Graft copolymerization of ethyl acrylate with alkyl methacrylates onto amylose initiated by cerium(IV). Microstructure of graft copolymers with respect to statistical copolymers

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The graft copolymerizations of ethyl acrylate (A) with ethyl methacrylate (E) and butyl methacrylate (B) via redox initiation with cerium(IV) in water at 30°C are described. The kinetic parameters of the grafting reaction such as yield of the graft copolymer, grafting efficiency and total conversion were evaluated comparatively and the microstructures of the graft copolymers were analysed by ^{13}C n.m.r. spectroscopy. The results obtained are compared with the microstructural characteristics of statistical A–E and A–B copolymers prepared by free radical copolymerization at low conversion using 2,2′-azobisisobutyronitrile as the initiator at 60°C.

(Keywords: graft copolymerization; microstructure; statistical copolymers)

INTRODUCTION

The modification of polymeric materials (natural or synthetic) to prepare selective membranes for biomedical applications (dialysis, controlled release, etc.) has become one of the most attractive subjects for several research groups in the last 20 years. One of the most important factors in the selection of biomedical membrane materials is the relationship between the chemical and morphological structures and properties. These parameters depend on the nature of the functional groups on the polymeric backbone, i.e. the side substituents, which in addition controls the hydrophilic or hydrophobic character of the macromolecular system. The permeability through a biomedical membrane is related to the diffusivity, which in fact is governed by the interaction between the permeating species and the components of the polymeric system[1–3]. In this sense, water-swellable polymers have been extensively used for the preparation of biomedical devices including membranes, controlled release mechanisms, etc.[4].

In the case of polymers derived from polysaccharides, modification of the hydrophilic character has been mainly performed by the chemical substitution of the hydroxy groups or by grafting of hydrophobic, polymeric chains onto the polysaccharide backbone[5–7]. In this sense, the graft copolymerization of acrylic monomers onto carbohydrates (amylose, amylopectin, starch, cellulose) by means of the cerium(IV) redox initiation method has been closely studied in our laboratories[8–10]. The structural characterization of these complex systems is not easy because of the heterogeneity of the samples, and therefore the estimation of the true compositions of graft copolymers containing acrylate and methacrylate units is difficult by the usual analytical techniques[11] because of the similarity in the chemical structures of the constituent units. U.v. and *FT*i.r. spectroscopic methods are not very helpful, and other methods such as gas–liquid chromatography and radiometric[12] and isotopic[13] analysis are time consuming and not sufficiently sensitive. However, n.m.r. spectroscopy gives a simple and accurate evaluation and, in particular, ^{13}C n.m.r. spectroscopy has shown many advantages for the determination of the graft copolymer composition, avoiding the necessity of degrading the polymeric systems[14].

The main objective of the present work was to study the kinetic parameters that control the graft copolymerization of ethyl acrylate (A) with ethyl methacrylate (E) and butyl methacrylate (B) onto amylose. Also, the compositions of the graft copolymers prepared at high conversion were compared with those

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of the corresponding statistical A–E and A–B copolymers prepared by free radical copolymerization using 2,2'-azobisisobutyronitrile (AIBN) as the initiator.

EXPERIMENTAL

Materials

Amylose-V (Am; AVEBE, Holland) was used as received. Ethyl acrylate, ethyl methacrylate and butyl methacrylate (Merck) were washed with dilute alkali to remove the inhibitor, dried over calcium chloride and distilled under suitable conditions[14]. The initiator solution for the graft copolymerization was prepared by dissolving cerium(IV) ammonium nitrate (5.48 g, Fluka) in 1 M nitric acid (100 ml). 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. All other reagents (reagent grade) were used as supplied.

Methods

Graft copolymers A–E and A–B on amylose were synthesized using monomer ratios A/E or A/B of 80/20, 60/40, 50/50, 40/60 and 20/80. The polymerization reactions were carried out under a purified nitrogen (free of oxygen) atmosphere in a flask equipped with a magnetic stirrer and reflux condenser at a constant temperature of 30°C and under a constant light source (40 W lamps) (the graft copolymerization is affected by variations in irradiation[15]).

