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Microstructure of Copolymers of Methacrylonitrile/*n*-Alkyl Methacrylate Mixtures Grafted onto Amylomaize by ^{13}C-NMR Spectroscopy

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ABSTRACT: The microstructure and stereochemical configuration of copolymers of methacrylonitrile (MAN) with methyl methacrylate (MMA), ethyl methacrylate (EMA), and butyl methacrylate (BMA) grafted onto amylomaize are analyzed by ^{13}C-NMR spectroscopy. The graft copolymers were prepared at high conversion by free radical copolymerization in aqueous medium initiated by a redox mechanism with the amylomaize/Ce(IV) system. The composition and distribution of comonomeric units of these copolymers are compared with those of the bulk copolymerization at low conversion using AIBN as initiator. The results obtained indicate that random copolymers with a statistical distribution of comonomeric sequences are obtained at low conversion, but BMA–MAN copolymers prepared at high conversion seem to have relatively long sequences of BMA units in a wide feed composition interval. This behavior is explained taking into consideration the relative solubility of the corresponding alkyl methacrylate and methacrylonitrile in the reaction medium.

Introduction

In previous papers[1,2] we investigated the copolymerization and characterization of methacrylonitrile/*n*-alkyl methacrylate mixtures grafted onto amylomaize by using the ceric ion method. The graft copolymers were characterized by IR and NMR spectroscopies to obtain the average composition of the polysaccharide/acrylic copolymer chains and the kinetic parameters of the graft reaction initiated by the attack of Ce(IV) ions on the anhydroglucose rings of amylomaize according to a well-known mechanism.[3]

The purpose of this work was to study the effect of the initiation mechanism and the nature of the reaction medium, as well as the conversion, on the average composition, the microstructure, and the stereoregularity of copolymers of MMA, EMA, and BMA with MAN grafted onto amylomaize. The different solubility of monomers in the reaction medium was considered to explain the experimental results. On the other hand, as we knew the distribution of monomers along the copolymer chains for the three systems polymerized in bulk at low conversion with AIBN as initiator,[4,5] we thought that it would be interesting to accomplish a comparative study of both copolymerization processes.

Experimental Section

Materials. Commercial amylomaize starch (supplied by LAISA, Barcelona) was used without further purification. Methacrylonitrile (MAN), methyl methacrylate (MMA), ethyl methacrylate (EMA), and *n*-butyl methacrylate (BMA) (Merck) were purified by washing twice with dilute alkali and then several times with distilled water to remove the inhibitor before distillation under reduced nitrogen pressure. A solution of ceric ammonium nitrate (Fluka) 0.1 N in 1 N nitric acid was used as the initiator.

Grafting Procedure. Polymerization was carried out following the procedure described elsewhere.[1] Amylomaize (2 g) was dispersed in 290 cm^3 of bidistilled water in a three-necked flask, and this dispersion was purged with purified nitrogen for 30 min. Afterward, the required amounts of both monomers (0.047 mol total) were added to the reaction mixture and 5 min later 10 cm^3 of the initiator solution was introduced, performing the grafting reaction under magnetic stirring. This mixture was allowed to react for 4 h at 30 °C under a nitrogen atmosphere and then the reaction was stopped by the addition of a small quantity of hydroquinone.

Extraction. First, the ungrafted starch was separated by stirring the reaction mixture in 1 N NaOH and then the acrylic copolymer in the reaction solid was extracted from the dry product by the Soxhlet method with tetrahydrofuran and acetone as solvents.

Acid Hydrolysis of the Graft Copolymers. To separate the grafted acrylic copolymer from the starch, the graft copolymer was submitted to acid hydrolysis with perchloric acid as follows:[6] Approximately 2 g of amylomaize graft copolymer containing water-insoluble grafted chains was weighed accurately and added to 100 cm^3 of glacial acetic acid, which was then heated at 90–100 °C. Perchloric acid (2 cm^3, 60%) was added dropwise, and within 1–2 min the reaction was complete. The reaction mixture was immediately poured into ice/water to precipitate the vinyl polymer side chains. The acrylic polymer was dissolved in THF and reprecipitated in methanol to eliminate the trapped acid.

