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Microstructural Analysis of Methacrylonitrile–Methyl Methacrylate Copolymers by ^{13}C NMR Spectroscopy

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ABSTRACT: The microstructure and stereochemical configuration of methacrylonitrile, N, and methyl methacrylate, M, copolymers prepared by free-radical polymerization at 60 °C are analyzed on the basis of the classical terminal copolymerization model and with the assumption of Bernoullian statistics for the distribution of the stereochemical configuration of monomer units. From the analysis of ^{1}H NMR spectra the reactivity ratios were determined, their values being $r_N = 0.883$ and $r_M = 0.892$. From the analysis of the ^{13}C NMR resonance signals assigned to the quaternary carbon and the carbonyl group of M units and the α-CH_3 group of both the M and N units, the statistical parameters $\sigma_{NN} = 0.37$, $\sigma_{MM} = 0.24$, and $\sigma^* = \sigma_{NM} = \sigma_{MN} = 0.87$ were determined. The coisotacticity parameter σ^* is observably higher than the isotacticity parameters of the corresponding homopolymers, σ_{NN} and σ_{MM}, which indicates some strong interactions between the nitrile and carbonyl groups of neighboring N and M units.

Introduction

Numerous studies of the copolymerization of acrylonitrile with vinyl monomers such as styrene,[1–6] methyl acrylate,[7] and methacrylic acid[8] have been published during the last 4 decades, and the distribution of monomer sequences along the macromolecular chains of acrylonitrile copolymers has been carefully analyzed by ^{13}C NMR spectroscopy by Schaefer et al.[5,6] and by Pham et al.[8] However, little attention has been given to the study of methacrylonitrile polymer and copolymer systems, although poly(methacrylonitrile) and random copolymers of methacrylonitrile with other acrylic monomers such as methacrylic acid seem to have potential uses as photoresist materials.[9] In this regard, Grassie et al.[10] published in 1959 a comprehensive study of the free-radical copolymerization of a homologous series of methacrylic esters with methacrylonitrile. This compound was chosen because of the possibility of analyzing the copolymer systems through the nitrogen content and because of the interest of these systems in thermal degradation processes. Later, Block and Spencer[11] and more recently Suggate[12] published interesting results concerning the free-radical copolymerization of methacrylonitrile with vinylidene chloride, including an exhaustive analysis of monomer sequences in terms of diad and triad distribution by 60-MHz ^{1}H NMR spectroscopy, and some information on the tetrad and hexad sequences was tentatively considered from 220-MHz ^{1}H NMR spectra of copolymers.

Since NMR spectroscopy has become the most powerful tool for the study of structural features in polymer and copolymer systems, this paper describes the microstructural analysis of methacrylonitrile/methyl methacrylate copolymers by 75-MHz ^{13}C NMR spectroscopy, taking into consideration not only the composition of the copolymer chains but also the stereochemical configuration of the monomer sequences.

Experimental Section

Reagents. Methacrylonitrile, N (Merck), and methyl methacrylate, M (commercial), were purified by washing three times with 5% NaOH aqueous solution and then several times with distilled water. After separation and drying over calcium chloride, the monomers were filtered, distilled, and stored at low temperatures. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol (mp = 104.0 °C).

Polymerization. The bulk copolymerization reactions were carried out in glass ampules at 60 ± 0.5 °C. The ampules containing the required amount of monomers and initiator were degassed twice by the usual freezing–thawing cycles under high vacuum ($>10^{-4}$ mmHg) and then sealed. After the desired reaction time (see Table I), the mixtures were immersed in liquid nitrogen. The samples were then diluted with DMF and poured into a large excess of cool methanol. The precipitated products were purified by dissolving the isolated samples in DMF and precipitating in excess methanol. Finally, they were dried to constant weight under vacuum at a temperature of 40 °C.

Characterization. The copolymers obtained were characterized by ^{1}H and ^{13}C NMR spectroscopy. The spectra were recorded at 80 °C on 20% (w/v) perdeuterated dimethyl sulfoxide (DMSO-d_6), with a Varian VXR-300 spectrometer operating at 300 MHz for ^{1}H NMR experiments and 75.5 MHz for ^{13}C NMR experiments. TMS was used as an internal reference. In order to have a quantitative response, the ^{13}C NMR spectra were recorded by using a flip angle of 80° (pulse width of 13 μs) and a relaxation delay of 4 s with inverse-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. The relative peak intensities were measured from peak areas calculated by means of an electronic integrator or by triangulation and planimetry.