In a typical experiment, Am (2.0 g) was dispersed in doubly distilled water (290 ml). The stirred mixture was deoxygenated by bubbling a slow stream of nitrogen through for 30 min. A monomer mixture of known composition was then added to the reaction medium (0.05 mol). After 5 min, a 0.1 N solution of cerium(IV) ammonium nitrate (5 ml) in 1 M nitric acid was added. The mixture was allowed to react over a period of 4 h.

The reaction products were separated by filtration and washed with dilute nitric acid and then with distilled water. The ungrafted Am was extracted with a 0.5 M sodium hydroxide solution (100 ml). The homopolymers produced were removed by Soxhlet extraction with tetrahydrofuran. The purified graft copolymers were analysed by ^{13}C n.m.r. spectroscopy. In order to obtain acrylic copolymers free from Am, the graft copolymers were hydrolysed with perchloric acid (60%) after swelling in glacial acetic acid, following a procedure described elsewhere[16].

Statistical copolymers were prepared by the free radical copolymerization of A/E and A/B monomer mixtures in bulk at high vacuum and 60°C. The composition of the monomer feed was varied from 15 to 85 mol% of A. AIBN was used as the free radical initiator with a concentration of 0.3 mol% with respect to the total amount of monomers in the feed. A reaction time of 30 min was used for copolymerizations with a molar fraction of A in the feed lower than 0.5, and for monomer mixtures with a molar fraction of A higher than 0.5 a reaction time of 45 min was used.

The polymerization reactions were stopped by quenching the reaction medium in liquid nitrogen and then adding methanol (5 ml). The mixtures were diluted with chloroform (20 ml) and reprecipitated in a large excess of cool methanol. The copolymer samples were then filtered, washed and finally dried in vacuum at room temperature to constant weight.

Characterization

Graft and statistical copolymers were analysed by ^{13}C n.m.r. spectroscopy with a Varian VXR 300 MHz spectrometer operating at 75.5 MHz. The conditions of operation were: pulse width 14 μs; acquisition time 1 s; delay time 3 s; spectral width 16 kHz; and 32 K data points for the Fourier transformation. The spectra were recorded after 40 000 scans. The spectra of the graft copolymers were recorded after swelling the sample in a mixture of dimethyl sulfoxide-d_6 and deuterated pyridine until a homogeneous gel was obtained. The spectra of the grafted acrylic copolymers after hydrolysis, and those of the statistical copolymers prepared at low conversion, were recorded using solutions (10% w/v) in chloroform-d_1. In all experiments the temperature was 40°C and tetramethylsilane (TMS) was used as the internal reference standard.

RESULTS AND DISCUSSION

Gravimetric analysis of the graft copolymers and the hydrolysed products provides a series of kinetic parameters that characterize the average structure of the two macromolecular systems with respect to the polysaccharide chains and the grafted acrylic copolymers. The characteristic parameters that define the length and number of grafted chains can be expressed by means of several percentage yields defined as follows[17].

Grafting efficiency

$$\%GE = \frac{\text{Total weight of graft copolymer}}{\text{Total weight of graft copolymer} + \text{Total weight of ungrafted acrylic copolymer}} \times 100$$

Percentage of grafting

$$\%G = \frac{\text{Total weight of grafted acrylic copolymer}}{\text{Total weight of grafted amylose}} \times 100$$

Percentage of grafted acrylic copolymer

$$\%GP = \frac{\text{Total weight of grafted acrylic copolymer}}{\text{Total weight of monomers added}} \times 100$$

Total conversion

$$\%CT = \frac{\text{Total weight of grafted and ungrafted acrylic copolymer}}{\text{Total weight of monomers added}} \times 100$$

These parameters can be determined from gravimetric data and analysis of the extracted polymer and the products formed by hydrolysis according to the method described in the Experimental section and in an earlier report[17].

