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COPOLYMERS OF CYANO COMPOUNDS WITH CAPTODATIVE MONOMERS. STUDIES OF THEIR MICROSTRUCTURES

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ABSTRACT

Copolymers of vinylidene cyanide, methacrylonitrile, and acrylonitrile with various captodative monomers such as cyanovinyl acetate, methyl α-acetoxyacrylate or methyl 1-(methoxy carbonyl) vinyl carbonate were synthesized by radical copolymerization. The microstructures of these copolymers were studied by means of ^{13}C NMR. The copolymers of vinylidene cyanide are rich in alternating structure, and the copolymers of methacrylonitrile and acrylonitrile are rather statistical than alternating. The measurements of reactivity ratios for three copolymerization reactions, vinylidene cyanide, methacrylonitrile, and acrylonitrile with methyl α-acetoxyacrylate, confirm these conclusions.

INTRODUCTION

Due to the piezoelectric properties of the amorphous and alternating copolymer of vinylidene cyanide and vinyl acetate, first described by Miyata et al. [1], a growing interest in the copolymerization of cyano monomers with various acrylic, vinylic, or styrenic compounds has been observed in order to study either their microstructures or their pyroelectric and piezoelectric properties. Vinylidene cyanide **1a** has been copolymerized with numerous vinylic esters [2], styrene [3], substituted styrenes [4], and methacrylic derivatives [5], and the best piezoelectric properties have been characterized with copolymers including vinylic esters [6]. Other current monomers such as methacrylonitrile **1b** and acrylonitrile **1c** have also been studied after copolymerization reaction with vinyl or isopropenylacetate [7]. An overlooked monomer, methylvinylidene cyanide **1d**, copolymerizes with styrene [8] or vinyl acetate [9], and some of the resulting copolymers have interesting pyroelectric properties [7].

The amorphous copolymers have to be poled to active noncentrosymmetricity, deriving their piezo-or pyroelectric properties from the cyano dipole. This poling is carried out at a temperature just below the glass transition temperature. After cooling, a fraction of dipole is aligned in the field section.

The properties of copolymers containing cyano groups could perhaps be improved with a higher concentration of dipoles. The copolymerization reaction of cyano monomers with captodative monomers such as 1,1-disubstituted ethylene, having an electron-withdrawing (capto) and an electron-donor (dative) substituant on the same carbon, could provide new materials with interesting piezo-or pyroelectric properties. Recently, the kinetic study of various captodative substituted methyl α-(acyloxy) acrylates [10] was described, and the polymer from methyl α-acetoxy acrylate has a high refractive index with higher second harmonic generation values than the alternating copolymer of vinylidene cyanide with vinyl acetate [11].

In this article we describe the copolymerization of vinylidene cyanide, methacrylonitrile, and acrylonitrile with captodative monomers such as cyanovinyl acetate (systematic name: 1-acetoxy-1-cyanoethylene), methyl α-acetoxyacrylate, and methyl 4-(methoxy carbonyl) vinyl carbonate. The microstructures of the resulting copolymers have been studied by using ^{13}C NMR, and the measurements of some reactivity ratios have also been carried out.

EXPERIMENTAL

Material Characterization of Copolymers

Methacrylonitrile, acrylonitrile, and cyanovinyl acetate are commercial products (Aldrich) and were distilled under reduced pressure, then stored below 5°C. Vinylidene cyanide was synthesized by pyrolysis of tetracyano-1,1,3,3-propane according to the procedure of Bogomolova et al. [12] and kept at −18°C in a sealed ampule with a small amount of phosphorus pentoxide as inhibitor of polymerization. Methyl α-acetoxy acrylate was prepared by reaction of acetic anhydride with methyl pyruvate and *p*-toluenesulfonic acid as a catalyst [13]. Methyl 1-(methoxy carbonyl) vinyl carbonate was prepared by reaction of methyl chloroformate on methyl pyruvate in basic medium (triethylamine in anhydrous tetrahydrofuran) using a procedure described by Tamariz et al. [14].

Elemental Analyses

The elemental analyses were carried out at the Service Central d'Analyse C.N.R.S. Vernaison (France), and the copolymer compositions were calculated from the nitrogen percentage of the copolymers.

Glass Transition Temperature (T_g) Determination

The glass transition temperatures were recorded with a D.S.C. 92 Setaram using a mass sample of 10–15 mg and a heating rate of 10°C/min. The T_g value has been taken as the initial onset of the change of slope in the D.S.C. curve.

Molecular Masses

The molecular weights of the copolymers have been characterized by viscosimetry by means of a Ubbelohde apparatus at 25 ± 0.1°C in dimethylformamide as solvent. Molecular masses of the copolymers have also been measured with a Waters Apparatus and Ultrastyragel columns (10^4, 10^5, and 10^6 Å) using dimethylformamide as solvent and monodisperse polystyrene as standards.