Results and Discussion

Copolymerization reactions were carried out, as is indicated in the Experimental Section, to conversions of about 1–2 wt % (see the fourth column of Table I) in order to satisfy the conditions for the application of the general copolymer equation, assuming that the copolymerization reaction follows the classical terminal unit scheme.[13,14] This was also done in order to obtain copolymer samples with a homogeneous distribution of both monomeric units, which would be altered if the composition of the reaction mixture changes during the polymerization.

The molar fraction of monomer units incorporated in the copolymer was determined from the ^{1}H NMR spectra

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Table I
Experimental Data and Conditional Probabilities, p_{ij}, for the Free-Radical Copolymerization of Methacrylonitrile (N) with Methyl Methacrylate (M) at 60 °C[a]

f_N		reaction	convn,		
feed	copolymer	time, min	wt %	p_{NM}	p_{MN}
0.100	0.11_0	55	1.25	0.911	0.111
0.200	0.20_9	96	2.40	0.819	0.219
0.400	0.41_0	78	1.25	0.629	0.428
0.600	0.59_5	126	1.14	0.430	0.627
0.800	0.79_1	171	1.57	0.221	0.817
0.900	0.89_0	159	1.28	0.112	0.910

[a] $p_{MM} = 1 - p_{MN}$, $p_{NN} = 1 - p_{NM}$.

Table II
Copolymerization Parameters for the Free-Radical Polymerization of Methacrylonitrile (N) and Methyl Methacrylate (M) at 60 °C

method	r_N	r_M
Fineman–Ross	0.908 ± 0.030	0.905 ± 0.020
Kelen–Tüdős	0.892 ± 0.020	0.903 ± 0.020
Tidwell–Mortimer	0.883	0.892
literature[10]	0.70	0.74

of copolymer samples prepared with various monomer feeds. The analysis was carried out by comparing the integrated intensities of a set of signals between δ 3.55 and 3.85, which were assigned to the resonances of the $-OCH_3$ protons of methyl methacrylate units, with those of signals between δ 0.80 and 1.60, assigned to the resonances of the α-CH_3 groups of both monomers. The results obtained are given in the second column of Table I, the composition of copolymer samples being rather close to the corresponding monomer feed in the whole interval analyzed, which indicates that the system approaches ideal behavior.[15]

From the composition data shown in the first and second columns of Table I we have determined the reactivity ratios of both monomers by the application of the Fineman–Ross[16] and Kelen–Tüdős[17] linearization methods, as well as by the application of the nonlinear least-squares analysis suggested by Tidwell and Mortimer.[18] The values of r_N and r_M determined by these methods are given in Table II, together with those reported by Grassie et al.,[10] determined by elemental nitrogen analysis. In Table I are also given the conditional probabilities of monomer addition to growing polymeric chains, p_{ij} (i, j = N, M).[19] These values are useful in determining the statistical distribution and length of monomer sequences considering the classical terminal model of copolymerization proposed by Lewis and Mayo[13] and Alfrey and Goldfinger.[14] According to this model, the values of p_{ij} can be expressed as a function of the reactivity ratios and the molar ratio of the concentration of monomers.[19,20] Values of these parameters are collected in the fifth and sixth columns of Table I and have been calculated from the reactivity ratios determined by the method of Tidwell and Mortimer (see Table II). As shown in Table II, the application of different methods for the determination of reactivity ratios gives similar values. Perhaps this is a result of the ideal character of this copolymerization system, since both reactivity ratios are very close to unity and the corresponding composition diagram is practically coincident with that of ideal behavior. We stress here that the reactivity ratios determined by the application of the nonlinear least-squares analysis suggested by Tidwell and Mortimer[18] are the most probable values for this system. In this sense, the 95% confidence limit gives an idea of the experimental error and the correctness of the experimental conditions used to generate the composition data.[18] When the experimental error is reasonably small and the data have been taken under the appropriate conditions, the approximation can be remarkably good. This is illustrated by the dimensions of the elliptical diagram generated by the application of the mathematical treatment suggested by Behnken[21] and Tidwell and Mortimer.[18] The application of this treatment to the copolymerization data reported in Table I and the reactivity ratios quoted in Table II provides the 95% confidence limits defined by the area of the elliptical diagram drawn in Figure 1. This diagram confirms the excellent approximation of the values of r_N and r_M as is indicated by the reduced dimensions of the ellipse.