Figure 1 shows the variation in *%GE* with feed composition for both kinds of graft copolymer. It can be seen that the plots obtained have a rather similar trend. The addition of methacrylic esters to the reaction medium produces an increase in the grafting efficiency with respect to the homopolymerization of ethyl acrylate over a wide range of compositions, reaching a maximum for reactions carried out with a composition of about 20% E or B in the feed. A similar result was also obtained for the copolymerization of A with methyl methacrylate under

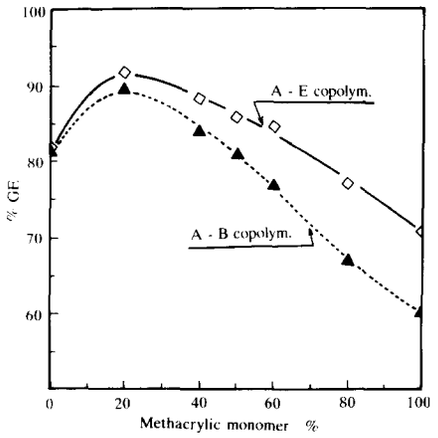

Figure 1 Variation in the grafting efficiency *%GE* with feed composition for (◇) A–E and (▲) A–B copolymers

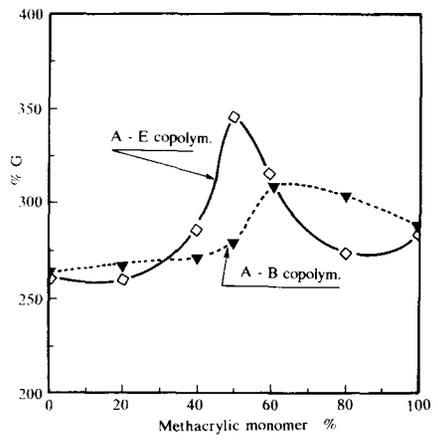

Figure 2 Percentage of grafting *%G* against feed composition for (◇) A–E and (▼) A–B copolymers

the same experimental conditions[18], again indicating a decrease in the formation of ungrafted homopolymer.

Figure 2 shows the variation in the percentage of grafting *%G* with feed composition for both copolymerization systems. The experimental results for the two copolymers are rather different when the molar fraction of the corresponding methacrylic monomer in the feed is higher than 50%. In the case of the A–E copolymers, it seems that a clearly defined maximum is reached for an equimolar mixture of A and E, whereas in the case of the A–B copolymers the maximum is not so clear and apparently is reached for a feed composition of 60% B. An explanation for this phenomenon based on the solubilities of the acrylic monomers in the reaction medium must be ruled out because all the monomers used in this study were not soluble in the hydrated dispersion of amylose, and therefore the copolymerization was initiated heterogeneously for both systems. On the other hand, the mechanical stirring was enough to keep a homogeneous distribution of droplets of the acrylic components dispersed in the hydrated medium. Perhaps it could be related to differences in the reactivities of the corresponding methacrylic monomers towards the free radicals generated on the anhydroglucose rings of the amylose chains via reaction with cerium(IV).

Figures 3 and *4* show the variations in the percentage of grafted acrylic copolymer *%GP* and total conversion *%CT* with feed composition for the A–E and A–B copolymers, respectively. It is clear from *Figure 3* that both parameters present a similar trend with a clearly defined maximum for an equimolar mixture, as in *Figure 2*. However, the plots shown in *Figure 4* indicate that the effect of composition is more noticeable for the graft copolymerization of A/B mixtures, and although the average percentage of grafted copolymer remains rather constant over the whole composition range, the total conversion increases monotonically over a wide range of compositions, reaching conversions higher than 80%.

The data presented in *Figures 1* to *4* are the average values of results obtained from the gravimetric analysis of the different components of the copolymerization systems and those obtained from analysis of the ^{13}C n.m.r. spectra of the swollen graft copolymers and the acrylic copolymers freed from polysaccharide chains by hydrolysis with perchloric acid. *Figure 5a* shows the ^{13}C n.m.r. spectrum of the graft copolymer amylose-*g*-(A–E) prepared from an acrylic monomer feed with an A/E ratio of 40/60, and *Figure 5b* shows the spectrum of the graft copolymer amylose-*g*-(A–B) prepared from a monomer feed with an A/B ratio of 40/60. For copolymers prepared with other compositions similar spectra were obtained, with corresponding changes in the intensities of the signals assigned to the monomeric units with composition. The resolution of the spectral lines is good and the assignments to the different components of the graft copolymers were performed as reported elsewhere[14], providing accurate information on the