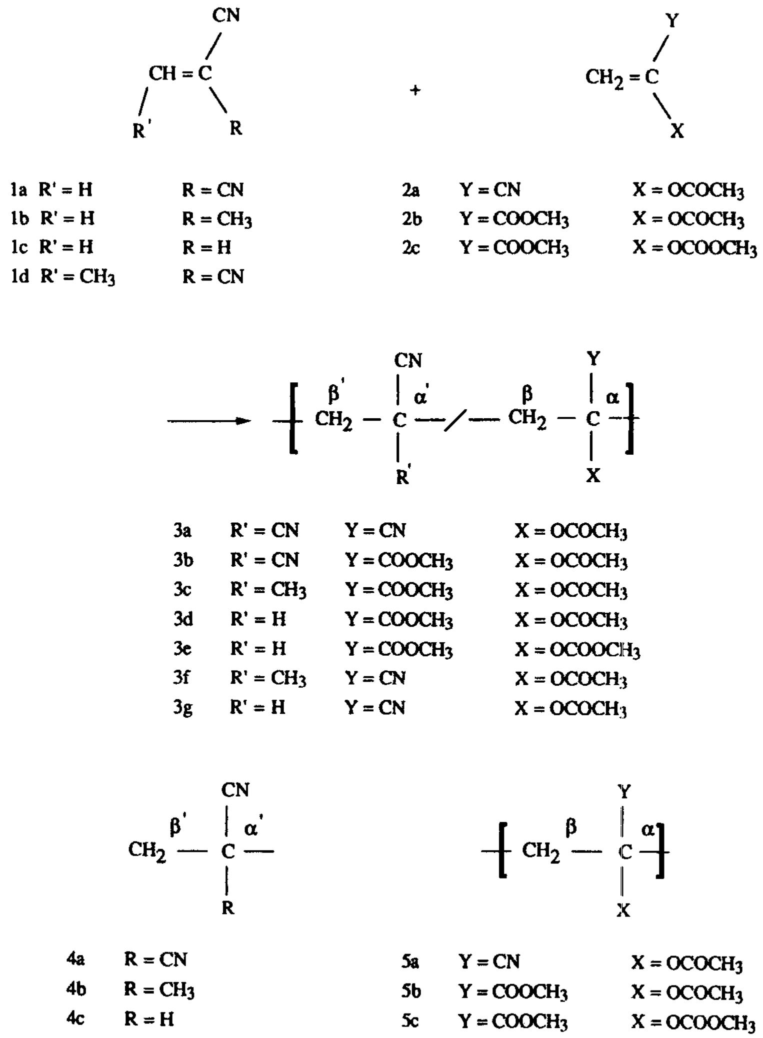
^{13}C NMR

^{13}C-NMR spectra have been recorded using a Bruker A.C. 200 spectrometer at 50.3 MHz with a 50% solution in deuterated dimethylformamide d_7 or dimethylsulfoxide (DMSO) d_6 with tetramethylsilane (TMS) as internal reference. The probe temperatures were 100°C for the DMSO d_6 solution. $Cr(Acac)_3$ has been used as a relaxing agent, 50 mg for a 2.5 or 3 mL/solution. Typical analysis conditions have been the following: pulse angle = 800 repetition, time = 6 seconds, acquisition time = 3 seconds for 32 kwords. Sweep width = 1000 Hz, number of scans = 6000–7000. ^{13}C peak assignments have been aided by using DEPT spectra.

Copolymerization

Copolymers were prepared as follows: equimolar proportions of cyano monomer and captodative monomer were mixed with 0.2 wt% of initiator (2,4-dichlorobenzoyl peroxide (DCBP) or azobisisobutyronitrile (AIBN) and dissolved in a minimum of benzene and heated at 45°C for 24 hours or heated in bulk (AIBN) at 75°C for 24 hours. The contents of the tubes were dissolved in dimethylformamide (DMF) and precipitated with methanol, then dried. The yields of the copolymerization were close to 50%. See Scheme 1.

For the determination of reactivity ratios the yield of the copolymerization was less than 10% and the duration of the reaction was generally less than 2 hours.



SCHEME 1. Synthesis routes of the copolymers.

RESULTS AND DISCUSSION

Characterization of the Copolymers

Copolymers **3a–e** have been characterized by their elemental analyses, their glass transition temperatures, their viscosities, or their molecular masses (Table 1). The glass transition temperature of copolymers **3a** and **3b** are of 143 and 146°C, respectively, and are in the range of observed temperatures for numerous copolymers of vinylidene cyanide [15, 16].

^{13}C-NMR Studies

The knowledge of the microstructure of the copolymers needs the assignments of the chemical shifts of the corresponding homopolymers: poly(vinylidene cyanide)

TABLE 1. Characteristics of the Copolymers **3a–3g**: Elemental Analyses, Glass Transition Temperatures T_g, Viscosities, Molecular Masses, Polydispersities, and Percentages of Incorporation of Captodative Monomer[a]

			C	H	N	O	T_g, °C	η, L/g	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	%[b]	%[c]
3a	$(C_4H_2N_2)_n(C_5H_5NO_2)_n$	Found	55.36	4.11	19.63	20.47	142	—	240	826	3.4	62	54
	$(78.07)_n(111.10)_n$	Calcd	57.14	3.73	22.21	16.92							
3b	$(C_4H_2N_2)_n(C_6H_8O_4)_n$	Found	52.73	5.17	11.79	29.96	146	24×10^{-3}	64	180	2.8	54	54
	$(78.07)_n(144.12)_n$	Calcd	54.05	4.54	12.61	28.80							
3c	$(C_4H_5N)_n(C_6H_8O_4)_n$	Found	54.44	6.49	7.69	30.89	60	49×10^{-3}	75	368	4.9	50	55
	$(67.09)_n(144.12)_n$	Calcd	56.86	6.20	6.63	30.30							
3d	$(C_3H_3N)_n(C_6H_8O_4)_n$	Found	53.11	6.02	7.12	32.92	59	48×10^{-3}	82	289	3.5	50	51
	$(53.06)_n(144.12)_n$	Calcd	54.82	5.62	7.10	32.46							
3e	$(C_3H_3N)_n(C_6H_8O_5)_n$	Found	48.35	5.20	4.27	41.33	93	17×10^{-3}	44	118	2.68	63	57
	$(53.06)_n(160.12)_n$	Calcd	50.70	5.16	6.57	37.55							
3f	$(C_4H_5N)(C_5H_5NO_2)$	Found	59.7	5.67	15.46	19.69	129	120×10^{-3}	260	1320	5	56	50
	$(67.09)_n(111.10)_n$	Calcd	60.66	5.66	15.72	17.96							
3g	$(C_3H_3N)(C_5H_5NO_2)$	Found	56.99	4.94	16.13	21.15	131	130×10^{-3}	300	1270	4.2	57	56
	$(53.06)_n(111.10)_n$	Calcd	58.53	4.91	17.06	19.49							

[a] The calculated values are given for an equimolar incorporation of the two monomers in the copolymer.

[b] Values of the percentage of incorporated captodative monomer calculated from the arithmetic mean of oxygen and nitrogen percentage.

[c] Calculated from measurements of areas in the ^{13}C-NMR spectra.

4a is unstable but its ^{13}C-NMR spectrum was first described by Stille et al. [17] with the study of the alternating copolymer of **4a** with styrene. Due to the lack of tacticity, only three single peaks were observed: at 113.6 ppm (CN), 66 ppm (CH_2), and 30.2 (quaternary carbon). The assignments of the chemical shifts of polymethacrylonitrile **4b** and polyacrylonitrile **4c** have been studied [18, 19].

The polymerizations and copolymerizations of the two captodative monomers **5a** and **5b** were previously studied [20, 21], but their ^{13}C-NMR spectra have never been described. The monomer **5c** seems to be new. The main characteristics of these five homopolymers are given in Table 2. Several values of chemical shifts for the C_α of **5a, b, c** are observed and are due to the tacticity effects of the triads. As the polymerization was carried out with a radical initiator due to the steric effect, the most important peak could generally be referred to the triad *rr* and the least important peak to the triad *mm* (Scheme 2).

The ^{13}C chemical shifts assignments of copolymers **3a–g** are given in Table 3.

Copolymer **3a** [poly(1a-*co*-2a)]

The composition of the copolymer can also be calculated by measuring areas due to the quaternary carbon of the **1a** unit and to the CH_3 of the **2a** unit: the percentage of incorporated captodative monomer **2a** is close to 54%. By increasing the starting proportions of **2a** in copolymerizations (66% for **2a** and 33% for **1a**), an increasing percentage of incorporated **2a** with chemical shifts due to homosequence of **2a** was observed in the resulting ^{13}C-NMR spectrum. The microstructure of copolymer **3a** is mostly alternating and probably terminated by homosequences of **2a**: no chemical shift at 66 ppm corresponding to the CH_2 group of polyvinylidene cyanide **4a** was observed (Fig. 1).

The examination of the CN groups is in good agreement with this proposition: Three CN peaks are observed for the **2a** unit due to the three different pentads denoted $M'M'$, $R'M'$, and $R'R'$ (Scheme 3). The most important peak is probably due to the $R'R'$ pentad.