Characterization. Graft copolymer and hydrolyzed grafted acrylic chains were characterized by ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectra were recorded with a Varian VXR-300 spectrometer. The samples were analyzed as 15% (w/v) solutions in DMSO-d_6 at 80 °C or Cl_3CD at 40 °C, using a pulse width of 13 μS, a relaxation delay of 5 s and inversed gated decoupling in the acquisition, and a spectral width of 16K data points. These conditions ensure the complete relaxation of all the ^{13}C nuclei analyzed. Relative peak intensities were measured from peak areas calculated by means of an electronic integrator or by triangulation and planimetry.

Results and Discussion

Copolymers of MMA, EMA, and BMA with MAN grafted onto amylomaize were prepared in aqueous medium by free radical copolymerization initiated by the reaction of Ce(IV) ions with the anhydroglucose rings of the polysaccharide chains according to a well-known mechanism described elsewhere.[3] The graft copolymers obtained at high conversion were analyzed by recording

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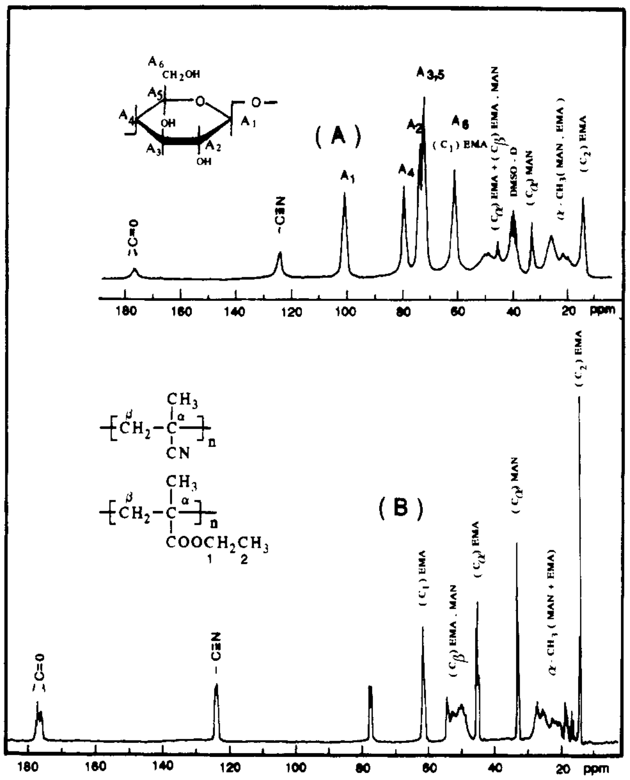

Figure 1. ^{13}C-NMR spectra of amylomaize/EMA-MAN graft copolymer in DMSO-d_6 (A) and EMA-MAN copolymers after hydrolysis recorded in Cl_3CD (B).

their proton-decoupled ^{13}C-NMR spectra. Figure 1 shows the ^{13}C-NMR spectra of an amylomaize-EMA-MAN graft copolymer before and after the hydrolytic treatment. The spectra were recorded under quantitative conditions, i.e., long delay time, minimum NOE, and a high number of scans. Similar spectra for the other copolymer systems and different compositions were obtained. It is interesting to note here that the characteristic resonance signals of the acrylic copolymer chains are apparently not affected by the hydrolytic treatment, but the spectra of the hydrolyzed starch-acrylic system present a better resolution than the original grafted copolymer, as can be seen clearly in the spectra in Figure 1. This provides higher accuracy for a detailed analysis of the acrylic-methacrylonitrile copolymer chains. Therefore, the microstructural and stereochemical parameters of the copolymer chains were determined by the analysis of samples after acid hydrolysis. The grafting percentage (% *G* = percent weight of grafted polymer with respect to grafted amylomaize) was determined by the comparison of the integrated intensities of signals assigned to amylomaize chains and those of the corresponding copolymer system indicated in Figure 1. The data of the average grafting percentage (% *G*) obtained from the acid hydrolysis method and ^{13}C-NMR spectra are collected in Table I. The good agreement of values obtained indicates that the ^{13}C-NMR spectra are suitable for quantitative determinations under the conditions used in the present work. It is also interesting to consider that the grafting reaction is favored for the alkyl methacrylate rich composition of the reaction medium as reflected by the % *G* values obtained.