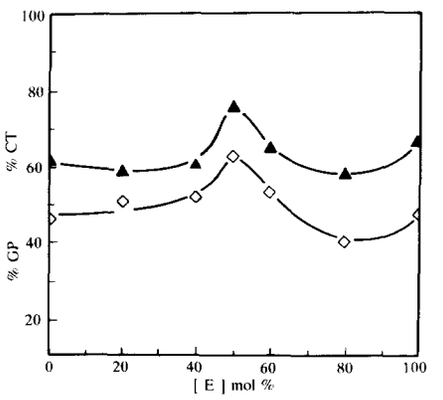

Figure 3 Percentage of grafted acrylic copolymer *%GP* (◇) and total conversion *%CT*(▲) against feed composition for A–E graft copolymers

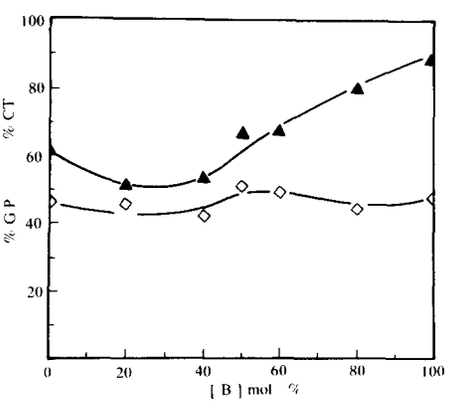

Figure 4 Percentage of grafted acrylic copolymer *%GP* (◇) and total conversion *%CT*(▲) against feed composition for A–B graft copolymers

average composition of the graft copolymer system. For example, as shown in *Figure 5a* the anomeric Am_1 carbon of the anhydroglucose ring of the amylose chain gives a sharp signal at 101.5 ppm, and other signals clearly assignable to the methyleneoxy carbons of ethyl methacrylate at 54.5 ppm and ethyl acrylate at 47.5 ppm are easily evaluated under the experimental conditions used to record the quantitative n.m.r. spectrum. In fact, these data give the percentages of grafting $\%G$, without hydrolysis of the copolymer sample, from the areas of the peaks outlined above. The value obtained by spectroscopy, $\%G = 303$, is very close to that obtained by the gravimetric method, $\%G = 311$. Similarly, for the system amylose-*g*-(A–B) the spectrum drawn in *Figure 5b* gives a value of $\%G = 335$, whereas the gravimetric method gives a value of $\%G = 334$.

One interesting result reflected in *Figures 1, 2* and *4* is that the kinetic parameters of the graft copolymerization reaction are rather similar for both systems when the acrylic mixture is rich in ethyl acrylate. However, the behaviour changes when the acrylic feed becomes richer in ethyl or butyl methacrylate. This result cannot be explained in terms of the solubility of the corresponding alkyl methacrylate in the hydrated medium, since both alkyl methacrylates are completely insoluble in water at the reaction temperature[19]. Therefore, it is necessary to consider the effect of conversion and the relative reactivities of the monomers and radicals in the propagation step of the free radical copolymerization, rather than any specific effect on the initiation step.

In order to study these parameters we prepared statistical A–E and A–B copolymers by free radical copolymerization in bulk with AIBN as the free radical initiator at 60°C. The reaction times were regulated to reach conversions of about 5 wt% in order to avoid the influence of conversion on the compositions and sequence distributions of the copolymers prepared[20]. The compositions of the copolymer chains were determined from the ^{13}C n.m.r. spectra using the same resonances as for the graft copolymers. The results obtained are collected in *Table 1* for the A–E copolymers and *Table 2* for the A–B copolymers. As expected, the average compositions of the A–E and A–B copolymers prepared at low conversions are rather similar, and the molar fractions of A and B units in the copolymer chains are sensibly higher than those in the monomer feeds over the whole range of compositions. The conditional probabilities p_{ij} (i, j = E, A or B), defined as the probabilities for the additions of monomer units j to free radical i ends[21], were calculated statistically from the best values of the corresponding reactivity ratios. These values are useful in determining the statistical compositions of A-centred, E-centred and B-centred sequences along the copolymer chains.

From the average composition data and using the general copolymer equation according to the classical terminal model of copolymerization suggested by Mayo and Lewis[22] and Alfrey and Goldfinger[23], the reactivity ratios of both systems were calculated by application of the linearization methods suggested by Fineman and Ross[24] and Kelen and Tüdös[25], as well as by application of the non-linear method reported by Tidwell and Mortimer[26]. The values obtained are collected in *Table 3*, together with those reported for the free radical copolymerization of A and B initiated with benzoyl peroxide at 60°C in methyl ethyl ketone[27]. We have found rather similar values for the copolymerization of ethyl acrylate with methyl methacrylate under the same experimental conditions[28].