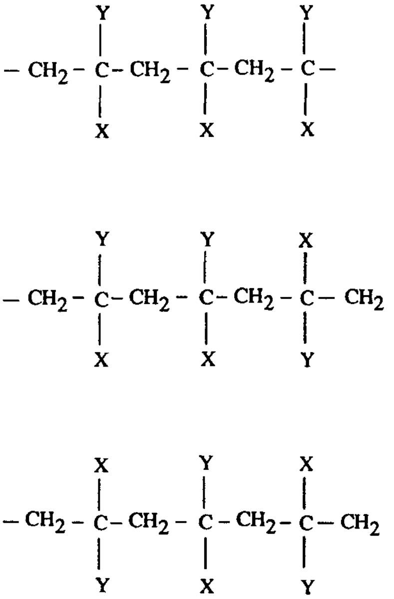
Three groups of three peaks are also observed for the **1a** unit in the 113.3–114.6 range, which can be explained by the nine centered **1a** heptads denoted $M'M'M'M'$, $M'M'R'M'$ or $M'R'M'M'$, $R'M'M'M'$ or $M'M'M'R'$, $R'M'R'M'$ or $M'M'R'M'$, $R'M'M'R'$, $M'R'R'M'$, $R'R'R'M'$, or $M'R'R'R'$ because of the almost alternate structure and the symmetry of **1a**, $n - 1$, and $n + 1$ units. The chemical shifts of C_α, CN of the central **2a** n unit, should only be affected by the spatial orientations of the **2a**'s $(n - 2)$ and $(n + 2)$ units. The capital letters M' (*co* meso triad) and R' (*co* racemic triad) are used here. The small letters *r* and *m* are usually reserved for classical configurational dyads.

Copolymer **3b** [poly(1a-*co*-2b)]

Vinylidene cyanide **1a** is known to give chiefly alternating structures with a variety of monomers such as styrene [16], vinyl acetate [22], vinyl esters, or substituted styrenes [23]. Only a few statistical copolymers seem to have been described with methyl vinyl ketone [15] or acrylonitrile [15] but no details concerning their structures have been given. The results of elemental analysis show that the percentages of the two monomers are similar and close to 50%. The examination of the

TABLE 2. ^{13}C Chemical Shifts Assignments for Polymers **4a, b, c** and **5a, b, c**

	4a	**4b**	**4c**	**5a**	**5b**	**5c**
C_α or $C_{\alpha'}$	30.2	33.2	28.2; 27.7; 27.3	67.3; 67.5; 67.6	80.3; 80.8; 81.2	80.9; 81.7; 82.2
C_β or $C_{\beta'}$	66	47–51	33.5	42.6; 44	39.8	38.3
CH_3		25.6–27.5				
CH$_3$COO				20.5	21.7	
COO*CH*$_3$					52.6	52
OCOO*CH*$_3$						54.1
CN	113.6	123.2	119.9; 120.2; 120.4	115.1; 115.2; 115.4		
CH$_3$*CO*O				168	169–171	
					169–171	168.8; 168.9
*CO*OCH$_3$						
O*CO*OCH$_3$						152.7



$$-CH_2-\overset{Y}{\underset{X}{C}}-CH_2-\overset{Y}{\underset{X}{C}}-CH_2-\overset{Y}{\underset{X}{C}}-$$

mm

$$-CH_2-\overset{Y}{\underset{X}{C}}-CH_2-\overset{Y}{\underset{X}{C}}-CH_2-\overset{X}{\underset{Y}{C}}-CH_2$$

mr

$$-CH_2-\overset{X}{\underset{Y}{C}}-CH_2-\overset{Y}{\underset{X}{C}}-CH_2-\overset{X}{\underset{Y}{C}}-CH_2$$

rr

SCHEME 2. Triads of the homopolymers **5a**, **5b**, and **5c**. a: Y = CN, X = $OCOCH_3$. b: Y = $COOCH_3$, X = $OCOCH_3$. c: Y = $COOCH_3$, X = $OCOOCH_3$.

chemical shifts of the CN groups shows three main peaks at 114.4, 114, and 113.8 ppm, but the shape of these peaks is different from those observed from the perfect alternating copolymer of **1a** with vinyl acetate [22] or with styrene [24]. These three peaks are due to the two defined triads as *m'm'* and *m'r'* (Scheme 4), but the shoulders of the peaks also suggest a statistical sequence of **1a** with the captodative monomer. Two chemical shifts (78.6 and 79.44 ppm) are assigned to the methylenic carbon (CH_2): a fully alternating copolymer should only give one chemical shift for this carbon. The composition of the copolymer between statistical sequence and alternating structure can be calculated by an examination of the chemical shifts of the two carbonyl groups. Two major peaks assigned to the $OCOCH_3$ and to the $COOCH_3$ are observed at 169.9 and 167 ppm, respectively, and two other peaks are also observed at 169.5 and 167.9 ppm, also due to the two carbonyls. The major and minor peaks are in an approximate 65/35 ratio which roughly corresponds to the proportion between an alternating structure and a statistical product (Fig. 2).

Copolymer **3c** [poly(1b-*co*-2b)]

The results of elemental analysis and of the measurements of the areas due to the CN groups of **1b** and the CH_3 of **2** are similar, and the percentages of incorporation of the monomer is in the 50–55% range. The expanded resonance patterns of the CN group show three broad main peaks at 122.9, 122.75, and 122.5 ppm with minor peaks at 122.2 and 122 ppm (Fig. 3). The main peaks are due to the triad effects here noted: *r'r'*, *m'm'*, and *rm* or *mr*. Three peaks are also observed for the methyl group in the 24–25 ppm range and are assigned to the three positions of

TABLE 3. ^{13}C Chemical Shifts Assignments for the Copolymers **3a-g**

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
C_α	67.2; 68	79.4; 78.6	81.1	79.6; 80; 80.7	8.14; 81.9	69.5–71.1	69–73
$C_{\alpha'}$	28.4; 28.5	79.4; 78.6	[b]	[b]	[b]	33.2–34	[b]
C_β	42.7	[b]	40–50[a]	39.8	40	44.4–49.8	43–43 .5
$C_{\beta'}$	42.7	[b]	40; 50	[b]	40	44.4–49.8	39–40
$\mathrm{CH_3}$			24.9			26.1–27.2	
$\mathit{CH}_3\mathrm{COO}$	20.2–20.8	20.7	20.9	20.3	20.7	21.9	21.5–21.7
$\mathrm{COO}\mathit{CH}_3$		52.6	51.9	52	52.3		
$\mathit{CH}_3\mathrm{OCOO}$					55		
CN	112.7; 120.5 (1a and 2a)	113.8; 114; 114.4	122.5; 122.8; 123	119–121.7	118.3; 121	117.2–118.6 123.3–124.8 (2a and 1b)	117.3–121.4 (1a and 2a)
$\mathrm{CH_3}\mathit{COO}$	168.2	167 or 169.9	169.3 or 169.4	169.3		170.2	170–170.3
$\mathit{COO}\mathrm{CH_3}$		169.9 or 167	169.4 or 169.3	169.3	168.8		
$\mathrm{CH_3O}\mathit{COO}$					152.7		

[a] The dash means that the chemical shifts are in a range.

