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COPOLYMERIZATION REACTIONS OF VINYLIDENE CYANIDE WITH STYRENES CARRYING A FLUOROCARBON SEGMENT: PRELIMINARY STUDIES OF THEIR MICROSTRUCTURE

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ABSTRACT

In order to prepare piezoelectric copolymers, vinylidene cyanide has been copolymerized with two styrenes bearing a fluorinated chain in the para position of the aromatic nucleus. The microstructure of the resulting copolymers has been studied by ^{13}C NMR, with decoupling of fluorine and hydrogen. These copolymers are perfectly alternating and for one copolymer, a partial cristallinity is observed, due to the side fluorinated chain.

INTRODUCTION

Since high piezoelectric activity was observed in poled amorphous copolymer of vinylidene cyanide (VCN) and vinylacetate [1] P(VCN-VAC), many syntheses of new copolymers of VCN with various monomers have been described : Styrene [2], methylmethacrylate [3], vinylesters [4], methacrylonitrile [5] and cyanovinylacetate [5] react easily with VCN giving generally alternating copolymers. But the piezoelectric activity has chiefly been observed with copolymers of VCN and vinylacetate or vinylesters.A mesophase glass structure has been proposed for these copolymers [6] allowing cooperative motions around the glass transition temperature. Other polymers or copolymers which have a crystalline structure with large dipoles moments can also exhibit high piezoelectricity when their main chain has an all-trans conformation. The main examples are the polyvinylidene fluoride (PVDF)[7] (ß type) and the crystalline copolymers of vinylidene fluoride and trifluoroethylene [8]. Recently new fluorinated styrenes have been synthesized by reaction of fluoro alcohols with 4-vinylbenzylchloride (VBC). Their polymerizations and copolymerizations with styrene provide macromolecules having a partial crystallinity due to side chain crystallization[9]. This phenomenon decreases when a growing percentage of styrene monomer is incorporated in to the copolymer. As the piezoelectric activity can also depend on the partial crystalline structure and on the dipolar rotation of the nitrile group it should be useful to prepare new copolymers of VCN with fluorinated styrenes. The syntheses characterizations and preliminary studies of their microstructure are now given.

EXPERIMENTAL

Products :
4 Vinylbenzylchloride (Kodak, USA) has been distilled under reduced pressure (1mmHg) before use.VCN has been synthesized according to a modification of the procedure describing the pyrolysis reaction, at 170°-230°C, of 1,1,3,3 tetracyanopropane [10].
1H,1H-perfluoro-1-octanol (Janssen Chemical) and 1H,1H,2H,2H-perfluoro 1-hexanol (Fluorine Chem.) have been used without purification.

Materials :
^{13}C NMR spectra have been recorded with a Brucker DR X 400 apparatus at the frequency of 100,6MHz, by using a simultaneous decoupling of hydrogen and fluorine. Impulsion angle ~ 40°; acquisition time = 1,01 sec. (32 k. words); scan numbers = 4100. Deuterated acetone has been used as a solvent and tetramethylsilane as an internal reference.

Thermal characterization
Differential scanning calorimetry was performed on a Setaram DSC 92 at a heating rate of 10°C.min^{-1} under nitrogen. Dynamic thermogravimetric runs were made using a Setaram G70 thermal analyzer under a dry helium atmosphere (50 ml.min^{-1}) at a heating rate of 10 °C.min^{-1}.

Preparations of the monomers.
The fluorostyrenes F_1S and F_2S have been synthesized by using the described procedure by J. Höpken et al [9] with a phase transfer catalysis(Fig.1). As the substitution reaction is not complete and provides residual VBC and starting fluoroalcohols, the two liquid fluoroethers have been purified by means of a column chromatography (silicagel support, elution with petroleum ether) to eliminate the residual VBC then with mixture of petroleum ether and chloroform (10/90 - 20/80) to eluate the fluoroalcohols F_1S (liquid) and F_2S (mp = 17°C D.S.C.). The yields (pure products) are close to 45 %.