Figure 6 shows the 95% confidence limit diagrams for the values of the reactivity ratios obtained by the different methods[29]. These diagrams give a clear idea of the experimental errors in and the correctness of the experimental conditions used to generate the composition data. When the experimental error is reasonably small

Table 1 Average compositions, conditional probabilities and copolymer conversions of A–E copolymers prepared in bulk with AIBN at 60°C

F_E (feed)	f_E (copolymer)	p_{EA}	p_{AE}	Conversion (wt%)
0.850	0.91_5	0.07_0	0.95_9	5.30
0.700	0.87_0	0.15_2	0.92_8	4.20
0.500	0.75_5	0.29_5	0.84_7	4.80
0.300	0.58_1	0.49_3	0.70_5	5.40
0.150	0.42_3	0.69_9	0.50_0	5.05

Table 2 Average compositions, conditional probabilities and copolymer conversions of A–B copolymers prepared in bulk with AIBN at 60°C

F_B (feed)	f_B (copolymer)	p_{EA}	p_{AE}	Conversion (wt%)
0.850	0.93_1	0.06_8	0.96_0	5.60
0.700	0.86_2	0.14_8	0.91_0	4.90
0.500	0.74_5	0.28_8	0.81_3	4.20
0.300	0.56_3	0.48_5	0.65_2	4.60
0.150	0.39_1	0.69_2	0.43_9	5.15

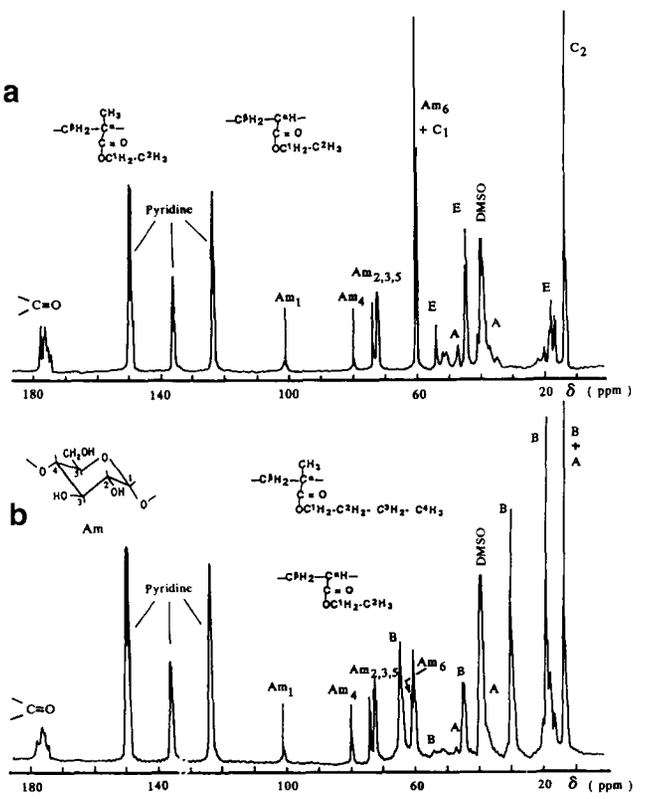

Figure 5 ^{13}C n.m.r. (75.5 MHz) spectra of graft copolymers: (a) amylose-*g*-(A–E); (b) amylose-*g*-(A–B)

Table 3 Reactivity ratios for the AIBN-initiated free radical copolymerizations of A/E and A/B mixtures in bulk at 60°C

Method	A/E		A/B	
	r_A	r_E	r_A	r_B
Fineman and Ross	0.16±0.02	2.26±0.22	0.22±0.02	2.39±0.13
Kelen and Tüdös	0.12±0.03	2.10±0.26	0.21±0.04	2.36±0.10
Tidwell and Mortimer	0.18	2.39	0.23	2.47
Pitchumani *et al.*	–	–	0.35	2.69

