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Microstructure of copolymers of vinylidene cyanide, methacrylonitrile and acrylonitrile with methyl α acetoxyacrylate, a captodative monomer

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SUMMARY :

Copolymers of vinylidene cyanide (**1a**) methacrylonitrile (**1b**) and acrylonitrile (**1c**) with a captodative monomer, methyl α acetoxyacrylate were synthesized by radical copolymerization and their microstructures were studied by ^{13}C NMR spectroscopy.

The copolymer of **1a** with methyl α-acetoxyacrylate (**2**) has mostly an alternating structure but the copolymers of **1b** and **1c** with **2** are rather statistical. The measurement of their reactivity ratios for these two reactions is in agreement with the proposed structures.

INTRODUCTION

Numerous studies have been devoted to the microstructure of polymers and copolymers bearing cyano groups such as vinylidene cyanide (**1a**), methacrylonitrile (**1b**), acrylonitrile (**1c**) with various comonomers. This interest, chiefly for the vinylidene cyanide copolymers, is due to their piezoelectric properties described in 1980 by S.Miyata et al [1] for the amorphous and alternating copolymer of **1a** with vinyl acetate. This material like, all the amorphous copolymers, has to be poled to give the non centrosymmetric active form in which the piezoelectric properties are derived from the cyanodipole. This poling is carried out at a temperature just below the glass transition temperature and after cooling, a fraction of the dipoles are aligned in the field direction. Other monomers with cyano groups have also been studied : **1b**,**1c**, and methylvinylidene cyanide (**1d**) react with vinyl acetate [2,3] and some of the resulting copolymers display pyroelectric properties. New applications of copolymers of **1a** or **1d** as materials for nonlinear optics or as photochromic material have recently been patented [4-8]. Only few copolymerizations of cyano monomers with captodative monomers have been described. Captodative monomers bear, on a same carbon , an electron-withdrawing group (captive) and an electron-donating group (dative). **1a** has been copolymerized with cyanovinyl acetate providing a mostly alternating copolymer [9]. Copolymers of cyano compounds with captodative comonomers, due to the presence of strongly non centrosymmetric dipoles, could provide new piezo and pyroelectric copolymers. Therefore the copolymerization reactions of **1a, b ,c** with a captodative monomer have been carried out and the microstructures of the resulting copolymers have been studied.

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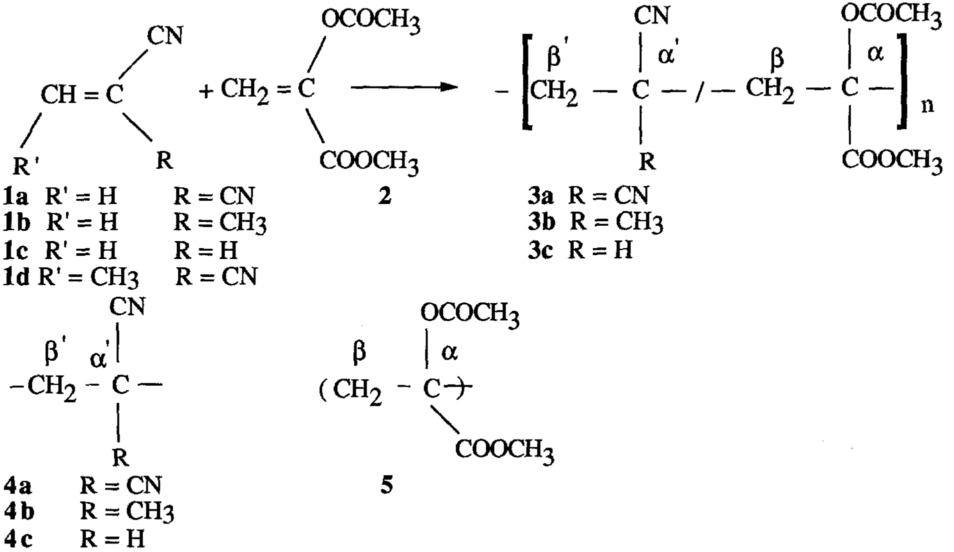
EXPERIMENTAL

Characterization and measurements

Elemental analyses were performed by the Service Central d'Analyse CNRS, Vernaison-France. The glass transition temperatures (Tg) were recorded using a D.S.C. 92 Setaram using a sample mass of 10-15 mg and a heating rate of 10 °C min^{-1}. The Tg value was taken as the initial onset of the change of slope in the D.S.C. curve. The viscosities of the sample were determined by means of a Ubbelohde viscosimeter at 25 ± 0,1 °C in dimethylformamide as solvent. ^{13}C NMR spectra were recorded using a Brüker A.C. 200 spectrometer at 50,3 MHz with a 50 % concentration of the copolymers dissolved in deuterated dimethylformamide d$_7$ or dimethylsulfoxide 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 relaxing agent, 50 mg for 2,5 or 3 ml solution. Typical analysis conditions have been the following : pulse angle = 80°, repetition time = 6s, acquisition time = 3s for 32 kwords, sweep width = 1000 Hz, number of scans = 6000-7000. ^{13}C peak assignments have been aided by DEPT spectra.