Figure 2 shows the composition diagram of three copolymerization systems prepared at low (<10 wt %) and high conversion (>30 wt %). It is clear from this figure that whereas the MMA-MAN system fits an ideal behavior, independently of the conversion, the other two systems deviate appreciably, and the results obtained depend on the conversion reached during the polymerization process. Moreover, in the case of the EMA-MAN system, the diagrams obtained seem to correspond to a random copolymerization, but the copolymers are richer in EMA than the monomer feed. This behavior is enhanced for the BMA-MAN system, in which the copolymers prepared in the whole range of composition studied present a BMA molar fraction quite higher than the monomer feed.

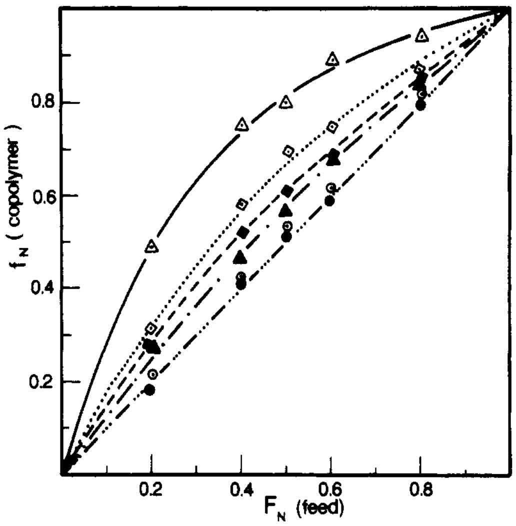

Figure 2. Composition diagrams for the free radical copolymerization of MMA-MAN (●, ○), EMA-MAN (♦, ◇), and BMA-MAN (▲, △) prepared in bulk with AIBN at low conversion (black symbols) and in the presence of the polysaccharide/Ce(IV) at high conversion (white symbols).

Table I. Percent Grafting of Different Copolymers of Methacrylonitrile/Alkyl Methacrylate Mixtures onto Amylomaize by ^{13}C-NMR and by Acid Hydrolysis

grafted copolymer	molar ratio in the feed	% G acid hydrolysis	% G ^{13}C-NMR
MAN/MMA	20/80	153	156
MAN/MMA	40/60	83	83
MAN/MMA	80/20	70	63
MAN/EMA	20/80	187	193
MAN/EMA	50/50	97	99
MAN/EMA	80/20	58	59
MAN/BMA	80/20	76	73
MAN/BMA	50/50	190	196

The composition diagrams for the copolymerization of these systems in bulk at low conversion have been determined from experimental data reported previously[7] and taking into consideration the reactivity ratios $r_{MMA} = 0.89$ and $r_{MAN} = 0.88$ for the MMA-MAN system, $r_{EMA} = 1.03$ and $r_{MAN} = 0.44$ for the EMA-MAN system, and $r_{BMA} = 1.16$ and $r_{MAN} = 0.43$ for the BAM-MAN system. These parameters were determined from the analysis of the ^{1}H-NMR spectra (300 MHz) of copolymer samples prepared in bulk (with AIBN as the free radical initiator) at conversions lower than 5 mol % by the application of different treatments of the general copolymer composition equation described in a previous report.[7]

To make a correct interpretation of the change of composition diagrams from low- to high-conversion polymerizations, it is necessary to take into consideration not only the variation of the average composition of the reaction medium with the conversion but also the different solubilities of the monomers in the reaction medium, since under the experimental conditions used in the present work, the polysaccharide is dispersed in the reaction medium in small semihydrated particles in all three systems. Thus, whereas both methacrylonitrile and methyl methacrylate are soluble in the aqueous phase, ethyl methacrylate is less soluble in the reaction medium and

