6
50/50	4.22	67.4	46.3	18.0	45.7
40/60	4.24	68.2	43.5	17.5	45.2
20/80	4.34	69.9	56.4	22.5	49.8
0/100	4.82	71.6	67.5	29.6	58.8

Table 2 Grafting yields of the copolymerization of HPMA/MMA onto amylopectin

HPMA/MMA (%)	Solid (g)	%GE	%G	$\%Pol_g$	%CT
100/0	8.03	53.8	129	36.5	90.7
90/10	7.73	54.0	73.9	21.2	90.8
80/20	5.03	53.3	38.9	12.2	49.6
60/40	3.61	58.2	19.6	5.85	30.3
55/45	4.35	54.8	27.2	8.85	42.6
50/50	5.20	56.5	54.4	17.6	58.8
45/55	4.60	53.7	40.7	12.7	50.2
40/60	3.41	67.6	22.0	7.91	22.0
30/70	3.84	68.2	37.9	13.6	36.5
20/80	3.89	63.1	47.7	15.6	43.6
0/100	4.82	71.6	67.5	29.6	58.8

Table 3 Grafting yields of the copolymerization of HEMA/EMA onto amylopectin

HEMA/EMA (%)	Solid (g)	%GE	%G	$\%Pol_g$	%CT
100/0	4.31	86.1	129	39.2	50.4
80/20	4.52	85.2	151	42.2	54.6
60/40	5.20	84.0	140	47.1	61.7
50/50	5.32	85.9	129	47.6	61.5
40/60	5.48	77.6	124	43.6	63.0
20/80	5.36	77.6	124	43.6	63.0
0/100	5.96	72.1	129	43.1	73.5

Table 4 Grafting yields of the copolymerization of HPMA/EMA onto amylopectin

HPMA/EMA (%)	Solid (g)	%GE	%G	$\%Pol_g$	%CT
100/0	8.03	53.8	129	36.5	90.7
90/10	6.75	53.1	85.7	25.0	72.9
80/20	4.12	64.0	29.6	9.16	32.2
70/30	3.89	67.8	26.8	8.84	28.8
60/40	6.64	62.2	99.8	32.0	74.6
50/50	3.91	73.3	34.8	12.0	30.2
40/60	3.40	73.7	23.8	8.3	23.0
20/80	4.33	72.9	57.0	19.8	40.7
0/100	5.96	72.1	129	43.1	73.5

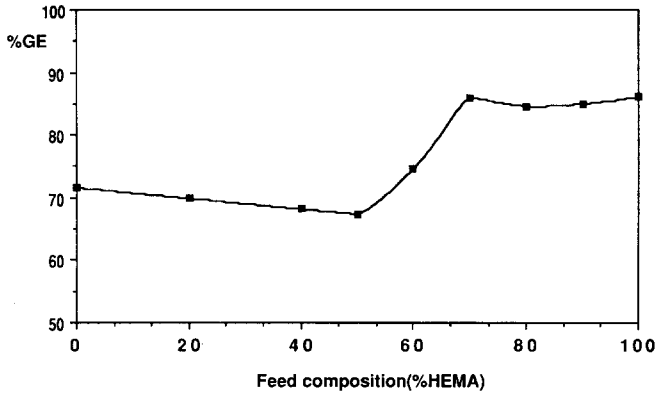

Figure 1 Plot of per cent grafting efficiency *versus* feed composition on grafting of HEMA/MMA mixture onto amylopectin

HEMA/MMA mixture

The evolution of %GE (*Figure 1*) and %G (*Figure 2*) is very similar. Consequently, the plots of $\%Pol_g$ and %CT (*Figure 3*) also have similar shapes. In all of these plots a maximum can be observed at a feed composition of HEMA/MMA = 80/20. That is to say, this feed concentration seems to be optimum to achieve the best grafting yields. Above and below this point, the values obtained are considerably lower. It is seen that the reactivity of the hydroxylic monomer is higher than that of the hydrophobic monomer[3–5] as found in the grafting of mixtures HEMA/EMA and HPMA/EMA[1].