1a R' = H R = CN
1b R' = H R = CH_3
1c R' = H R = H
1d R' = CH_3 R = CN

2

3a R = CN
3b R = CH_3
3c R = H

4a R = CN
4b R = CH_3
4c R = H

5

Scheme 1. Synthesis routes of the copolymers

Materials

Vinylidene cyanide (**1a**) was synthesized according to a modification of the procedure described by L.I. Bogomolova et al [10] and kept at -18 °C in a sealed ampoule with a small amount of phosphorus pentoxide as inhibitor.

Methyl α-acetoxyacrylate (**2**) was prepared by reaction of acetic anhydride with methyl pyruvate and p-toluenesulfonic acid as catalyst [11].

Methacrylonitrile **1b** and acrylonitrile **1c** (Aldrich) were distilled before use.

Synthesis of the copolymers

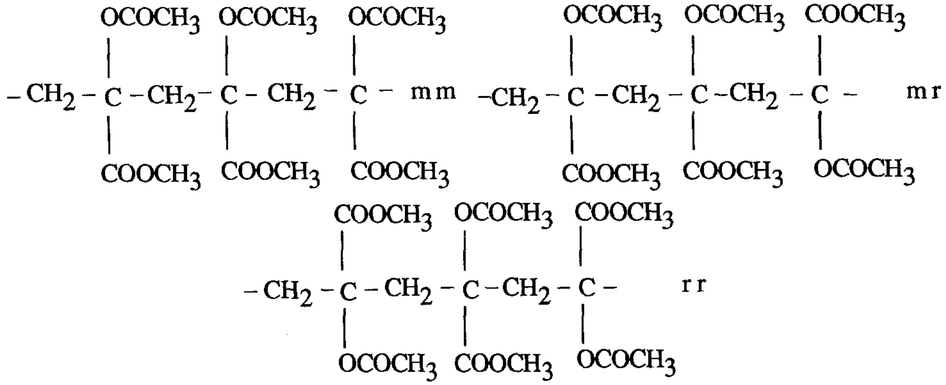
Monomers **1a** or **1b** or **1c** and comonomer **2** in equal molar proportions with 0,2 wt. % of azobisisobutyronitrile (AIBN) were heated during 24 hours, without solvent, at 75 °C in a sealed and degassed tube. Then the content of the tube was dissolved in dimethylformamide (DMF) and precipitated with methanol then dried. The yields of the copolymerization were close to 45 %. For the determination of reactivity ratios, the yields of the copolymerization were less than 10 %.

Synthesis of polymer **5**

Polymer 5 was prepared, by using a similar procedure, with AIBN as initiator and was purified by solubilization in DMF and precipitation by methanol.The synthesis routes are shown in Scheme 1.

RESULTS AND DISCUSSIONS

Before detailing the ^{13}C NMR spectra of the three new copolymers **3a,b,c,** it is necessary to give the main spectral data of the corresponding homopolymers of **1a, b, c** and of **2**. Poly(vinylidene cyanide) **4a** is unstable but its ^{13}C NMR spectrum was first described by J.K. Stille et al [12] with the study of the alternating copolymer of **1a** 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 ppm (quaternary carbon). The assignments of the chemical shifts of polymethacrylonitrile **4b** and polyacrylonitrile **4c** synthesized with a radical initiator have often been studied [13,14]. The polymerization of **2** has been recently described [15] but without its ^{13}C NMR spectrum. Tab. 1 summarizes the chemical shifts of these four homopolymers. Several values of chemical shifts for the Cα of **5** are observed and are due to the tacticity effect of the triads : as the polymerization was carried out with a radical initiator, and because of the steric hindrance of the monomer, the major peak could generally be assigned to the triad rr, and the minor peak to the triad mm (Scheme 2). The characteristics of the copolymers of **1a, b, c** with **2**, elemental analyses, glass transition temperature Tg and viscosity are given in Tab.2.