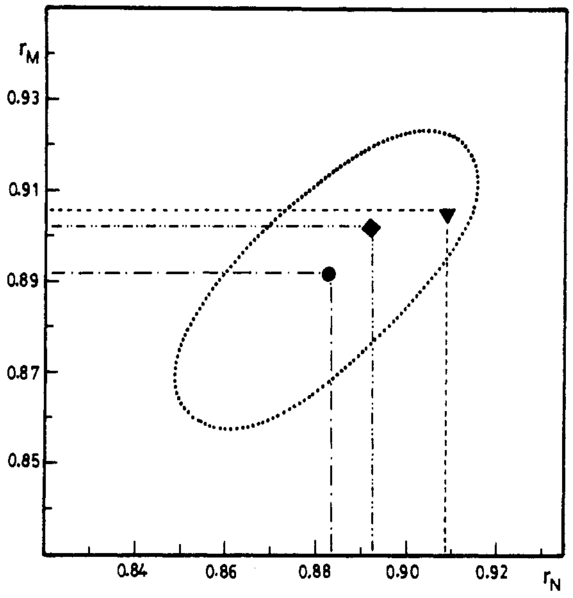

Figure 1. 95% confidence diagram for the reactivity ratios of N and M, determined by the nonlinear least-squares method suggested by Tidwell and Mortimer. Values of reactivity ratios: (●) Tidwell–Mortimer; (◆) Kelen–Tüdős; (▼) Fineman–Ross.

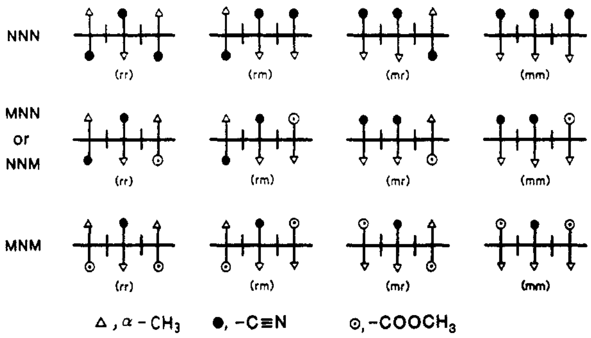

Figure 2. Schematic representation of N-centered triads in methacrylonitrile–methyl methacrylate copolymers.

For a complete description of the monomer sequence distribution and relative stereochemical configuration of monomer sequences, at least in terms of N- and M-centered triads, it is necessary to take into consideration as many as 10 different triads with a central N unit, which may be magnetically distinguishable, as is shown in the scheme of Figure 2. Since both monomeric repeating units have a quaternary pseudoasymmetric carbon, from a stereochemical point of view 10 triads with a central M unit sensitive to tacticity must also be considered. The statistical analysis of the monomer sequence distribution and of the stereochemical configuration of the copolymer sequences has been carried under the following assumptions: With respect to the chemical composition of copolymer sequences, it has been assumed that the copolymerization process is described correctly by the

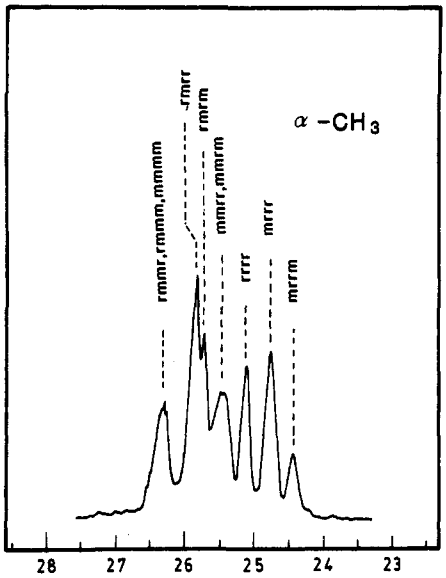

Figure 3. Enlarged ^{13}C NMR resonance signals of the α-CH$_3$ carbon of poly(methacrylonitrile); solvent, DMSO-d_6, $T = 80$ °C.

terminal unit model.[13,14] From a stereochemical point of view, we assume that the configurational sequence distribution (tacticity) may be described according to Bernoullian statistics, with the isotacticity and coisotacticity parameters σ_{NN}, σ_{MM}, σ_{NM}, and σ_{MN} as defined by Bovey[22,23] and Coleman,[24] where σ_{ij} is the probability of generating a meso diad between an i-ended growing radical and the incoming j monomer.