HPMA/MMA mixture

As seen in *Table 2*, the evolution of this reaction, excluding the values for pure monomers, shows a maximum for a feed composition of HPMA/MMA = 50/50. To corroborate this, grafting onto amylopectin was carried out at feed compositions of HPMA/MMA = 45/55 and 55/45. In both cases, the yields obtained were greater than those obtained for feed compositions of HPMA/MMA = 40/60 and 60/40, respectively (*Figures 4–6*), and so the maximum point was confirmed.

It can be seen from *Table 2* that the parameter %GE remains practically constant for feed concentrations rich in HPMA. From a composition of HPMA/MMA = 40/60, %GE increases to a value of 71.6% for pure MMA. This means that as the feed composition is enriched in the hydrophobic monomer, the homopolymer formation is lower.

Comparing these results with those for HEMA/MMA,

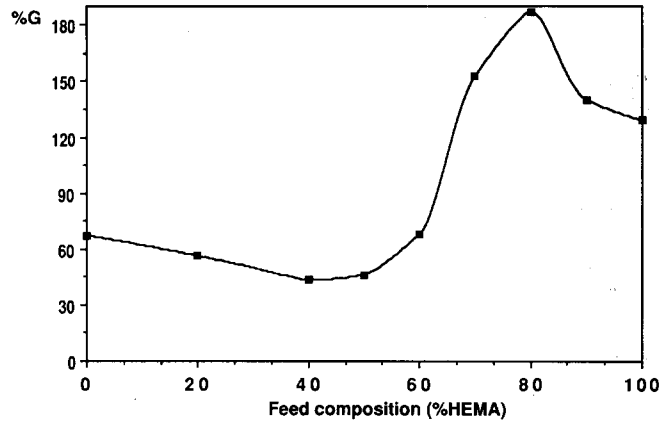

Figure 2 Plot of per cent grafting *versus* feed composition on grafting of HEMA/MMA mixture onto amylopectin

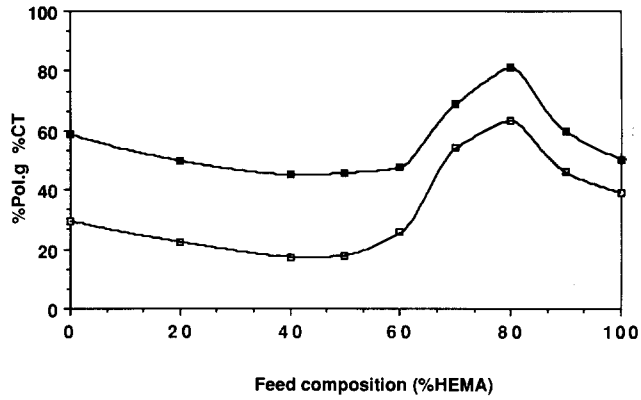

Figure 3 Plot of per cent grafted polymer (□) and per cent total conversion (■) *versus* feed composition on grafting of HEMA/MMA mixture onto amylopectin

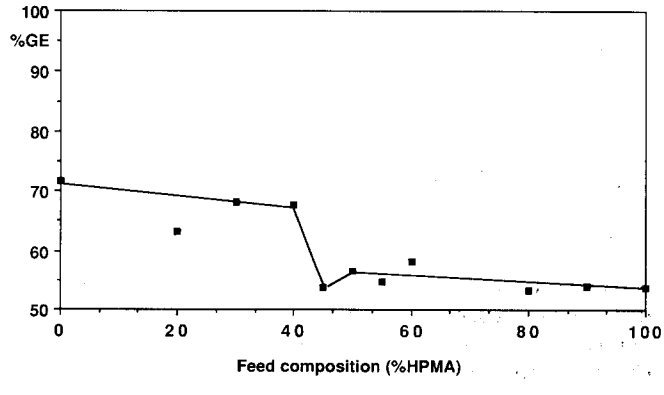

Figure 4 Plot of per cent grafting efficiency *versus* feed composition on grafting of HPMA/MMA mixture onto amylopectin