Scheme 2 : Tactic triads of homopolymer **5** = $OCOCH_3$

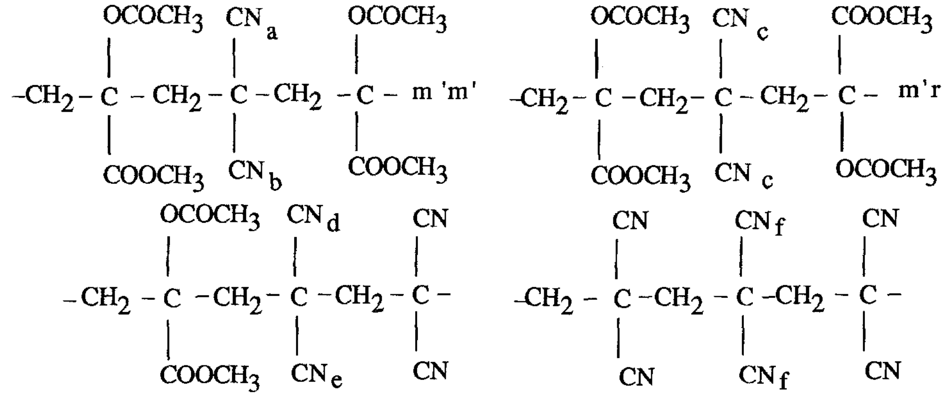
Table. 1.
^{13}C chemical shifts assignments for polymers **4a, b, c** and **5**

Carbon [a]	δ in ppm			
	4a[12]	**4b**[13]	**4c**[13]	**5**
Cα or Cα'	30,2	33,2	28,2, 27,7, 27,3	81,2, 80,8, 80,3
Cβ or Cβ'	66	47-51	33,5	39,8
CH_3	-	25,5-27,5		
CN	113,6	123,2	119,9, 120,2, 120,4	
$CH_3O\underline{CO}$				169-171[b]
$CH_3\underline{CO}O$				169-171
$\underline{CH_3}OCO$				52,6
$\underline{CH_3}COO$				21,7

[a] Carbon atoms are denoted as in Scheme 1

b) Peaks are badly resolved

a) Copolymer **3a** [poly (**1a** - co - **2**)] :Vinylidene cyanide **1a** is known to give chiefly alternating structures with a variety of monomers such as styrene [12], vinyl acetate [16] vinyl esters [17] or substituted styrenes [18]. A few statistical copolymers seem to have been described with methyl vinylketone [19] or acrylonitrile [19] but no details concerning their structures were given. The results of elemental analysis show that the percentages of the two monomers are similar and close to 50% The examination of the 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 in the perfect alternating copolymer of **1a** with vinylacetate [16] or with styrene [20]. These three peaks are due to the two triads defined as m'm' and m'r' (Scheme 3) 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 referred to the methylenic carbon (CH_2) : a fully alternating copolymer should give only one chemical shift for this carbon. The composition of the copolymer between statistic sequence and alternating structure can be calculated by an examination of the chemical shifts of the two carbonyl groups. Two major peaks are assigned to the $O\underline{CO}OCH_3$ and to the $\underline{CO}OCH_3$ are respectively observed at 169,9 and 167 ppm 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 approximately in a ratio 65/35, which roughly corresponds the proportion between an alternating structure and a statistical product.



Triads with homosequence of **1a**

Scheme 3 : Triads of the copolymers of vinylidene cyanide (**1a**) with methyl α-acetoxyacrylate.

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

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 range 50-55 %. The expanded resonance patterns of the CN group show three broad main peaks at 122.9 ppm 122.75 and 122.5 ppm with minor peaks at 122.2 and 122 ppm The main peaks are due to the triad effects here noted mm', m'm' and rm or mr . Three peaks are also observed for the methyl group in the range 24-25 ppm and are assigned to the three positions of the methyl groups in the triad but the broadness of the CN pattern comparatively to that of CN groups in the copolymer **3a** or in the copolymer of **1a** with vinylacetate do not suggest an alternating structure. Three chemical shifts for the CH_2 groups are observed at 40, 44 and 48 ppm and are respectively referred to (**1b**-**1b**), (**1b**-2) and 2-2 diads respectively. The ratio of their areas gives the percentage of alternating structure which is approximately 46 %.

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

Elemental analysis and measurement of various peaks due to the **1c** and **2** 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, whether alternating or statistical is just as difficult. The expanded resonance pattern of CN group gives three complex chemical shifts divided in nine badly separated peaks in the range 119-121,5 ppm and the assignment of these chemical shifts to monomer triads is not possible .The nine peaks could be assigned to the nine pentads resulting from three triads noted mm, mr and rr but no evidence for an alternating structure could be found after careful examination of the other peaks.

Table. 2
Characteristics of the copolymers of **1a, b, c** with **2a,b** : elemental analyses, glass transition temperature Tg, viscosity, percentage of incorporation.