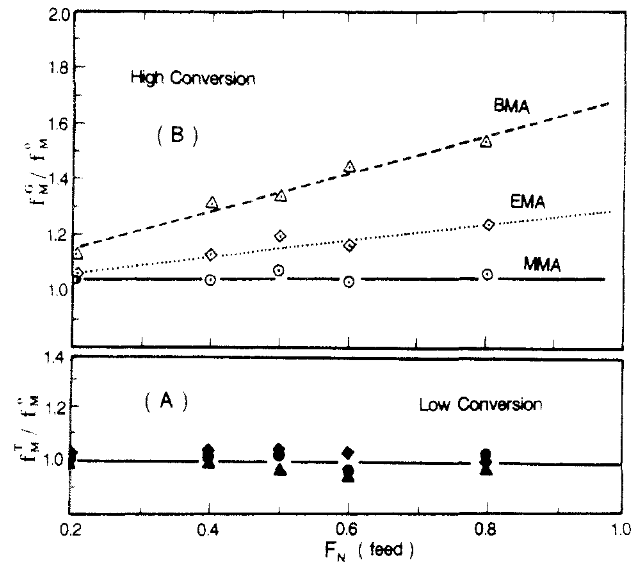

Figure 3. Variation of the ratio of the molar fraction of alkyl methacrylate with respect to that of copolymers polymerized in bulk f^o_M with the molar fraction of methacrylonitrile in the feed: (A) ratio of the theoretical molar fraction according to the reactivity ratios f^T_M and the experimental ones f^o_M for the bulk copolymerization; (B) ratio of the molar fraction of alkyl methacrylate in the graft copolymers f^G_M and the experimental f^o_M.

butyl methacrylate is not soluble at all. Therefore, the polymerization reaction of the MMA–MAN system takes place in a homogeneous phase, but for the other two systems the copolymerization occurs in a heterogeneous phase once the radicals are generated by the mechanism of Ce(IV)[3] on the carbohydrate chains.

Figure 3 shows the relative change of the molar ratio of the corresponding alkyl methacrylate with respect to systems studied previously in bulk.[7] In Figure 3A the molar ratio of the fraction of the alkyl methacrylate calculated theoretically from the values of the reactivity ratios for each system f^T_M and the experimental molar fraction f^o_M is plotted versus the experimental molar fraction of MAN in the feed, F_N. It can be clearly seen that the ratio f^T_M/f^o_M remains practically equal to unity over the whole range of compositions. This means that the copolymerization in bulk at low conversion of the three systems follows the classical kinetic terminal model of copolymerization with a good fitting of the experimental data to the expected results according to the reactivity ratios given above and the general composition copolymer equation. However, the diagrams presented in Figure 3B indicate clearly that this behavior is only observed for the MMA–MAN system prepared at conversions higher than 30 wt %, in which the polymerization medium is homogeneous, due to the solubility of both monomers in the interval of concentrations used in the present work. Therefore, the average composition of the reaction medium does not change with conversion, since the system approaches the ideal behavior with reactivity ratios very close to unity. For EMA–MAN copolymers prepared at high conversion, the molar fraction of EMA in the copolymer increases with respect to that of copolymers prepared in bulk at low conversion as the concentration of MAN in the reaction medium increases. This effect is even more enhanced in the BMA–MAN system. It could be though that there is a relationship between the solubility of the corresponding alkyl methacrylate and the deviation of the composition data from those obtained at low conversion.