[b] The chemical shift of this carbon is not visible due to the overlapping of the solvent.

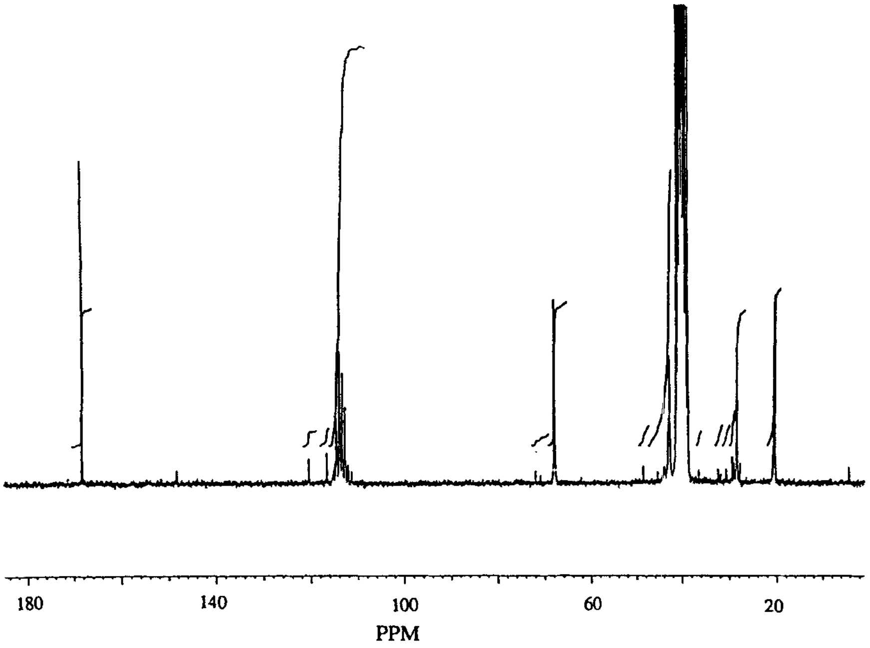
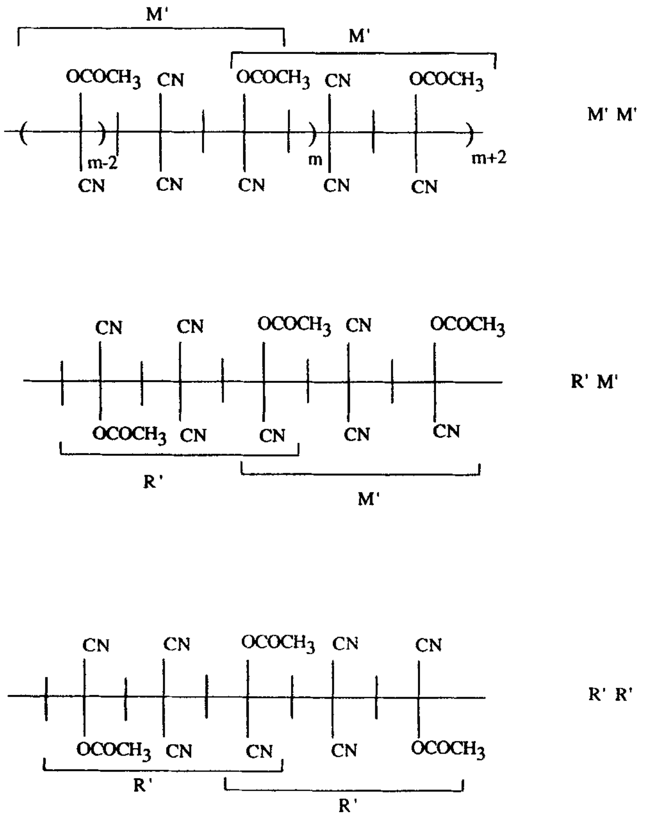
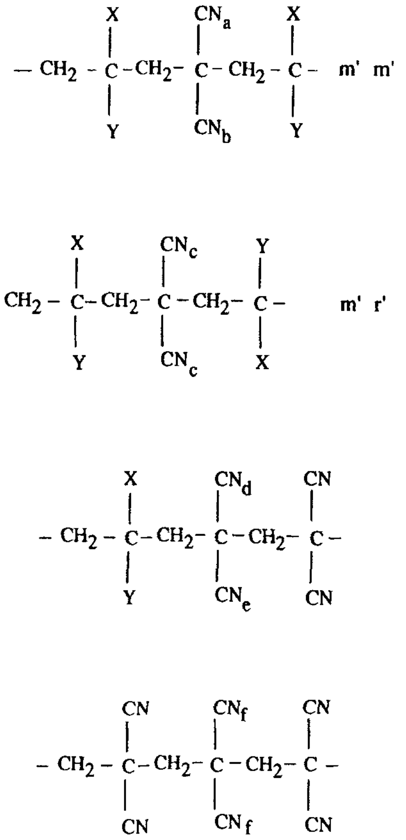


FIG. 1. ^{13}C-NMR spectrum of copolymer **3a**. Solvent: deuterated dimethylsulfoxide.



SCHEME 3. Cyanovinylacetate (**2a**)-centered pentads of the copolymer **3a**.



SCHEME 4. Triads *m'm'* and *m'r'* and triads of homosequence in the copolymer (**3b**): X = $OCOCH_3$, Y = $COOCH_3$.

the methyl groups in the triad, but the broadness of the CN pattern compared to those of CN groups in the copolymer **3b** or in the copolymer of **1a** with vinyl acetate do not suggest a fully alternating structure. Three chemical shifts for the CH_2 groups are observed at 40, 44, and 48 ppm and are referred to respectively as (**1b**-**1b**), (**1b**-**2b**) and (**2b**-**2b**) diads. The ratio of their areas gives the percentage of alternating structure, which is approximate 46% (Fig. 4).

Copolymer **3d** [poly(1c-*co*-2b)]

Elemental analysis and measurement of various peaks due to the **1c** and **2b** unit are also in agreement with an equimolar incorporation of the two monomers in the copolymers, but the determination of the nature of the copolymer, alternating or statistical, is also difficult (Fig. 5). The expanded resonance pattern of the CN group gives three complex chemical shifts divided in nine peaks badly separated in the 119-121.5 ppm range, and the assignment of this chemical shift to monomer triad is not possible. The nine peaks could be referred to the nine pentads resulting from the three triads noted, *mm*, *mr*, and *rr*, but no evidence can be found for an alternating structure after careful examination of the other peaks.