It may be assumed that the isotacticity parameters σ_{NN} and σ_{MM}, to a very good approximation, are the isotacticity parameters for the free-radical polymerization of the corresponding monomers, whereas the coisotacticity parameters σ_{NM} and σ_{MN} are considered to be equal, i.e., $\sigma_{NM} = \sigma_{MN} = \sigma^*$.[25,26] These parameters can be determined from the analysis by NMR spectroscopy of the stereochemical configuration distribution of the corresponding homopolymers and that of the comonomer sequences in copolymers with different compositions, since NMR spectroscopy has become the most exact characterization technique for the microstructural description of polymer and copolymer systems, including determination of composition, stereochemical configuration, and sequence length distribution.

Regarding the isotacticity parameter for the free-radical polymerization of methyl methacrylate, we have found a value of $\sigma_{MM} = 0.24$,[27] which is similar to that reported by Bovey[23] for the free-radical polymerization of methyl methacrylate in toluene at 50 °C and very close to that suggested by Kobayashi et al.[28] ($\sigma = 0.25$) for the free-radical copolymerization of methyl methacrylate with methyl acrylate. In order to determine the isotacticity parameter for the free-radical polymerization of methacrylonitrile, we have analyzed the ^{13}C NMR spectrum of a polymer sample prepared under the experimental conditions used in the copolymerization. Unlike the ^{13}C NMR spectrum of polyacrylonitrile,[3,29] the nitrile carbon of poly(methacrylonitrile) is not sensitive to the stereochemical configuration of the pseudoasymmetric quaternary carbon, but, as is shown in Figure 3, the α-CH$_3$ group gives resonance signals in the interval δ 24.0–27.0, which, according to the analysis of the spectrum of poly(methacrylonitrile) reported by Pham et al.,[29] have been assigned to sequences of tactic pentads with the stereochemical configuration indicated in that figure. From the integrated intensities of the corresponding resonances and assuming a Bernoullian trial, we obtain a value of the isotacticity parameter $\sigma_{NN} = 0.37$. Table III presents the molar fraction of tactic pentads determined experimentally from the ^{13}C NMR spectrum together with those calculated statistically with this isotacticity parameter. The good agreement between experimental and calculated values justifies the statistical model used in this work and verifies the assignment suggested in part by Pham et al.[29]

Table III
Experimental and Calculated Molar Fractions of Tactic Pentads of Poly(methacrylonitrile), Prepared by Free-Radical Polymerization in Bulk at 60 °C[a]

	molar fraction	
tactic sequence	exptl	calcd
mmmm mmmr + rmmm rmmr	0.13_2	0.137
rmrr + rmrm	0.29_6	0.294
mmrr + mmrm	0.19_0	0.173
rrrr	0.15_1	0.158
mrrr	0.17_1	0.185
mrrm	0.06_0	0.054

[a] Values calculated correspond to $\sigma_{NN} = 0.37$.

The isotacticity parameter determined is also very close to that calculated from the ^{13}C NMR spectrum of poly(methacrylonitrile) reported by Pham,[29] $\sigma = 0.39$, but is somewhat lower than values of the isotacticity parameter of poly(acrylonitrile), $\sigma = 0.51$, determined from the stereochemical configuration data reported by Pichot and Pham[3] for the free-radical polymerization of acrylonitrile in DMF at 60 °C, $\sigma = 0.53$, determined from data reported by Inoue and Nishioka,[30] or $\sigma = 0.55$, determined from the spectrum reported by Schaefer[31] for the free-radical polymerization of acrylonitrile in aqueous medium. The difference between the isotacticity parameters of methacrylonitrile and acrylonitrile polymerizations could arise from the relative steric hindrance of the α-CH$_3$ group in poly(methacrylonitrile) chains, with respect to poly(acrylonitrile) chains, since the dipolar interactions between the active growing end and incoming monomer molecules must be similar in both cases (they have the same side nitrile group). It is possible that the presence of the α-CH$_3$ provides additional difficulties to the isotactic addition of methacrylonitrile units with respect to the polymerization of acrylonitrile. The determination of the coisotacticity parameter $\sigma_{NM} = \sigma_{MN} = \sigma^*$ is feasible from the analysis of the ^{13}C NMR spectra of copolymer samples prepared with different feed composition, on the basis of the assumptions indicated above. In this sense, we are interested in the analysis of resonance signals assigned to the quaternary carbon and carbonyl groups of M-centered sequences, as well as the resonance signals assigned to α-CH$_3$ groups of both M- and N-centered sequences.