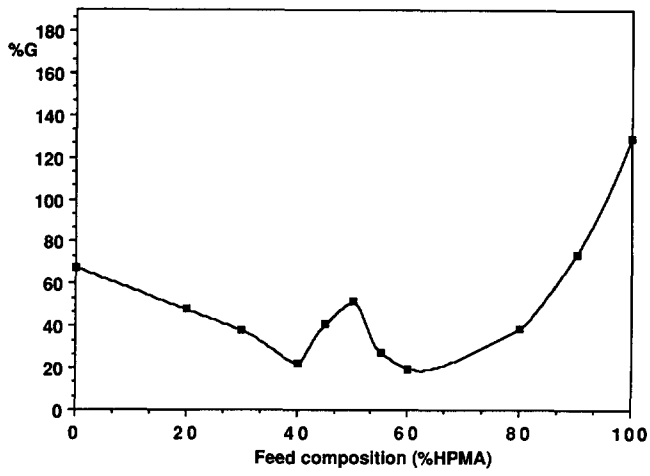

Figure 5 Plot of per cent grafting *versus* feed composition on grafting of HPMA/MMA mixture onto amylopectin

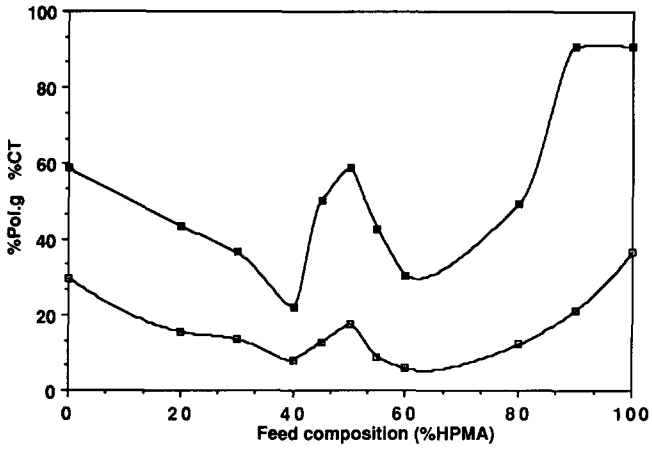

Figure 6 Plot of per cent grafted polymer (□) and per cent total conversion (■) *versus* feed composition on grafting of HPMA/MMA mixture onto amylopectin

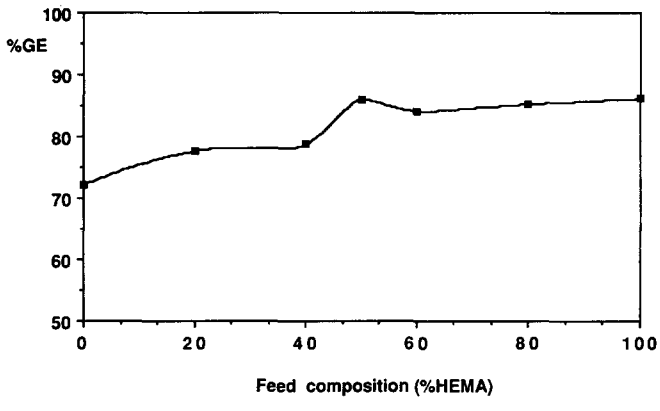

Figure 7 Plot of per cent grafting efficiency *versus* feed composition on grafting of HEMA/EMA mixture onto amylopectin

it can be observed that the %G yields are of the same order in both cases, as found when comparing the grafting of mixtures HEMA/ethyl acrylate (EA) with HPMA/EA[1]. On the other hand, comparison with HEMA/MMA shows that homopolymer formation is higher when the hydroxylic monomer is HPMA.