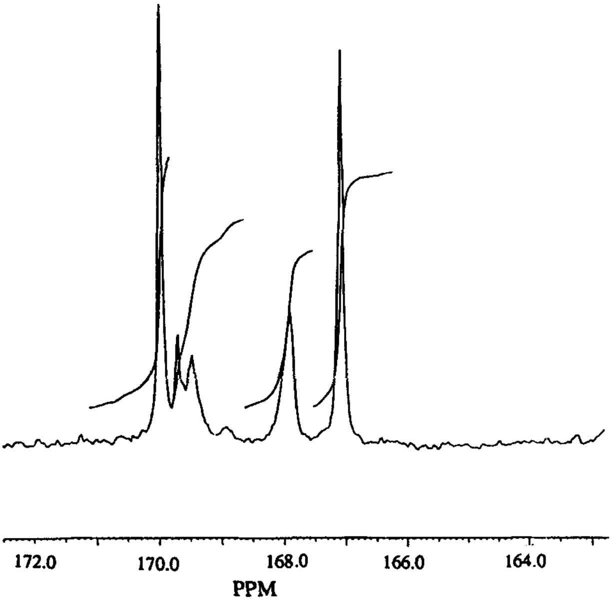


FIG. 2. ^{13}C-NMR spectrum of copolymer **3b**. Expanded resonance of carbonyl groups.

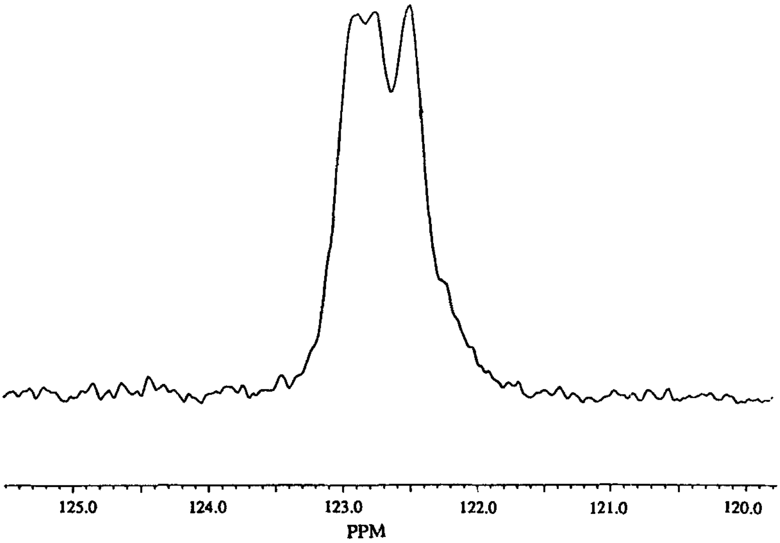


FIG. 3. ^{13}C-NMR spectrum of copolymer **3c**. Expanded resonance of CN groups. Solvent: deuterated dimethylformamide.

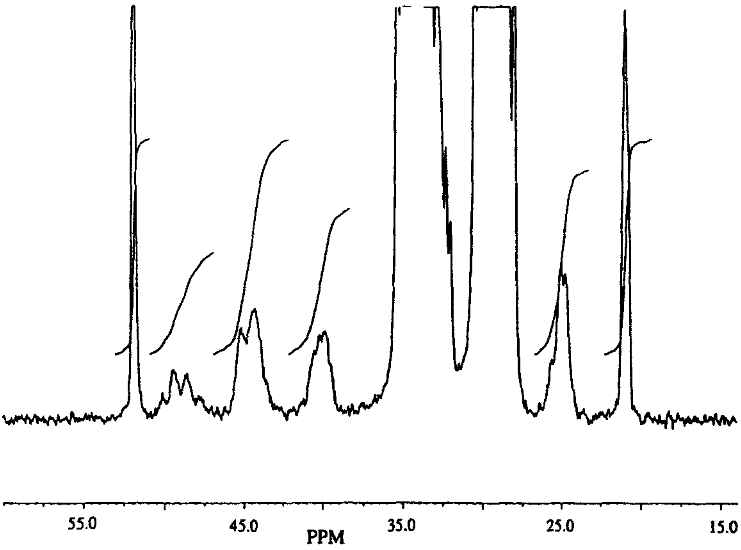


FIG. 4. ^{13}C-NMR spectrum of copolymer **3c**. Expanded resonance of CH_2 groups. Solvent: deuterated dimethylformamide.

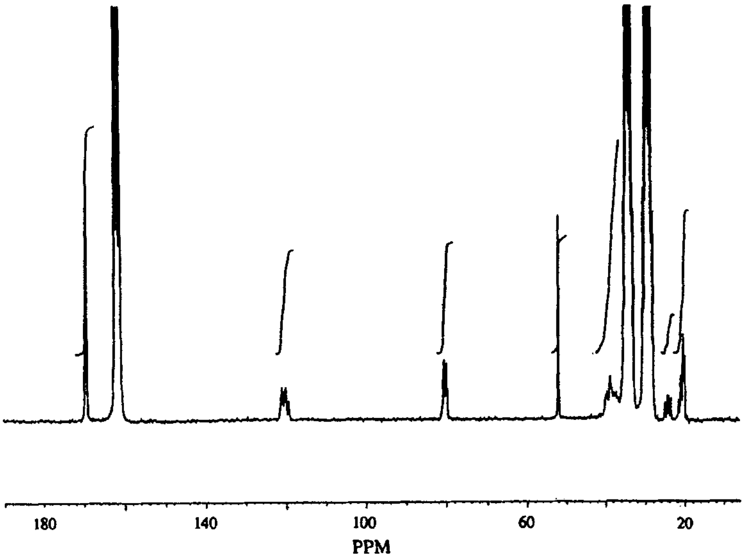


FIG. 5. ^{13}C-NMR spectrum of copolymer **3d**. Solvent: deuterated dimethylformamide.

Copolymer **3e** [poly(1c-*co*-2c)]

The results of elemental analysis and the measurements of various areas due to the two monomers show that the percentage of incorporation of **2c** is equal to 63%. The complexity of the expanded resonance pattern of CN groups (three main peaks divided into nine peaks badly separated in the 119–121.5 ppm range) also suggests a statistical structure.

Copolymer **3f** [poly(1b-*co*-2a)]

The assignments of the chemical shifts have been carried out by comparison with those of the polymethacrylonitrile **4b** and of the polycyanovinyl acetate **3a**. Measurements of the areas due to the CN groups or to the carbonyl function show an equal incorporation of the two monomers [the elemental analysis (Table 1) gives a slightly different result].

Examination of the expanded (Fig. 6) spectrum of the cyanide carbon region can explain the microstructure: three main peaks are observed for the cyano group of the methacrylonitrile unit at 124.8, 124.1, and 123.5 ppm, and can be respectively referred to *mm*, *mr*, and *rr* triads (Scheme 5). The last peak is split with a minor peak at 123.3 ppm. Similar observations are made for the nitrile group of the cyanovinyl acetate unit with chemical shifts at 118.5, 117.8, and 117.2 ppm, also with a splitting of the last peak into two minor peaks (Fig. 7).

The nature and the shape of the peaks of the CN region suggest a mostly alternating structure of the copolymer **3f** with homosequences of polymethacrylonitrile **4b** or of polycyanovinyl acetate **3a**.