			C	H	N	O	Tg °C	η l/g	%[a]	%[b]
3a	$(C_4H_2N_2)_n (C_6H_8O_4)_n$	Found	52,73	5,17	11,79	29,96	146	24.10^{-3}	54	54
	$(78,07)_n (144,12)_n$	Calc.	54,05	4,54	12,61	28,80				
3b	$(C_4H_5N)_n (C_6H_8O_4)_n$	Found	54,44	6,49	7,69	30,89	60	49.10^{-3}	50	55
	$(67,09)_n (144,12)_n$	Calc.	56,86	6,20	6,63	30,30				
3c	$(C_3H_3N)_n (C_6H_8O_4)_n$	Found	53,11	6,02	7,12	32,92	59	48.10^{-3}	50	51
	$(53,06)_n (144,12)_n$	Calc.	54,82	5,62	7,10	32,46				

a) The percentages of incorporation of 2 have been calculated from the arithmetic mean of elemental analyses of nitrogen and oxygen.
b) by analysis of the ^{13}C NMR spectra, see text.

Table. 3
^{13}C Chemical shifts assignments for the copolymers **3a, b, c**.

Carbon [a]	δ in ppm		
	3a	**3b**	**3c**
Cα	79,4, 78,6	81,1	80, 79,6, 80,7
Cα'	79,4, 78,6	b	b
Cβ	b	40-50 [c]	39,8
Cβ'	b	40-50 [c]	b
CH_3		24,9	
CN	113,8, 114,114,4	122,5, 122,8, 123	119-121,7
$CH_3O\underline{CO}$	167 or 169,95	169,3 or 169,4	169,3
$CH_3\underline{CO}O$	169,95 or 167	169,4 or 169,3	169,3
$\underline{CH_3}OCO$	52,6	51,9	52,0
$\underline{CH_3}COO$	20,7	20,9	20,3

a) Carbon atoms are denoted as scheme 1
b) This carbon is overlapped with solvent and cannot be used for analysis
c) The hyphen means that several peaks are observed in the range.40-50 ppm.

Monomer reactivity ratios

As knowledge of the microstructure is not always certain after examination of the ^{13}C NMR spectra, reactivity ratios have been measured for two copolymers, **3b** and **3c**, using the methods of Kelen-Tudös [21] and of Fineman-Ross [22].

Table 4 gives the composition and the conversion of **3b** and **3c** samples synthesized for the measurements of reactivity ratios and Figure 1 describes the monomer - copolymer composition for the two samples.

The reactivity ratio of **2** is less important than that of methacrylonitrile **1b** and higher than that of acrylonitrile **1c** and in this copolymerization one can observe an azeotropic point for $f'_1 \sim F'_1 \sim 0,5$. The values of these reactivity ratios are given in Tab. 5 and these results tend to show that the two copolymers **3b** and **3c** should be more statistic than alternating.

The measurement of reactivity ratios of **1a** with **2** (Copolymer **3a**) is difficult because of the strong reactivity of **1a** with **2** giving, in a short time, relatively high yields of copolymer. Nevertheless, several essays of the reaction have been carried out using various ratios of **1a** and **2** and the results of the elemental analyses show that an equal incorporation of the two monomers does not occur, this fact also means that copolymer **3a** cannot be fully alternating.

Table 4
Composition and conversion of **3b** and **3c** samples

Sample no	f_1*	F_1*	Conversion %	f_1'*	F_1'*	Conversion %
1	0,1015	0,0944	5	0,1024	0,2561	8
2	0,2964	0,2388	7	0,2039	0,3469	8
3	0,3988	0,3104	5	0,2924	0,4636	5
4	0,5008	0,4004	5	0,5011	0,5445	4
5	0,5981	0,4791	6	0,6056	0,7156	6
6	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

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

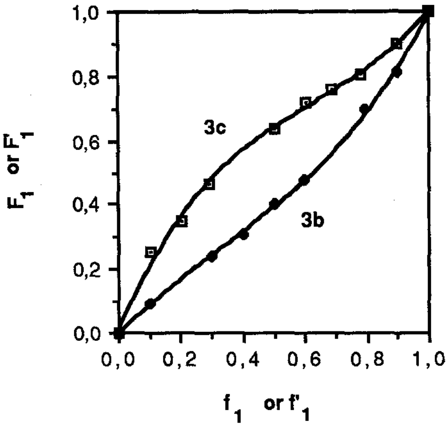


Fig.1 Monomer - Copolymer composition curve of copolymer **3b** (f_1 and F_1) and **3c** (f'_1 and F'_1)

f_1 and f'_1 are the mole fraction in the feed

F_1 and F'_1 are the mole fraction in the copolymer

Table 5

Reactivity ratios of methyl α acetoxy acrylate **2** (r_1) with methacrylonitrile **1b** (r_2) and of **2** (r_1) with acrylonitrile (**1c**) (r_2)

	Kelen-Tudös		Finemann-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)-methacrylonitrile (r_2)	0,432± 0,023	1,113± 0,049	0,436± 0,011	1,106± 0,053
methyl α acetoxyacrylate (r_1)-acrylonitrile (r_2)	1,000± 0,037	0,222± 0,044	0,947± 0,011	0,215± 0,082

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