HEMA/EMA mixture

Figures 7 and *8* show that there is no great variation between the values obtained for %GE and %G. The %GE decreases slightly as the HEMA content in the monomer feed decreases, thus it can be said that the presence of this monomer favours grafting onto amylopectin as opposed to homopolymer formation.

If *Figures 2* and *8* are compared it can be seen that the change of %G *versus* monomer feed composition is very similar in both cases; there is a maximum at about 80% hydrophilic monomer in the feed, and a practically steady state is reached when its content decreases to below 40%.

By comparison of the conversion plots (*Figure 9*), the previous observations are corroborated, since $\%Pol_g$ remains practically constant up to HEMA = 40% whereas %CT decreases. That is to say, as the hydrophilic content in the feed increases, homopolymerization decreases.

HPMA/EMA mixture

At a feed composition of HPMA/EMA = 60/40, a minimum value of %GE can be observed (*Figure 10*), whereas %G (*Figure 11*), $\%Pol_g$ and %CT (*Figure 12*) show a maximum. This means that at HPMA/EMA = 60/40 there is not only an increase in %G but also an increase in homopolymer formation. By comparison of the two curves in *Figure 12*, it can be observed that the maximum of the %CT curve is sharper than that of the $\%Pol_g$ curve, due to the related homopolymer increase.

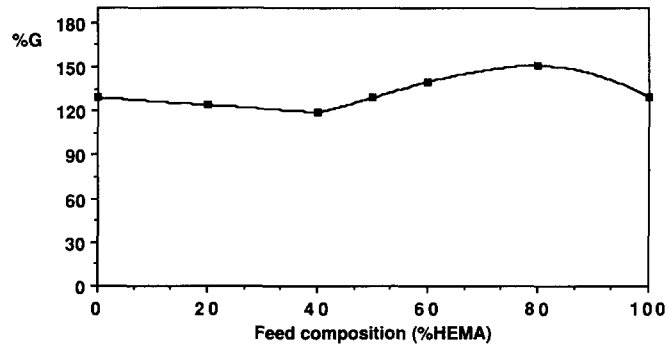

Figure 8 Plot of per cent grafting *versus* feed composition on grafting of HEMA/EMA mixture onto amylopectin

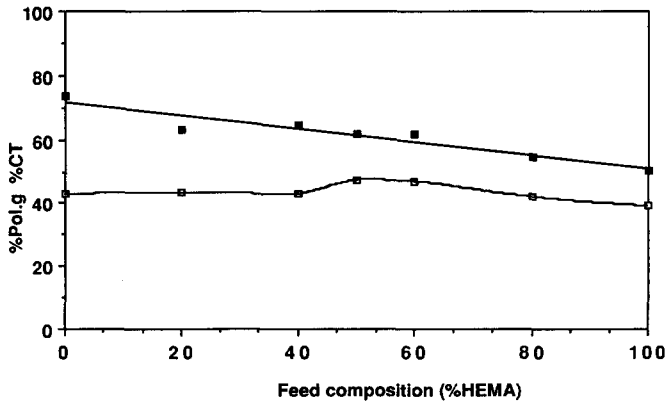

Figure 9 Plot of per cent grafted polymer (□) and per cent total conversion (■) *versus* feed composition on grafting of HEMA/EMA mixture onto amylopectin