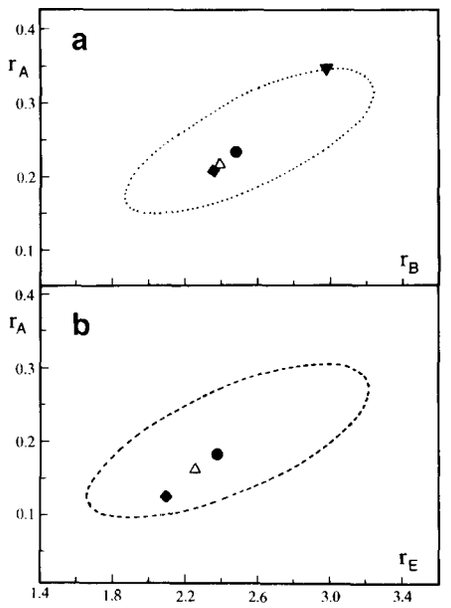

Figure 6 The 95% confidence limits for the reactivity ratios of the AIBN-initiated free radical copolymerizations of (a) A/B and (b) A/E mixtures in bulk at 60°C: (△) Fineman and Ross; (◆) Kelen and Tüdös; (●) Tidwell and Mortimer; (▼) Pitchumani *et al.*[27]

and the data have been taken under the appropriate conditions, the dimensions of the ellipse are reduced, and the experimental data are relatively centred. The best values are those determined by the method of Tidwell and Mortimer, which give a point around the centre of the ellipse. The values reported by Pitchumani *et al.*[27] for the A/B mixture are located just on the edge of the ellipse in *Figure 6a*. According to the reactivity ratios, the relative reactivity of ethyl acrylate towards growing chains ending in ethyl methacrylate radicals is 5.55; the relative reactivity towards butyl methacrylate radicals is somewhat lower, 4.35, indicating the strong tendency of ethyl acrylate towards cross-propagation reactions. However, the relative reactivities of ethyl methacrylate monomer towards ethyl methacrylate radicals and butyl methacrylate radicals are practically the same, 0.42 and 0.40, respectively, indicating the tendency of the alkyl methacrylates to form long sequences.

The difference in the reactivities of the monomeric units in the addition process of the propagation step of the free radical copolymerization has important effects on the change in the average composition of the reaction medium with conversion, and therefore it can be expected that the average compositions and mainly the distributions of comonomeric sequences along the copolymer chains for copolymers prepared at high conversions will be different from those of systems

Table 4 Average compositions of A–E and A–B graft copolymers prepared by grafting onto amylose initiated with cerium(IV) in water at 30°C

F_A (feed)	f_E (graft copolymer)	Conversion (wt%)	f_B (graft copolymer)	Conversion (wt%)
0.200	0.88_2	58.0	0.90_3	80.4
0.400	0.70_1	64.5	0.69_5	67.2
0.500	0.58_4	75.6	0.59_2	66.0
0.600	0.52_1	60.5	0.51_0	54.5
0.800	0.26_3	59.0	0.22_1	51.0

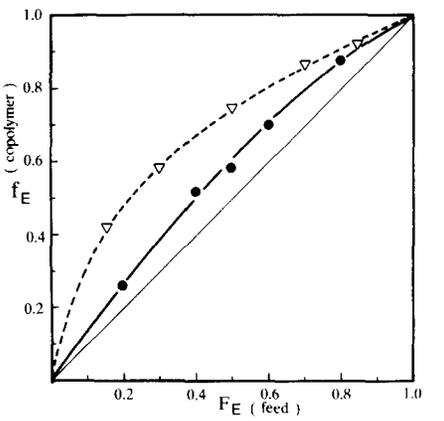

Figure 7 Composition diagrams of A–E copolymers: (▽) statistical copolymers prepared at low conversion; (●) graft copolymers prepared at high conversion

polymerized at low conversions in a homogeneous medium. The average compositions of the graft copolymers prepared at high conversions are collected in *Table 4*. It is clear from these data that the average compositions deviate sensibly from those of copolymers prepared at low conversions for both the A–E and A–B copolymers. *Figures 7* and *8* show the average composition diagrams for the A–E and A–B copolymers, respectively. The lines are the theoretical curves for the statistical copolymers, according to the terminal copolymerization model with the reactivity ratios collected in *Table 3*. The agreement between the experimental points and the theoretical curves indicates that the A–E and A–B copolymers are formed via the terminal model of copolymerization, with the addition of monomer units to growing chains according to the first-order statistics of Markov[21] with the conditional probabilities collected in *Tables 1* and *2* for A–E and A–B, respectively. There are different variations in average composition for the graft copolymers prepared at high conversion and those prepared at low conversion