To gain a deeper insight into the homogeneity and microstructure of the graft copolymers, we studied comparatively the effect of the reaction medium on the distribution of monomeric units along the copolymer chains. In this sense, the copolymers grafted onto the polysaccharide were submitted to hydrolysis in acid medium as reported elsewhere,[6] and their microstructure was studied by ^{13}C-NMR spectroscopy, taking into consideration the assignments of NMR signals established for copolymers prepared in bulk at low conversion.[4] Figure 4 shows the expanded ^{13}C-NMR signals of the quaternary carbons of ethyl methacrylate units in EMA–MAN copolymers prepared in the presence of polysaccharide at high conversion; similar spectra for the MMA–MAN and BMA–MAN systems were obtained. The resonance signals split into three peaks, the intensities of which change with the copolymer composition. Comparison of these signals with those of the corresponding copolymers prepared at low conversion allows us to assign them to the alkyl methacrylate centered triads with the following stereochemical configuration: I = isotactic (mm), II = heterotactic (mr + rm), and III = syndiotactic (rr) triads, in order of increasing field. As we have observed in other methacrylic copolymerization systems, the chemical shift of these signals is not affected by the chemical composition

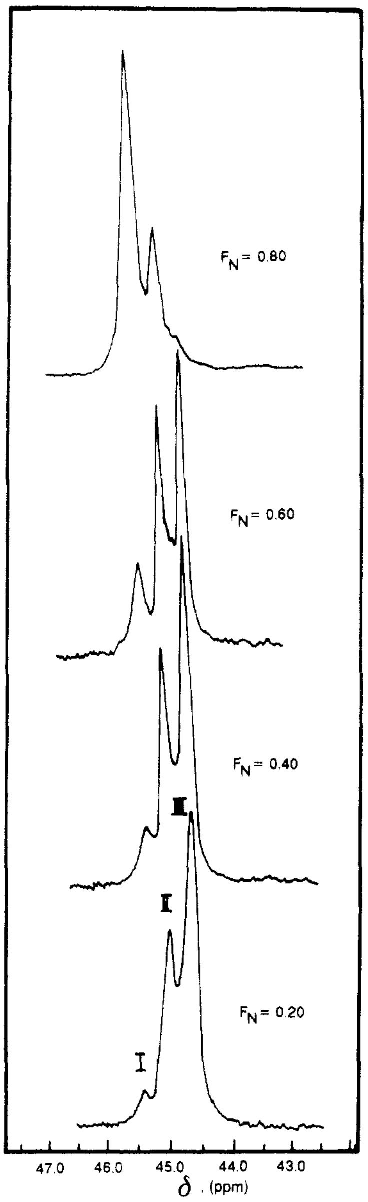

Figure 4. Expanded ^{13}C-NMR signals of the quaternary carbon of ethyl methacrylate units in EMA–MAN graft copolymers after hydrolysis for copolymers prepared with the molar fraction of methacrylonitrile in the feed indicated in the figure, F_N.

Table II. Experimental Values of Tactic Triads of Methacrylonitrile/Alkyl Methacrylate Copolymers Prepared by Free Radical Polymerization in Bulk at Low Conversion (LC) and in the Presence of Polysaccharide at High Conversion (HC)

		stereochemical sequence					
		mm		mr + rm		rr	
copolymer system	f_{MAN} (copolymer)	LC	HC	LC	HC	LC	HC
MAN–MAA	0.17_0		0.14_9		0.48_2		0.37_0
	0.20_9	0.12_5		0.44_0		0.43_4	
	0.38_5	0.28_8	0.25_0	0.46_2	0.51_9	0.25_0	0.23_0
	0.46_8		0.33_8		0.44_0		0.22_2
	0.59_0	0.43_2	0.42_8	0.45_5	0.42_3	0.11_4	0.14_9
	0.82_0	0.61_6	0.63_7	0.31_5	0.30_5	0.06_8	0.05_8
MAN–EMA	0.15_0	0.10_1	0.11_0	0.39_9	0.39_0	0.50_0	0.50_0
	0.25_2		0.240		0.50_4		0.25_6
	0.30_8		0.35_6		0.46_4		0.18_0
	0.38_9	0.35_2		0.44_0		0.20_7	
	0.48_4	0.45_6	0.43_7	0.42_1	0.45_7	0.12_2	0.10_6
	0.73_0	0.69_5	0.66_4	0.26_8	0.28_4	0.03_7	0.05_2
MAN–BMA	0.06_2		0.02_1		0.35_4		0.62_5
	0.10_5	0.07_0	0.02_4	0.40_7	0.39_0	0.52_4	0.58_6
	0.18_6	0.11_6	0.08_3	0.42_4	0.35_4	0.46_0	0.56_3
	0.25_0		0.13_7		0.38_2		0.48_0
	0.32_0	0.21_4		0.46_1		0.32_5	
	0.51_3	0.53_3	0.65_6	0.37_1	0.27_9	0.09_6	0.06_5