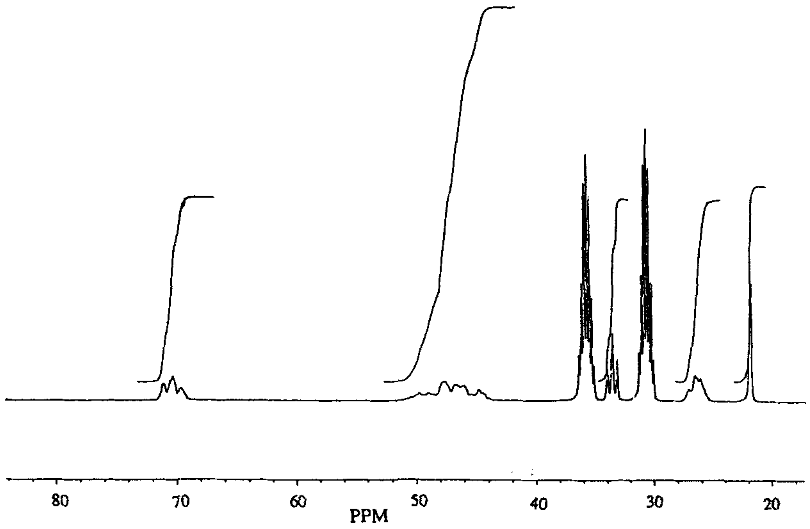
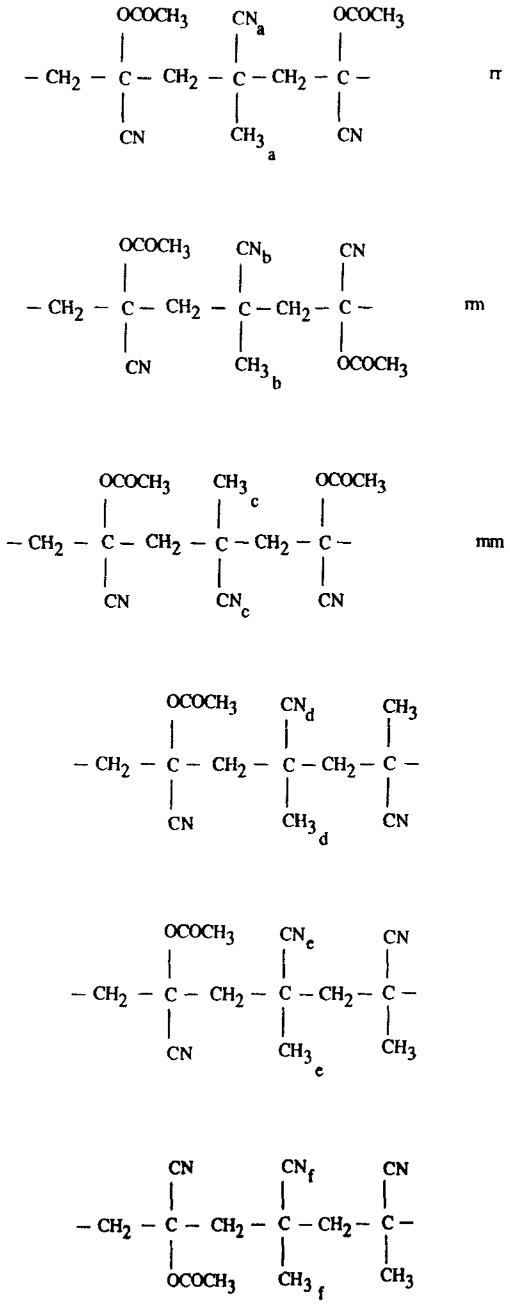


FIG. 6. ^{13}C-NMR spectrum of copolymer **3f**. Solvent: deuterated dimethylformamide.



SCHEME 5. Methacrylonitrile (**1b**)-centered triads of the copolymers (**3f**).

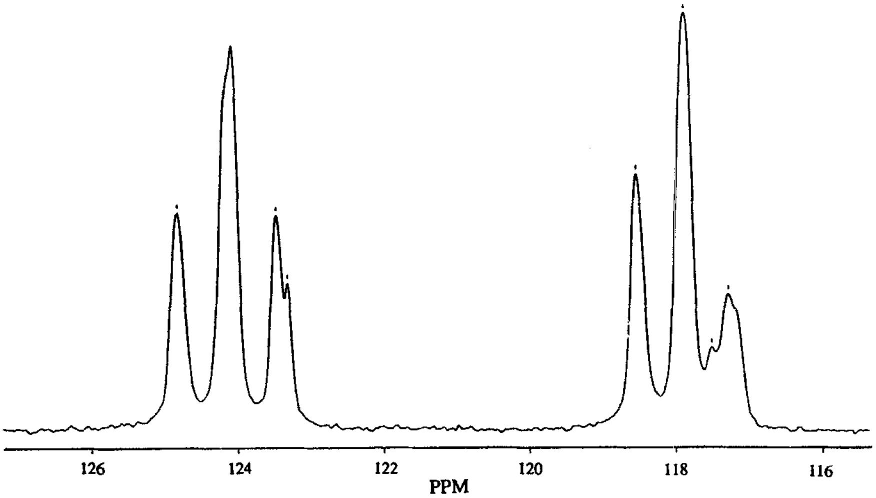


FIG. 7. ^{13}C-NMR spectrum of copolymer **3f**. Expanded: resonance of CN groups.

Copolymer 3g [poly(1c-*co*-2a)]

The composition of the copolymer has been calculated by elemental analysis (Table 1) or by measurements of the areas due to the CN group and to the carbonyl function. The results are similar and are 43 and 40%, respectively, for the acrylonitrile unit and 57 and 60% for the cyanovinyl acetate unit.

As for the previous copolymer **3f**, examination of the CN region can give some information about the microstructure of the product. Two groups of big peaks in the 116–118 and 120–122 ppm ranges are observed and are badly separated for the 120–122 ppm region. Therefore the copolymer could be mostly statistical (Fig. 8).

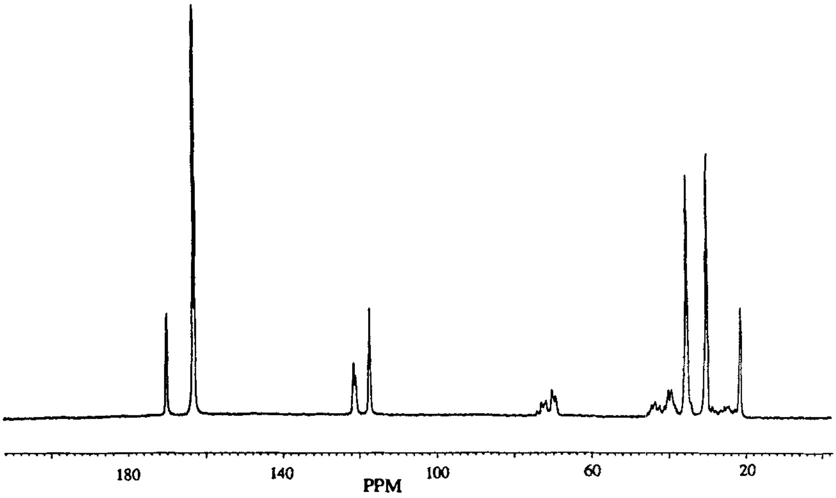


FIG. 8. ^{13}C-NMR spectrum of copolymer **3g**. Solvent: deuterated dimethylformamide.