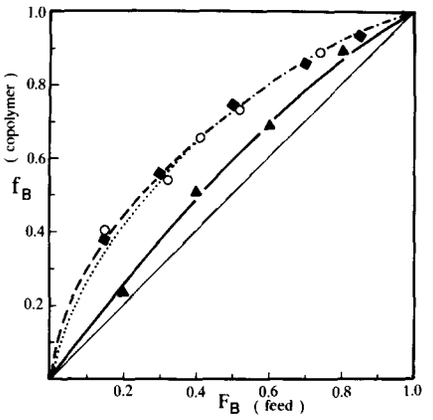

Figure 8 Composition diagrams of A–B copolymers: (◆) statistical copolymers; (▲) graft copolymers; (○) data taken from Pitchumani *et al.*[27]

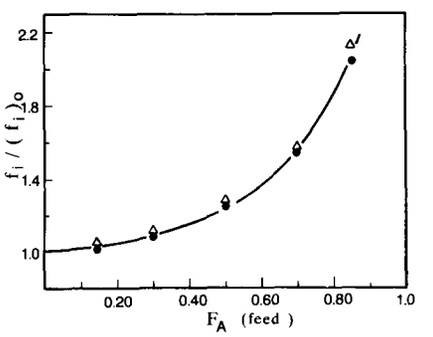

Figure 9 Variation in the ratio between the molar fraction of alkyl methacrylate units in the grafted copolymer f_i and the molar fraction in the statistical copolymer $(f_i)_0$ as a function of the concentration of ethyl acrylate in the feed: (●) A–E copolymers; (△) A–B copolymers

for both systems. The experimental composition diagram of the graft copolymers is rather close to the diagonal of the composition plot, which should correspond to the same composition for both copolymer and feed. This corresponds to a pure ideal system or a real system at total conversion.

More interesting is the study of the distributions of monomeric units along the copolymer chains that shows the differences between the statistical copolymers prepared at low conversion and the graft copolymers prepared at high conversion, since *Figure 9* shows that the ratio of the molar fraction of the alkyl methacrylate in the graft copolymer f_i to the corresponding molar fraction in the statistical copolymer $(f_i)_0$ increases exponentially with the molar fraction of ethyl acrylate in the feed, apparently giving the same diagram for both systems.

It is known that ^{13}C n.m.r. spectroscopy provides accurate information on the distribution of monomeric units along the copolymer chain[30,31]. We have analysed recently[28] the proton-decoupled ^{13}C n.m.r. spectra of statistical ethyl acrylate–methyl methacrylate copolymers. The spectra give information about the sequence distributions and stereoregularities of the monomer units along the macromolecular chains. Among other interesting signals, the carbonyl carbons give at least seven distinguishable signals, the intensities of which change drastically with composition. These signals were assigned to different ethyl acrylate centred and methyl methacrylate centred sequences, according to the distributions and stereochemical configurations of the units in the sequences.

Although an exhaustive study of these characteristics is out of the scope of this work, some very interesting information arises from the carbonyl carbon resonances of the copolymers in the accurate determination of the molar concentration of AAA homotriads along the macromolecular chain. This is possible because the C=O of ethyl acrylate gives a sharp peak at 174.6 ppm, assigned to the central A unit in the AAA sequence[28]. *Figure 10* shows the C=O resonances of A–E graft copolymers with different compositions. Similar spectra for A–B graft copolymers are obtained. The spectra were recorded from chloroform-d_1 solutions of the hydrolysed graft copolymers to give better resolution. A drastic variation in the intensity of the AAA signal is clearly seen in *Figure 10*. The other complex patterns of C=O resonances can be assigned to AAM, MAA, MAM and MMM sequences (M = E or B) with the stereochemical configurations reported for ethyl acrylate–methyl methacrylate copolymers[28].