Table III. Assignments of the Carbonyl Group Resonance Signals for the Grafted MMA/MAN, EMA/MAN, and BMA/MAN Copolymers

signal	δ, ppm	M-centered pentads
I	178.10	mrrm
II	177.65	mrrr
III	177.45	rrrr
IV	176.90	rmrm
V	176.65	mmrr + mrmr
VI	176.35	mmrm
VII	175.95	rmmr
VIII	175.60	mmmr + mmmm

of the alkyl methacrylate centered sequences (it is independent of the chemical nature of the neighboring units) but is strongly dependent on the relative stereochemical configuration of the central unit with respect to the neighboring units of the triad. The molar fractions of each kind of triad for the three copolymerization systems are collected in Table II. It is clear from the values reported in this table that the molar fraction of isotactic traids increases with increasing methacrylonitrile molar fraction in the copolymer chains, whereas the molar fraction of syndiotactic triads decreases. This result is similar to that found for copolymers prepared in bulk at low conversion.[4]

On the other hand, the carbonyl carbon of the alkyl methacrylate units is also sensitive to the stereochemistry of the corresponding alkyl methacrylate centered sequences, giving rise to the splitting of eight different peaks assigned to alkyl methacrylate centered pentads, independently of the chemical composition of the corresponding sequences and with the stereochemical configuration of pentads assigned as indicated in Table III. This assignment was carried out following the criterion described for copolymers prepared in bulk with AIBN.[4] Figure 5 shows the expanded resonance signals of the carbonyl group of four copolymers prepared with different compositions of the monomer mixture for the BMA–MAN system. Rather similar spectra are obtained for the other two copolymerization systems, i.e., MMA–MAN and EMA–MAN. It is noteworthy that, although the chemical shift of these signals does not depend on the chemical composition of the sequence, the intensity changes drastically with the composition, showing a clear tendency to increase the isotactic alkyl methacrylate centered sequences as the molar fraction of MAN in the copolymer increases. Therefore, the stereochemical distribution of alkyl methacrylate centered sequences is directly related to the chemical composition of the corresponding sequences.

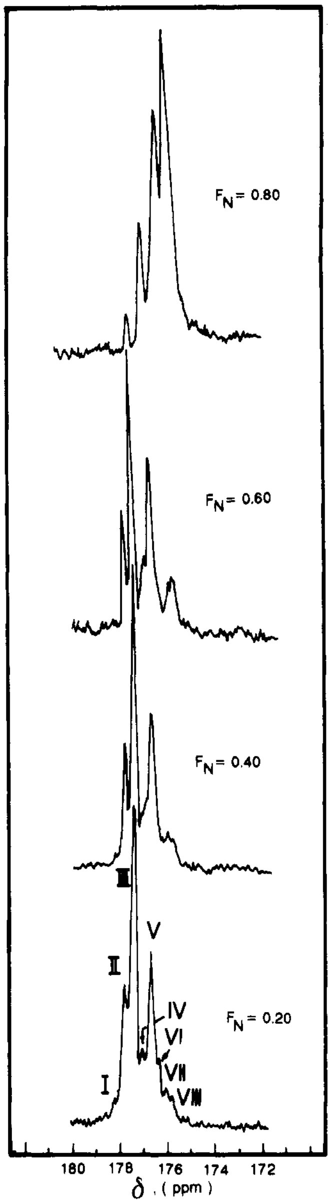

Figure 5. Expanded ^{13}C-NMR pattern of the carbonyl carbon of butyl methacrylate units in BMA–MAN graft copolymers after hydrolysis.