Monomer Reactivity Ratios

As the understanding of the microstructure is not always certain, after examination of the ^{13}C-NMR spectra the reactivity ratios have been measured for the three copolymers **3b**, **3c**, and **3d** by using the methods of Kelen-Tüdös (K.T.) [25] and of Fineman-Ross (F.R.) [26] (Fig. 9).

The equation for the Kelen-Tüdös method is

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$$

when

$$\eta = G/(\alpha + F)$$
$$\xi = F/(\alpha + F)$$

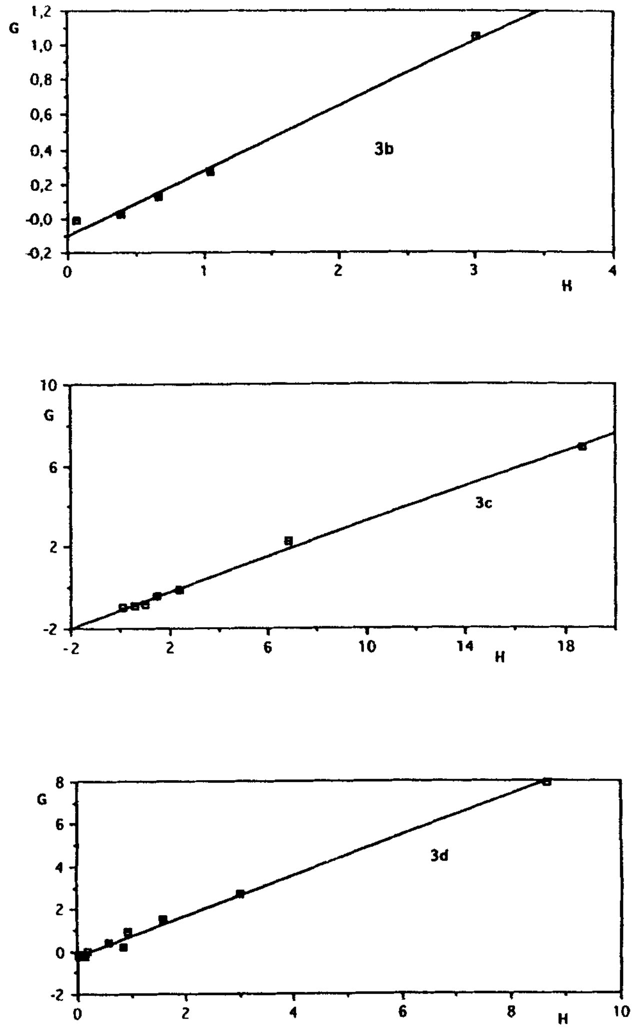


FIG. 9. Fineman-Ross plots of **3b**, **3c**, and **3d** copolymers.

$$\alpha = (F\text{max}{*}F\text{min})^{1/2}$$

$$G = \frac{[(M_1)/(M_2)][(dM_1/dM_2) - 1)]}{dM_1/dM_2}$$

$$H = \frac{((M_1)/(M_2))^2}{dM_1/dM_2}$$

The equation for the Fineman-Ross [22] method is

$$G = r_1H - r_2$$

where

$$G = [f_1(2F_1 - 1)]/(f_2 \times F_1)$$

$$H = (f_1^2 \times F_2)/(f_2^2 \times F_1)$$

where f_i and F_i are mole fractions of monomer i in the feed and in the copolymer, respectively.

Table 4 gives the composition and conversion of **3b**, **3c**, and **3d** samples synthesized for the measurements of reactivity ratios, and Fig. 10 describes the monomer-copolymer composition for the three samples of copolymers. The reactivity ratios (Table 5) in the copolymerization of vinylidene cyanide **1a** with methyl α-acetoxyacrylate are respectively in the 0.06–0.10 (r_2) and 0.30–0.37 (r_1) ranges with a value of the product of the reactivity ratios in the 0.02–0.04 range by using the F.R. and K.T. methods, respectively. These results are in agreement with a mainly alternating structure of the copolymer **3b**, and the monomer-copolymer composition curve (Fig. 10) shows a typical shape of the composition curve of a product rich in the alternating structure. The measured values for the two other copolymers **3c** and **3d** of the reactivity ratios of monomer **2b** with methacrylonitrile **1b** and acrylonitrile **1c** show that the two copolymers have a statistical structure. The 90–95% joint confidence intervals have been calculated according to the method of Carcano et al. [27] used for the copolymerization reaction of isobutylene and chlorotrifluoroethylene (Fig. 11).

The results of the Alfrey-Price *Q–e* scheme, which is commonly used to predict monomer reactivity ratios, do not appear to be in agreement with our experimental values.

The Alfrey-Price parameters are known for the monomers vinylidene cyanide **1a** [28], methacrylonitrile [28], acrylonitrile [28], and for cyanovinyl acetate [20]. They can be calculated for the captodative monomer **2b** (methyl α-acetoxyacrylate) from the reactivity ratios of **2b** with styrene [21], with methacrylonitrile **1b**, and with acrylonitrile **1c** by using the method described by Greenley [29] ($Q = 0.77$ $e = +0.47$).

The values of $r_1 \times r_2$ (Table 6) calculated from Alfrey–Price parameters and measured for polymers **3b**, **3c**, and **3d** are quite different. The calculated values of the product $r_1 \times r_2$ for copolymers **3a** and **3f** are different from zero in spite of a high percentage of alternating structure. The monomers **1a**, **1b**, and **1c**, which bear strong electron-withdrawing groups, exhibit repulsive effects when adding monomer or a copolymer chain containing high proportions of the same monomer. Their reactivities depend on the electron deficiency of double bonds arising from the electron-withdrawing characteristics of the attached group. The three monomers **1a**,

TABLE 4. Composition and Conversion of **3b**, **3c**, and **3d** Samples

Sample	f_1 [a]	F_1 [a]	Conversion, %	f'_1 [a]	F'_1 [a]	Conversion, %	f''_1 [a]	F''_1 [a]	Conversion, %
1	0.2056	0.4865	3.87	0.1015	0.0904	5	0.1024	0.2561	8
2	0.3908	0.5087	7.29	0.2964	0.2388	7	0.2039	0.3469	8
3	0.4684	0.5388	8	0.3988	0.3104	5	0.2924	0.4636	5
4	0.6998	0.6441	10.3	0.5008	0.4004	5	0.5011	0.5445	4
5	0.8206	0.7078	7.35	0.5981	0.4791	6	0.6056	0.7156	6
6	0.5389	0.5652	8	0.6493	0.5973	4	0.6892	0.7571	6
7				0.7982	0.6952	4	0.7797	0.8067	7
8				0.9001	0.8013	5	0.8991	0.9016	4

[a] f_1, f'_1, f''_1 and F_1, F'_1, F''_1 are, respectively, the mole fraction of **2b** (methyl α-acetoxy acrylate) in feed and copolymer **3b**, **3c**, and **3d**.