Quaternary Carbon Resonance Signals. The spectra shown in Figure 4 reproduce the resonance peaks of the quaternary carbon of the methyl methacrylate units. Three well-resolved signals can be observed, the intensities of which change drastically with copolymer composition. Comparison with the resonance signals of this carbon atom in pure poly(methyl methacrylate)[27,29] suggests that they correspond to M-centered triads, independently of the composition, but with the following stereochemical configuration: syndiotactic triads (rr), $\delta = 44.30$; heterotactic triads (mr + rm), $\delta = 44.70$; and isotactic triads (mm), $\delta = 45.20$, the chemical shifts being very close to those of the corresponding signals in the ^{13}C NMR spectrum of poly(methyl methacrylate).[27] This result indicates that

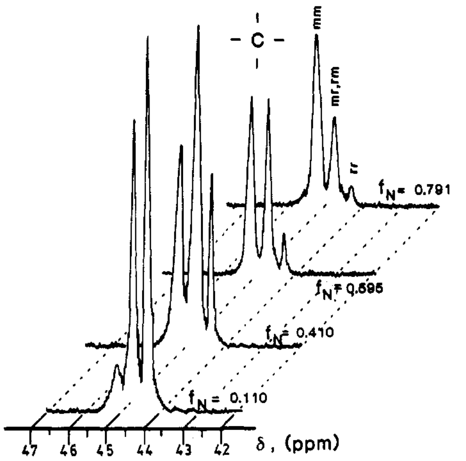

Figure 4. Expanded ^{13}C NMR signals of the quaternary carbon of M units in methacrylonitrile–methyl methacrylate copolymers.

Table IV
Distribution of the Stereochemical Configuration of M-Centered Sequences along the Copolymer Chains, for N–M Copolymers Prepared by Free-Radical Copolymerization[a]

f_N (copolymer)	tactic sequence	triad molar fraction	
		exptl	calcd
	mm	0.06_4	0.096
0.11_0	mr + rm	0.40_6	0.428
	mm	0.52_9	0.475
	mm	0.12_5	0.143
0.20_9	mr + rm	0.44_0	0.470
	rr	0.43_4	0.387
	mm	0.28_8	0.260
0.41_0	mr + rm	0.46_2	0.500
	rr	0.25_0	0.240
	mm	0.43_2	0.403
0.59_5	mr + rm	0.45_5	0.463
	rr	0.11_4	0.133
	mm	0.61_6	0.572
0.79_1	mr + rm	0.31_5	0.368
	rr	0.06_8	0.060

[a] Values calculated have been obtained with the copolymerization parameters indicated in the text.

the chemical shift of the quaternary carbon of the M units is sensitive to the stereochemical configuration in terms of M-centered triads, independent of the chemical composition. This means that the diamagnetic effect of the nitrile group on the quaternary carbon of neighboring M units is similar to that of the carbonyl ester group of M units. Therefore, the resonance signals of the quaternary carbons appear in nearly the same position as the corresponding signals of pure poly(methyl methacrylate).

It is noteworthy that the central M unit in sequences of triads for copolymers rich in methyl methacrylate has a predominantly racemic or syndiotactic stereochemical configuration, whereas in the methacrylonitrile-rich copolymers this trend is reversed and the M units have a predominantly meso or isotactic configuration. This variation permits the determination of the coisotactic parameter, σ^*. From the integrated intensities of these signals we have determined a value of $\sigma^* = 0.87$ on the basis of Bernoullian statistics. This value is higher than the coisotacticity parameters reported for the free-radical copolymerization of methyl methacrylate with other alkyl acrylic esters[27] and indicates some strong interactions between the nitrile group of the N units and the carbonyl ester residue of M neighbors.