Copolymerization of VCN with F_1S or F_2S
VCN and F_1S or F_2S in equal proportions, with 2 ‰ in weight of 2,4 dichlorobenzoylperoxide as in initiator and a minimum of dry petroleum ether (Eb 35°C - 60°C) are heated at 45° C and stirred during 24 hours in a degassed tube.

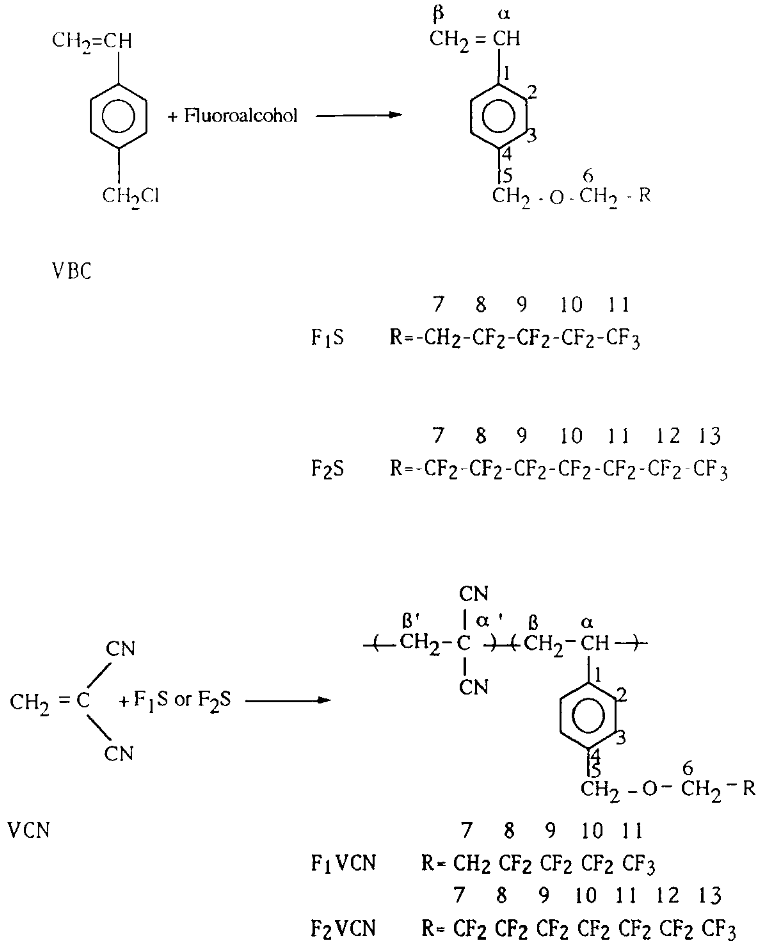


Fig. 1 - Scheme of preparation of the monomers F_1S and F_2S and of the copolymers F_1VCN and F_2VCN.

Table 1:

Chemical shifts (^{13}C NMR, δ ppm, after decoupling of fluorine) of the monomers F_1S and F_2S.

	F_1S	F_2S
C_α	138,3	137,4
C_β	114,6	114,6
C_1	138,4 or 137,5	138,9 or 137,1
C_2	128,8 or 127,3	128,8 or 127,3
C_3	127,3 or 128,8	127,3 or 128,8
C_4	137,5 or 138,4	137,1 or 138,9
C_5	74	75,1
C_6	63	67,7
C_7	32,5	118,3
C_8	111,5	116,8
C_9	118,6 or 118,7	116,3
C_{10}	118,7 or 118,6	112,2 or 112 or 111,5
C_{11}	109,9	112 or 112,2 or 111,5
C_{12}		111,5 or 112 or 112,2
C_{13}		109,5

The resulting copolymers are dissolved in dry acetone and precipitated by methanol. The yields are close to 35%.

RESULTS AND DISCUSSION

Structure of the monomers.