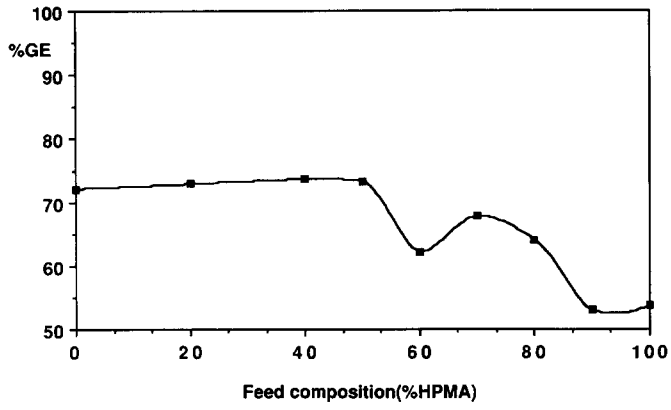

Figure 10 Plot of per cent grafting efficiency *versus* feed composition on grafting of HPMA/EMA mixture onto amylopectin

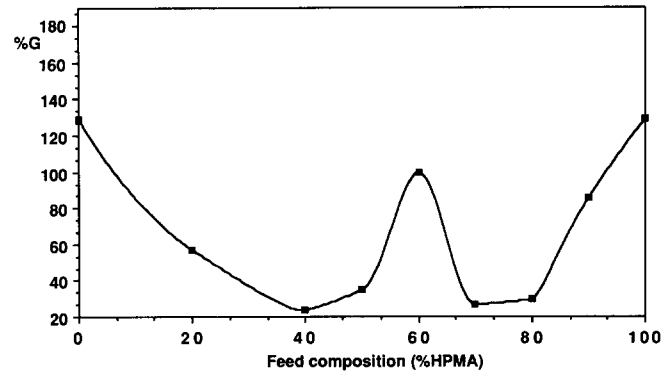

Figure 11 Plot of per cent grafting *versus* feed composition on grafting of HPMA/EMA mixture onto amylopectin

Here again, the evolution of %G is similar to that obtained in the grafting of the HPMA/MMA mixture (*Figure 5*). In both cases, after a rapid decrease of this parameter, a maximum point appears as the feed becomes richer in the hydrophylic monomer.

By comparison of *Tables 3* and *4* it can be seen, as in the two previous cases, that the amount of homopolymer is greater when HPMA is used instead of HEMA.

CONCLUSION

In this study, the homopolymerization tendency of the HPMA monomer is greater than that of the HEMA monomer, when they are grafted either alone or together

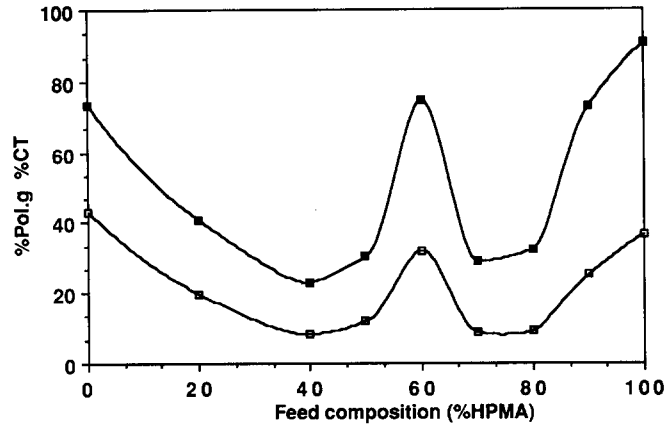

Figure 12 Plot of per cent grafted polymer (□) and per cent total conversion (■) *versus* feed composition on grafting of HPMA/EMA mixture onto amylopectin

with EA, MMA or EMA. However, the average %G values obtained are quite similar for the pairs formed between the hydroxylic monomers with each of the three hydrophobic monomers. However, when comparing the results for the mixtures HEMA/EMA and HPMA/EMA, it can be observed that those obtained with HEMA were higher, thus steric hindrance may be the cause of this behaviour.

Comparing the plots of yields obtained on the grafting of HEMA/EA and HPMA/EA mixtures, similar curves result. But when methacrylate mixtures were grafted, similar curves were observed between HEMA/MMA and HEMA/EMA on the one hand, and between HPMA/MMA and HPMA/EMA on the other.

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