The molar fractions of tactic M-centered triads (independent of the chemical structure, M or N, of neighboring units) of copolymer samples with different compositions are collected in Table IV. Experimental values have been determined from the integrated intensities of the three resonance signals assigned in Figure 4, whereas the values quoted in the fourth column have been determined by the sum of the contribution of MMM, MMN, NMM, and NMN triads, with the stereochemical configuration of interest according to the scheme of Figure 2, but using the parameters $r_N = 0.883$, $r_M = 0.892$, $\sigma_{NN} = 0.37$, $\sigma_{MM} = 0.24$, and $\sigma^* = 0.87$. The excellent agreement of experimental and calculated values in the whole range of composition analyzed makes it clear that this copolymerization model is useful for the microstructural analysis of this system.

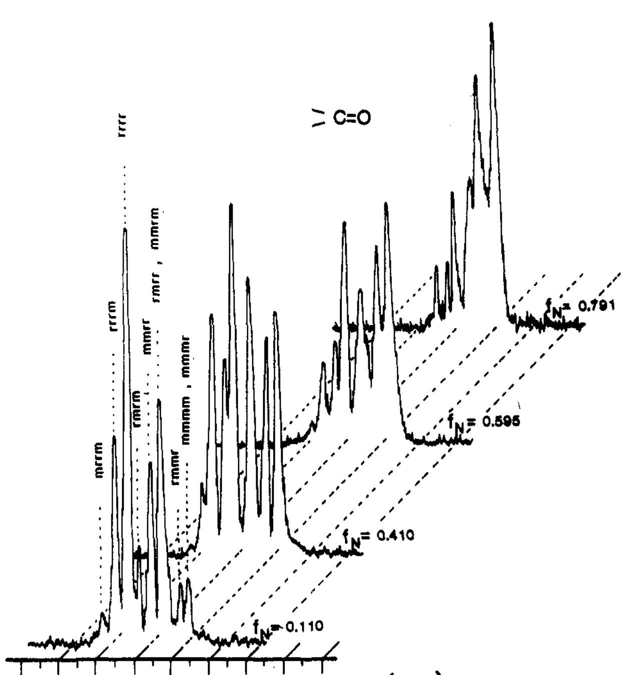

Figure 5. Expanded ^{13}C NMR pattern of the carbonyl carbon resonances of M-centered sequences in methacrylonitrile–methyl methacrylate copolymers.

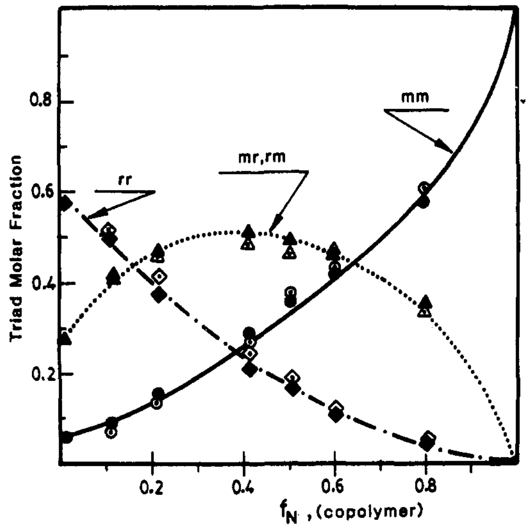

Figure 6. Variation of the tacticity of M-centered triads as a function of the methacrylonitrile mole fraction in the copolymer samples. Black points correspond to data obtained from carbonyl signals; white points correspond to data from quaternary resonances; lines correspond to theoretical diagrams with the statistical parameters indicated in the text.

Carbonyl Carbon Resonance Signals. The analysis of carbonyl carbon resonance signals may be of interest in providing information sequences longer than four units.