Only few details are given in the literature about the chemical shifts in ^{13}C NMR concerning various fluorinated monomers [11-12] and the assignments of the corresponding ^{13}C chemical shifts of F_1S and F_2S could provide useful informations about the microstructure of the fluoro copolymers. These assignments of chemical shifts of the carbons of styrenic skeletons have been carried out by comparison of that of para VBC [13] (table 1).

Micro Structure of the copolymers F_1VCN and F_2VCN

Figures 2 and 3 show the ^{13}C NMR spectra of the two copolymers, after decoupling of the fluorine atom, in deuterated acetone (CD_3COCD_3) solution. Due to the numerous copolymerizations reactions of VCN with various substituted styrenes [2,14] the probable structure of these copolymers should be alternating. The chemical shifts of the carbon of the copolymers F_1VCN and F_2VCN are given in the table 2 and their assignments are proposed after comparison with the chemical shifts of the carbons of various copolymers of styrenes with substituted

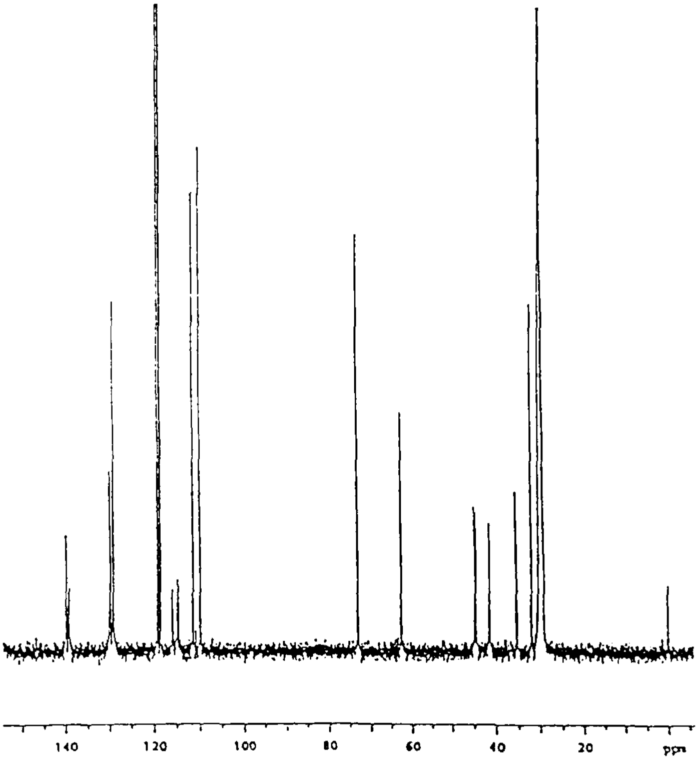


Fig.2: ^{13}C NMR spectrum of F_1VCN

styrenes[14). The usual unresolved peaks for the C_α and C_β of styrene units in polystyrene [15) are not observed and the sharpness and simpleness of each resonance suggest that the monomeric units are arranged in head-to-tail placements. The measurements of the areas of the peaks due to the $C_{\alpha'}$ of VCN (F_1VCN and F_2VCN) and to the C_1 and C_4 of the styrene unit also show equal proportions of VCN and styrene units.

As it was previously reported for numerous copolymers of VCN with vinyl esters such as vinyl acetate [16) or vinyl formate [17) three peaks are observed for the CN groups when the spectra are magnified in the range of 110-120 ppm. These three peaks are assigned to the three different CN groups in the co meso and the co racemo triad (Fig.4). In the first structure the CN groups are equivalent and different in the second structure (co racemo) therefore the assignments are respectively for F_1VCN and F_2VCN:

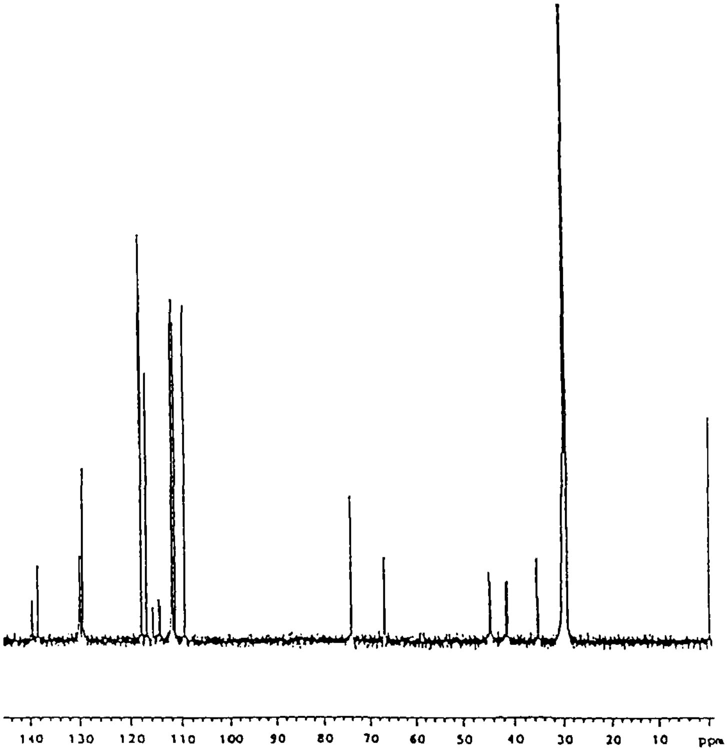


Fig.3: ^{13}C NMR spectrum of F_2VCN

CN_3	114,6 and 114,7
CN_2	114,3 and 114,6
CN_1	115,8 and 114,8

Similarly, in the two spectra the C_β and C_β', the C_α and C_α' show two thin peaks. These two peaks, for C_β and C_β', are due to the nature of the tetrads (Fig.5) of meso type or of racemo type. A similar explanation can be given for the assignments of C_α and C_α' by considering the two pentads (Fig.6). The most important peak in the two copolymers (respectively 35,6 and 35,5 for F_1VCN and F_2VCN) is probably due to the coracemic structure of the tetrad arising from a non stereospecific reaction of copolymerization.

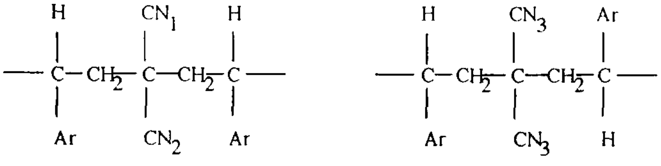
Table 2:

Chemical shifts (^{13}C NMR, δ ppm, after decoupling of fluorine) of the copolymers F_1VCN and F_2VCN.

	F_1VCN	F_2VCN
C_α	40,5 and 41,6 *	41,4 and 41,7 *
C_β	44,5 and 45 *	44,5 and 44,9 *
$C_{\alpha'}$	35,3 and 35,6 *	35,2 and 35,5 *
$C_{\beta'}$	44,5 and 45 *	44,5 and 44,9 *
C_1	139,1	139,6
C_2	129 or 129,9	129 or 130
C_3	129,9 or 129	130 or 129
C_4	139,8	138,4
C_5	73,1	74,3
C_6	62,6	67,1
C_7	32,1	114,7
C_8	119,2 **	114,6 **
C_9	118,5 **	112,3 **
C_{10}	111,5 **	111,3 **
C_{11}	109,9	110,2 **
C_{12}		110,1 **
C_{13}		109,5
CN	114,3 and 114,6 and 115,8	114,6 and 114,7 and 114,8

* : Observed after expansion of the spectra.

** : The assignments of these chemical shifts are probable.



$-\overset{H}{\underset{Ar}{C}}-CH_2-\overset{CN_1}{\underset{CN_2}{C}}-CH_2-\overset{H}{\underset{Ar}{C}}-$ $\quad$ $-\overset{H}{\underset{Ar}{C}}-CH_2-\overset{CN_3}{\underset{CN_3}{C}}-CH_2-\overset{Ar}{\underset{H}{C}}-$

Fig.4 : VCN-Centered dyads of the copolymers F_1VCN and F_2VCN (Ar= aromatic nuclei).