As we have indicated above, the free radical copolymerization of these systems in bulk initiated by AIBN follows the classical terminal model, giving rise to statistical copolymers with a random distribution of the monomeric units along the copolymer chains.[4,7] The microstructural analysis of copolymers by ^{13}C-NMR spectroscopy demonstrated that there is a clear tendency toward the formation of coisotactic sequences when the corresponding methacrylate unit is isolated between two methacrylonitrile units, i.e., MAN–N–MAN alternating triads.[4,5] This behavior provides an interesting way to analyze the microstructure of copolymers prepared in the presence of the polysaccharide, since both homopolymers and copolymers formed by long blocks of MAN and MMA, EMA, or BMA would predominantly give rise to syndiotactic or heterotactic chains.[10] In fact, as we reported previously,[4,5] the free radical homopolymerization of MMA, EMA, BMA, and MAN gives Bernoullian polymers with a stereoregularity that can be described by the isotacticity parameters

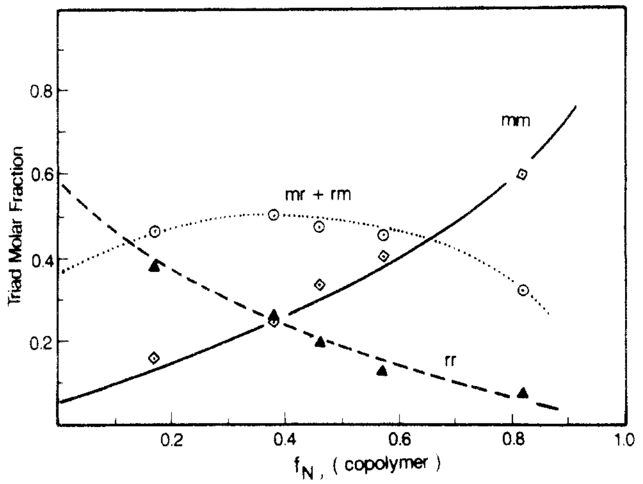

Figure 6. Variation of the tacticity of MMA-centered triads as a function of methacrylonitrile molar fraction in the grafted copolymer samples prepared at high conversion. Points correspond to average values obtained from carbonyl and quaternary carbon NMR signals. Lines correspond to the theoretical diagrams with the statistical parameters given in the text and in ref 5.

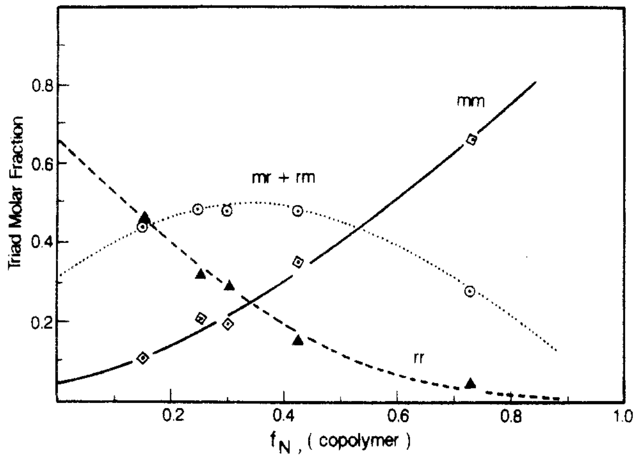

Figure 7. Distribution of tactic traids of EMA-centered sequences for EMA–MAN copolymers prepared at high conversion versus the methacrylonitrile molar fraction in the copolymer. Points correspond to the average values obtained from carbonyl and quaternary carbon NMR signals. Lines correspond to the theoretical diagrams.