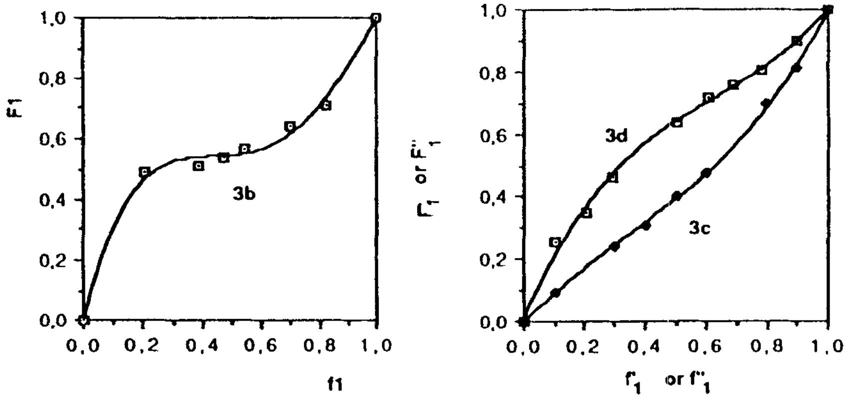


FIG. 10. Monomer-copolymer composition curve of copolymers **3b**, **3c**, and **3d**. f_1, f'_1, and f''_1 are the mole fraction of **2b** in the feed. F_1, F'_1, and F''_1 are the mole fractions of **2b** in the copolymers.

1b, and **1c** possess a strong dipole due to a nitrile group conjugated with the double bond, and this type of repulsion cannot be taken into account for a Lewis-Mayo copolymerization model. Therefore, the values of Alfrey-Price parameters could not be significant for calculating the reactivity ratios and for explaining the nature of the propagation step.

Similar observations have been made for the copolymerization of styrene and acrylonitrile [30], of methylacrylate and acrylonitrile [31], and of butylacrylate and acrylonitrile [32].

Steric factors are also neglected in the Alfrey-Price scheme. For a substituted styrene such as α-acetoxy styrene, which bears a bulky group on the double bond, the calculated values of these two parameters have little meaning and are not in agreement with the measured reactivity ratios of this monomer [33].

TABLE 5. Reactivity Ratios and Confidence Intervals of Methyl α-Acetoxyacrylate **2b** (r_1) with Vinylidene Cyanide **1a** (r_2), with Methacrylonitrile **1b** (r_2), and with Acrylonitrile **1c** (r_2)

	Kelen-Tüdös		Fineman-Ross	
	$r_1 \pm \Delta r_1$	$r_2 \pm \Delta r_2$	$r_1 \pm \Delta r_1$	$r_2 \pm \Delta r_2$
Methyl α-acetoxyacrylate (r_1)-Vinylidene cyanide (r_2)	0.30 ± 0.30	0.06 ± 0.05	0.37 ± 0.06	0.10 ± 0.09
Methyl α-acetoxyacrylate (r_1)-Methacrylonitrile (r_2)	0.43 ± 0.018	1.11 ± 0.10	0.43 ± 0.02	1.11 ± 0.16
Methyl α-acetoxyacrylate (r_1)-Acrylonitrile (r_2)	1.00 ± 0.17	0.22 ± 0.08	0.95 ± 0.05	0.21 ± 0.14

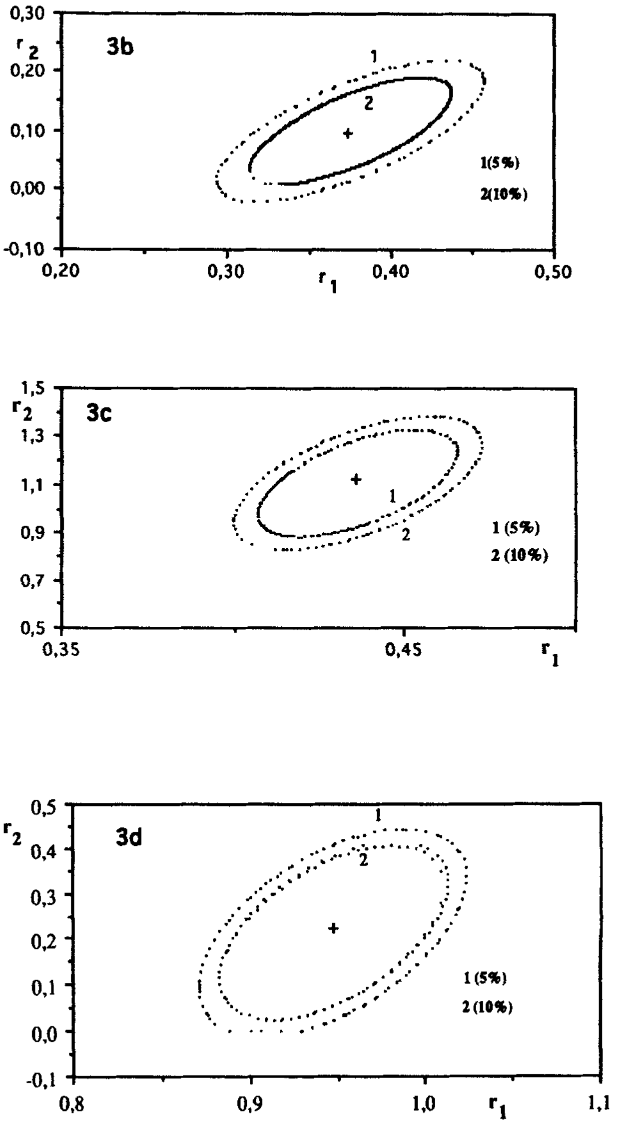


FIG. 11. 95% and 90% joint confidence intervals for the Copolymers **3b**, **3c**, and **3d**. The symbol "+" represents the estimated values of r_1 and r_2.

Further studies will be necessary to examine the nature of the copolymerization model of the reactions of cyano monomers with these captodative monomers.

CONCLUSION

Cyanocompounds such as vinylidene cyanide, methacrylonitrile, and acrylonitrile react with various captodative monomers. The structures of copolymers which were studied by ^{13}C NMR are mainly alternating for the copolymers of vinylidene

TABLE 6. Values of the Product $r_1 \times r_2$ Calculated with the Alfrey-Price Parameters or Measured

	$r_1 \times r_2$	
Copolymer	Calculated	Measured
3a	0.27	
3b	0.122	0.04
3c	0.902	0.47
3d	0.552	0.20
3f	1	
3g	0.8	

cyanide and statistical for the copolymers of methacrylonitrile and acrylonitrile. Measurements of reactivity ratios for three copolymerization reactions corroborate this hypothesis. The nature of the propagation step involving a terminal model or a penultimate model remains to be determined.

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