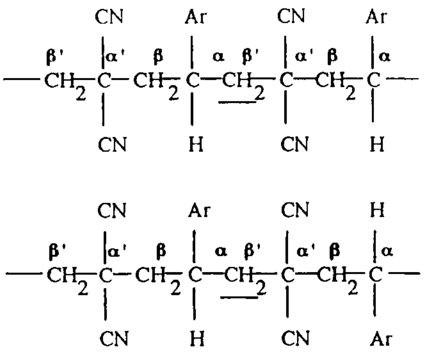


Fig.5: VCN centered tetrads of the polymers F_1VCN and F_2VCN(Ar= Aromatic nuclei)

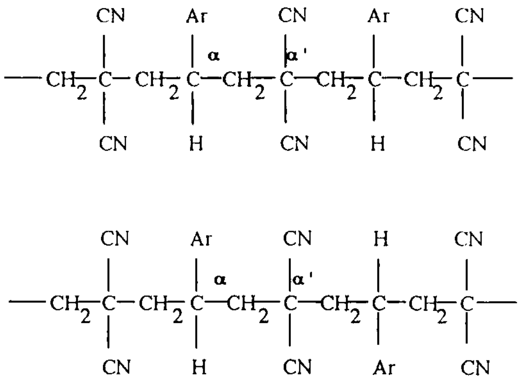


Fig.6: VCN centered pentads of the polymers F_1VCN and F_2VCN(Ar= Aromatic nuclei)

Thermal characterization:

The thermal behaviours of the two copolymers are quite different. DSC heating traces of the copolymers are shown in Fig.7 . The copolymer F_1VCN with a short chain of fluorocarbons, shows a glass transition at 88°C and no melting point after heating up to 220°C. We can see a weak exothermic peak at 180°C which indicates a probable degradation. The second copolymer F_2VCN with a longer chain of fluorocarbons shows a glass transition at an higher temperature(119°C) and an endothermic peak (melting point at 190°C). The enthalpy is very weak(1.67 $J.g^{-1}$). This partial cristallinity may be explained by the side chain cristallization of perfluorooctyl groups 9). The undercooling is about 30°C.