$\sigma_{MMA} = 0.24$, $\sigma_{EMA} = 0.19$, $\sigma_{BMA} = 0.17$, and $\sigma_{MAN} = 0.37$. These values indicate that predominantly syndiotactic polymer chains might be expected for the polymerization reactions that would give rise to homopolymers, block copolymers, and copolymers with long sequences of these monomers. However, this is not the case for the copolymerization systems initiated in the presence of polysaccharide as is shown by the spectra reported in Figures 4 and 5. It is clear from the expanded signals of the spectra shown in these figures that the intensity of signals assigned to stereochemical alkyl-centered sequences (related directly with the structural composition of copolymer sequences) does not change drastically until the feed composition is very rich in MAN. The effect is even more noticeable for BMA–MAN than EMA–MAN copolymer systems. This is better seen in Figures 6–8, which show the distribution of tactic triads for MMA-, EMA-, and BMA-centered sequences, respectively. The lines correspond to the distribution curves obtained for copolymers prepared in bulk at low conversion, which present a random distribution of alkyl methacrylate and methacrylonitrile units according to the classical Mayo–Lewis copolymerization model.[11] The points correspond to the concentration of tactic triads determined from the NMR spectra of graft copolymers prepared at high conversion in the presence of polysaccharide. It can be clearly observed in Figures 6 and 7 that the experimental points adequately fit the diagrams of the random copolymers taken as reference. Therefore, we can conclude that the copolymers grafted onto amylomaize present a rather uniform random distribution of MMA or EMA and MAN units along the copolymer chains, since the stereochemical distribution of MMA- or EMA-centered sequences depends directly on the MAN molar fraction in the copolymer chains as we have indicated above.

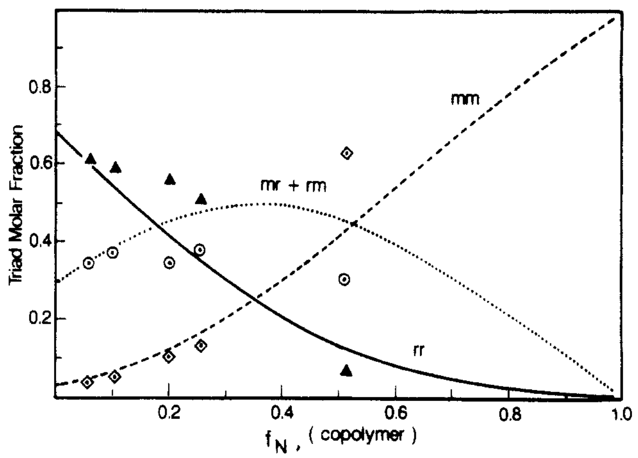

Figure 8. Variation of the tacticity of BMA-centered triads as a function of MAN molar fraction in the grafted copolymer samples prepared at high conversion. Points correspond to the average values obtained from carbonyl and quaternary carbon signals. Lines correspond to theoretical diagrams with the statistical parameters indicated in the text.

However, as shown in Figure 8, the distribution of tactic triads of BMA-centered sequences for BMA–MAN copolymers prepared at high conversion deviates sensibly from that of copolymers prepared in bulk at low conversion. It is clear that although the copolymer prepared with the highest content of BMA (>90% of BMA units) apparently fits the distribution diagrams of the reference random copolymers, for compositions lower than 80% of BMA units, the BMA–MAN system deviates from the copolymerization model in bulk at low conversion. Moreover, the copolymers obtained seem to be rather more syndiotactic than expected according to a random distribution of monomers for molar fraction of BMA lower than 0.85–0.90. These results indicate that for the free radical copolymerization of BMA with MAN relatively long sequences of BMA units could be expected, with a distribution that deviates from the copolymer system prepared at low conversion for a relative wide interval of compositions in the monomer feed.

The most interesting conclusions of this work are as follows: The free radical copolymerization of methyl methacrylate with methacrylonitrile in aqueous medium initiated by a redox mechanism using the amylomaize/Ce(IV) system gives rise to graft copolymers in which the comonomeric units are distributed at random, following the classical copolymerization terminal model. However, the copolymerization of ethyl methacrylate with methacrylonitrile is slightly different in the sense that a higher reactivity of ethyl methacrylate with respect to methyl methacrylate is observed, although the distribution of comonomeric units along the polymeric sequences seems to be rather similar to that of copolymers prepared by free radical copolymerization in bulk initiated by AIBN. Finally, the butyl methacrylate methacrylonitrile system deviates noticeably, giving rise to the formation of copolymers probably with long sequences of butyl methacrylate units along the copolymer chains.

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