Table V
Tacticity of M-Centered Pentads

resonance signal		pentad molar fraction				
δ, ppm	sequence	$f_N = 0.11_0$	$f_N = 0.20_9$	$f_N = 0.41_0$	$f_N = 0.59_5$	$f_N = 0.79_1$
178.10	mrrm	0.02_3	0.01_5	0.00_6	0.00_0	0.00_0
177.85	mrrr	0.15_8	0.10_4	0.04_6	0.01_9	0.00_0
177.55	rrrr	0.31_7	0.25_1	0.15_0	0.07_6	0.06_1
177.25	rmrm	0.07_7	0.10_7	0.12_2	0.10_0	0.06_7
176.90	mmrr	0.14_0	0.18_2	0.21_9	0.22_0	0.13_8
176.70	rmrr + mmrm	0.18_9	0.17_7	0.17_3	0.15_2	0.15_4
176.15	rmmr	0.04_7	0.08_1	0.13_3	0.20_0	0.26_0
175.90	mmmr + mmmm	0.04_9	0.08_3	0.15_2	0.23_6	0.32_0

Table VI
Assignment of Resonance Signals of ^{13}C NMR Spectra Recorded in DMSO-d_6 at 80 °C to the α-CH_3 Groups of N- and M-Centered Sequences[a]

signal			sequence molar fraction			
sector	δ, ppm	sequence	$f_N = 0.11_0$	$f_N = 0.41_0$	$f_N = 0.59_5$	$f_N = 0.79_1$
a	16.40	MMM (rr)	0.038_5	0.09_6	0.02_5	0.00_6
		MNM (rr)	(0.407)	(0.115)	(0.035)	(0.004)
	17.80	MMN + NMM (rr)				
b	18.40	MMN + NMM (mr + rm)	0.40_6	0.31_1	0.15_6	0.04_7
	18.90	MMM (mr + rm)	(0.411)	(0.338)	(0.198)	(0.060)
		MNM (mr + rm)				
	20.20	MMN + NMM (mm)				
c	20.40	MMM (mm)	0.14_0	0.20_5	0.22_3	0.12_1
	21.00	MNM (mm)	(0.145)	(0.194)	(0.220)	(0.082)
	23.60	NNN (rr)				
	24.20	NNM + MNN (rr)				
d	24.90	NMN (rr)	0.05_6	0.26_1	0.43_7	0.62_9
	25.40	NNM + MNN (rm + mr)	(0.023)	(0.202)	(0.399)	(0.633)
	25.80	NNN (mr + rm)				
		NMN (mr + rm)				
	26.60	NMN (mm)				
e	27.00	NNN (mm)	0.01_3	0.12_7	0.15_9	0.19_7
	28.00	NNM + MNN (mm)	(0.014)	(0.151)	(0.148)	(0.221)

[a] Values in parentheses correspond to the contribution of the sequences calculated statistically with the parameters indicated in the text.

In Figure 5 the expanded resonances of the carbonyl ester group of M units for copolymer samples with different compositions are drawn. This functional group gives rise to eight sharp peaks, whose intensities change drastically with the average composition of the copolymer samples. The assignment of these peaks, with chemical shifts between δ 176.0 and 178.5, has been carried out in terms of M-centered pentads, on the basis of similar signals for pure poly(methyl methacrylate) reported by Hatada et al.,[32] Peat and Reynolds,[33] and Ferguson and Ovenall,[34] as well as for other poly(aryl methacrylates)s.[35] It is clear from Figure 5 that the chemical shifts of these signals do not change with the composition of the copolymer samples, but according to the assignment suggested the M units have a predominant racemic or syndiotactic character for methyl methacrylate rich copolymers. The incorporation of N units in the copolymer chains gives rise to a drastic change in the intensity of the assigned M-centered pentads in such a way that for methacrylonitrile-rich copolymers the M units have a predominantly meso or isotactic configuration. This supports the results deduced from the analysis of the quaternary carbon resonances. In this sense, Figure 6 shows the variation of the mole fraction of methyl methacrylate centered triads, as a function of the methacrylonitrile mole fraction in the copolymer; the black points in the figure correspond to data derived from the carbonyl ester resonances and the white points to data obtained from the quaternary carbon resonances, whereas the lines are the statistical prediction on the basis of the terminal model for the addition of monomers to growing chain ends, with a stereochemical configuration according to the Bernoullian statistics with the parameters reported above. It is clear from this figure that the experimental points adequately fit the theoretical diagrams, justifying the parameters considered. The molar fractions of M-centered pentads for copolymers prepared with different compositions, according to the assignment of the C=O resonances, are collected in Table V.