This result provides valuable information on the distributions of ethyl acrylate sequences in A–E and A–B copolymers independent of the conversion and polymerization technique. Along these lines, *Figure 11* shows plots of the molar fraction of ethyl acrylate homotriads f_{AAA} as a function of the average concentration of ethyl acrylate units in the copolymer chain. There is an exponential increase in the concentration of AAA sequences with increasing concentration of A units in the copolymer chain. Although the trend of the plots is rather similar to that in *Figure 9*, the analysis at the level of the distribution of sequences is more selective and deeper, since in *Figure 11* different behaviour for each system can be detected, whereas the analysis of the average molar composition does not give such a level of sensitivity (see *Figure 9*). In any case, it can be clearly seen in *Figure 11* that the variation in f_{AAA} with composition for the statistical copolymers is smoother than that for the graft copolymers. The divergence of the plots obtained for the A–E and A–B statistical copolymers arises from the small differences in the reactivity ratios of the monomers

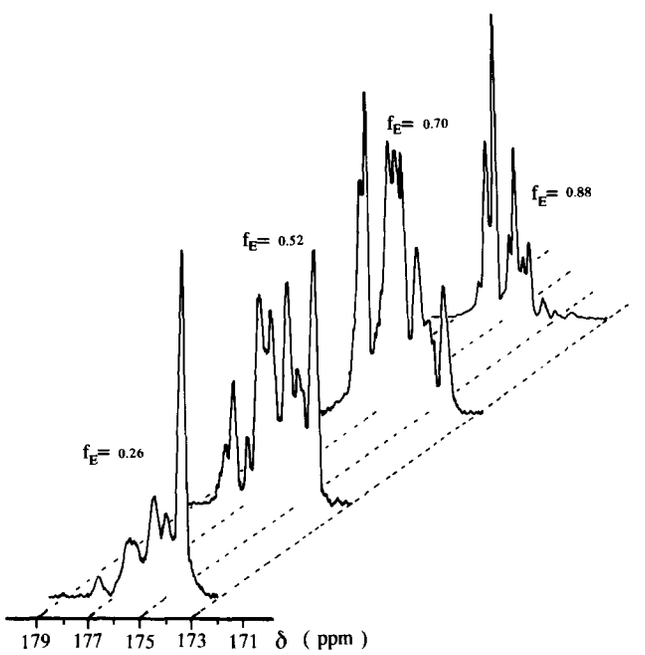

Figure 10 Enhanced ^{13}C n.m.r. carbonyl carbon signals of hydrolysed graft amylose-*g*-(A–E) copolymers with different compositions

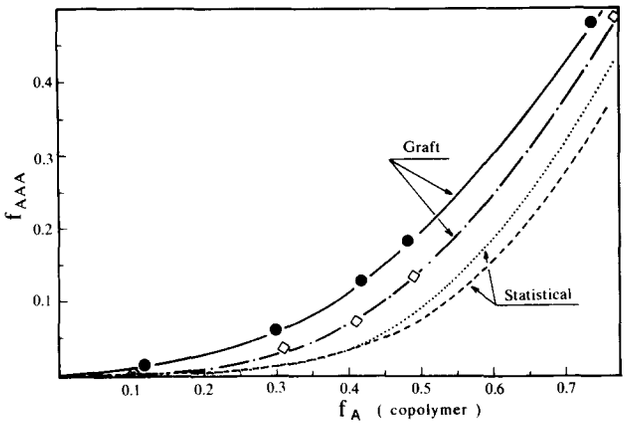

Figure 11 Variation in the molar fraction of ethyl acrylate homotriads f_{AAA} as a function of the ethyl acrylate molar fraction in the copolymer chain

(*Table 3*). However, it is clear that the concentrations of AAA homotriads in the graft copolymers are sensibly higher than those in the statistical copolymers, this situation being more noticeable for the A–E copolymers. Logically, this is a consequence of the different reactivities of ethyl acrylate towards ethyl methacrylate and butyl methacrylate radicals, as we have indicated above. The effect is cumulative as the conversion of monomers to copolymer chains increases. The effect should also be more enhanced for reaction media rich in A, giving an exponential variation as the concentration of A in the reaction medium increases.

Finally, the distribution of monomeric sequences has a considerable effect on the physical properties of the corresponding graft copolymers, such as the hydrophobic character, glass transition temperature, etc., thus determining the application of these kinds of polymeric systems as biomaterials. These aspects will be described in a future publication.

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