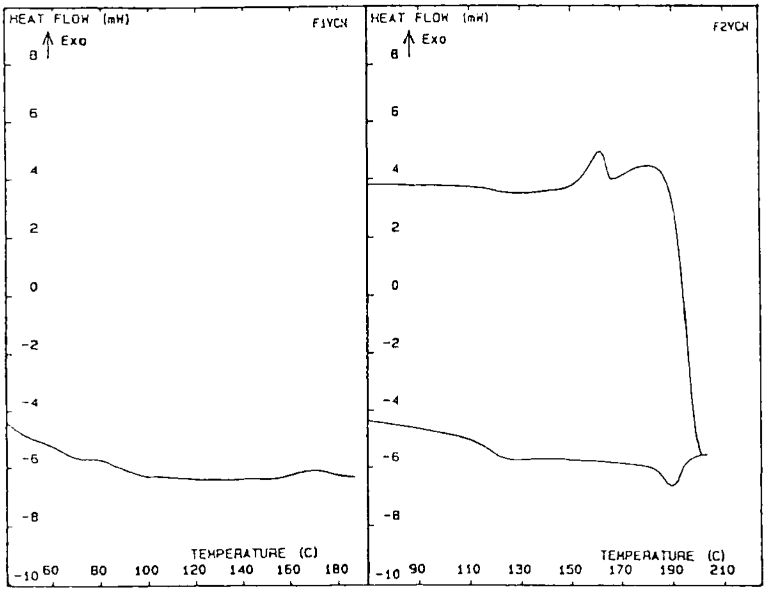


Fig.7:DSC traces of copolymers F_1VCN and F_2VCN

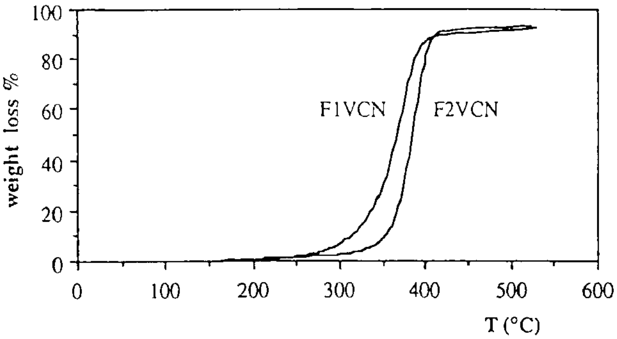


FIG.8 : Dynamic thermogravimetric curves for copolymers F_1VCN and F_2VCN heated in helium at 10°C.min^{-1}

Thermogravimetric analyses in programmed heating runs indicate that thermal degradation with weight loss occurs in a single step (Fig.8). The reaction begins at 200°C for F_1VCN and at 230°C for F_2VCN. At 550°C, the global weight loss is fairly complete for both polymers (i.e. 93%).
The characterizations of the electric properties of the two copolymers are now in progress and will be further detailed.

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REFERENCES

1) S.Miyata, M.Yoshikawa, S.Tasaka, M.Ko, Polymer J. 12,857 (1980).

2) Y.Inoue, A.Kashiwazaki, Y.Maruyama, Y.S.Jo, R.Chujo, I.Seo, M.Kishimoto, Polymer, 29,144 (1988).

3) Y.Maruyama, Y.S.Jo, Y.Inoue, R.Chujo, S.Tasaka, S.Miyata, Polymer, 28,1087 (1987).

4) Y.Ohta, Y.Inoue, R.Chujo, M.Kishimoto, I.Seo, Polymer, 31,1581 (1990).

5) J.P.Monthéard, A.Mesli, A.Belfkira, M.Raihane, Q.T.Pham, Macromolecular Reports A31 (Suppls) 1, (1994).

6) S.Tasaka, N.Inagaki, T.Okutani, S.Miyata, Polymer, 30,1639 (1989).

7) A.J.Lovinger, G.T.Davis, T.Furukawa, M.G.Broadhurst, Macromolecules 15,323 (1982).

8) M.Uchidari, T.Iwamoto, K.Iwata, M.Tamura, Rep. Prog. Polym. Phys. Jpn, 22,345 (1979).

9) J.Höpken, M.Möller, Macromolecules, 25,1461 (1992).

10) L.I.Bogomolova, I.A.Gorker, S.A.Kotchekova, G.I.Mikhailov, Metody Poluch Chem. Reaktitov Prep. 18,50 (1969) Chem. Abstr. 76,14964 (1969).

11)B.Boutevin, B.Youssef, S.Boileau, A.M.Garnault, J.Fluorine Chem. 35,399 (1987).

12) A.M.Garnault - Thèse Docteur-Ingénieur, Université Pierre et Marie Curie, Paris VI (1986).

13) J.P.Monthéard, M.Camps, M.Chatzopoulos, Q.T.Pham, Makromol. Chem. 186,2513 (1985).

14) J.P.Monthéard, B.Boinon, A.Belfkira, M.Raihane, Q.T.Pham, Makromol. Chem. 194,2839 (1993).

15) Q.T. Pham, R.Petiaud, H.Waton, N.F.Lauro-Darricades, Proton and Carbon NMR Spectra of Polymers, Penton Press London , p 312 (1991).

16) Y.S.Jo, Y.Inoue, R.Chujo, K.Saito, S.Miyata, Macromolecules, 18,1850 (1985).

17) Y.Inoue, Y.Ohta, M.Sakurai, R.Chujo, I.Seo, M.Kishimoto, Polymer, 35,718 (1994).