α-CH_3 Resonance Signals. The ^{13}C resonances of the α-CH_3 groups for several copolymer samples prepared with different feed compositions and the corresponding homopolymers are shown in Figure 7. As has been indicated above, the α-CH_3 resonances of poly(methacrylonitrile) are susceptible to analysis in terms of tactic pentads, their chemical shifts being somewhat different from those of the α-CH_3 resonances for poly(methyl methacrylate), which in turn can be analyzed in terms of tactic triads.

The spectra of copolymer samples present both kinds of signals with a very complex pattern that could be analyzed in terms of M- and N-centered triad to pentad sequences, but in the spectra shown in Figure 7 signals that are not present in the spectra of the corresponding homopolymers may be identified. The appearance of these new signals, i.e., δ 17.80, 18.40, 20.20, 20.40, 27.00, 28.00, etc., is associated with the formation of M- and N-centered sequences, with the composition and stereochemical configuration outlined in the scheme of Figure 2. The complexity of the NMR pattern of these signals does not allow us to establish accurately the assignment of resonance signals to individual sequences because it is not appropriate to consider only the composition of N-centered sequences but also their stereochemical configuration. Therefore, on the basis of the assignment of signals for both homopolymers and taking into consideration the distribution and stereochemical configuration of N and M sequences of triads, according to the scheme of Figure 2, we have considered the resonance pattern tentatively divided into five sectors (named a–e), which correspond approximately

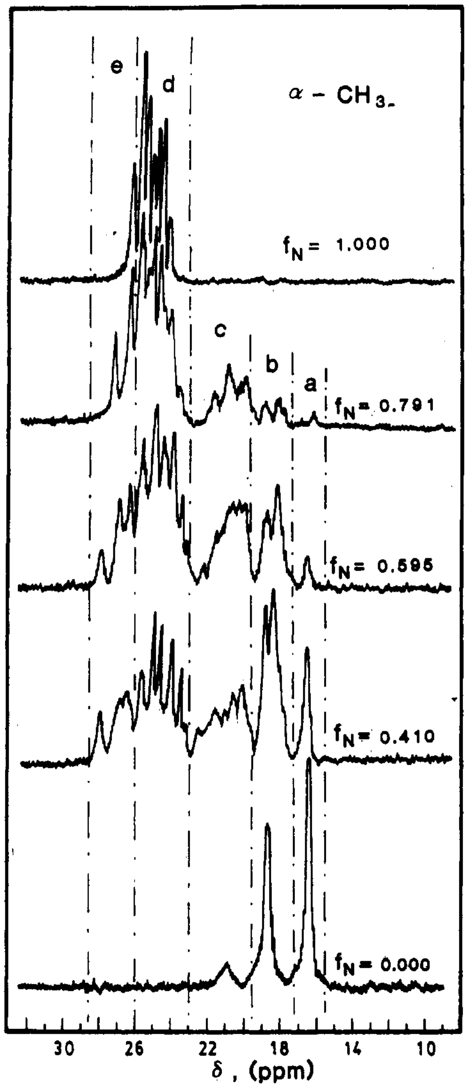

Figure 7. Expanded ^{13}C NMR signals of the α-CH$_3$ groups of M- and N-centered sequences.

to homogeneous tactic sequences of triads. The chemical shifts of the main NMR signals considered are collected in the second column of Table VI, and the sequences considered in each sector are collected in the third column. The fourth to seventh columns display the experimental data of each one of the sectors for copolymer samples with different compositions. Values in brackets correspond to the total contribution of the molar fraction of sequences collected in the third column and have been calculated considering the copolymerization parameters $r_N = 0.883$ and $r_M = 0.892$ and the statistical parameters $\sigma_{NN} = 0.37$, $\sigma_{MM} = 0.24$, and $\sigma^* = \sigma_{NM} = \sigma_{MN} = 0.87$.

We stress here that the tentative analysis of the α-CH$_3$ resonance signals gives the most conclusive information since they are sensitive to the composition and stereochemical configuration of N- and M-centered sequences. The agreement between experimental and calculated values for the sectors considered supports the validity of the model considered for this free-radical copolymerization system.

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Registry No. (Methacrylonitrile)(methyl methacrylate) (copolymer), 26813-25-2; methacrylonitrile, 126-98-7; methyl methacrylate, 80-62-6.