Dielectric studies of amorphous vinylidene cyanide alternating copolymers

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Alternating copolymers of vinylidene cyanide with substituted styrenes (mixtures of *meta* and *para*) and with *para*-substituted styrenes have been synthesized and characterized by means of d.s.c. and g.p.c. The lowest values for T_g have been observed with the copolymers which include both *meta*- and *para*-substituted styrenes. The values of permittivities of these copolymers at 30°C are in the range 3-6 and dielectric losses are close to 10^{-2}. Some of these copolymers could have piezoelectric properties.

(Keywords: vinylidene cyanide copolymers; dielectric properties; glass transition temperature)

INTRODUCTION

Vinylidene cyanide (VCN) is known to polymerize with a wide variety of monomers such as vinyl acetate, styrene or dienes to form chiefly alternating copolymers[1], and their mechanical properties have been studied extensively[2]. New applications of VCN were found in 1980 by Miyata *et al.*[3] who observed piezoelectric properties for the amorphous copolymer of VCN with vinyl acetate (VCN–VAC). Therefore, studies which include the copolymerization reactions of VCN with various monomers have assumed a growing relevance in the last few years; the copolymerization reactions of VCN with methyl methacrylate[4], isopropenyl acetate[5], vinyl benzoate[4], styrene[6] and vinyl esters of fatty acids[7] have been described along with studies of the microstructures by [13]C n.m.r.

Fundamental studies of the piezoelectric properties of some copolymers take into account the chain mobility in the macromolecules[8], their dielectric properties[9] and their enthalpy relaxation[10]. Recent industrial patents give the main characteristics of piezoelectric copolymers of VCN[11–13].

In order to find new materials with piezoelectric or pyroelectric properties, the copolymerization of VCN with various substituted styrenes and studies of their dielectric properties (permittivities, dielectric losses and relaxations) are now described.

EXPERIMENTAL

Monomers

VCN has been synthesized according to a modification of the procedure described by Bogomolova *et al.*[14] for the pyrolysis of 1,1,3,3-tetracyanopropane between 180 and 250°C.
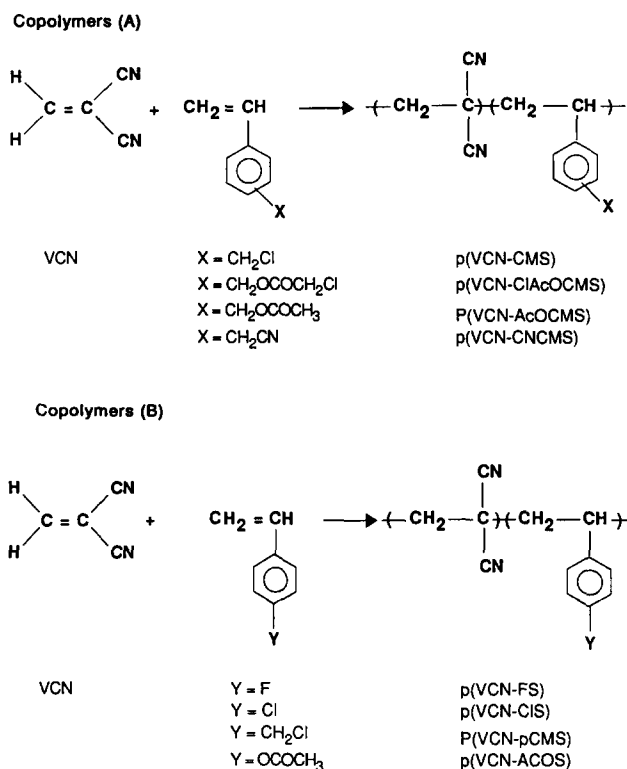
(Chloromethyl)styrene (CMS) is a commercial product (mixture of *meta* and *para* 60/40; Dow Chemical, USA). The pure *para* isomer (*p*CMS) is also commercially available (Kodak, USA). (Acetoxymethyl)styrene (AcOCMS), (chloroacetoxymethyl)styrene (ClAcOCMS) and (cyanomethyl)styrene (CNCMS) have been prepared by nucleophilic substitution of CMS using previously described methods[15]. 4-Fluoro- and 4-chlorostyrenes (FS and ClS) are commercial products; 4-acetoxystyrene (ACOS) is a generous gift of the Hoechst–Celanese Company.

Copolymerizations

Two types of products have been synthesized by the copolymerization reaction of CMS (mixture of *meta* and *para*) or its derivatives with VCN giving terpolymers (A) and by the copolymerization of VCN with 4-substituted styrenes (B). The copolymers were prepared by dissolving a mixture of VCN (0.025 mol), the substituted styrene (0.025 mol) and 2,4-dichlorobenzoylperoxide (2 wt‰) in 20 ml of benzene and heating in a sealed tube for 24 h at 45°C. Then the contents of the tube were poured into tetrahydrofuran (THF) and the copolymer precipitated

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with methanol. All the copolymers are soluble in THF except for p(VCN–CNCMS) and p(VCN–ACOS) which are dissolved in dimethylformamide and precipitated with methanol. The yields are close to 50%. The formulae of the copolymers are given in *Scheme 1*.

Copolymers (A)

VCN	X = CH₂Cl	p(VCN-CMS)

	X - CH₂Cl	p(VCN-CMS)
	X = CH₂OCOCH₂Cl	p(VCN-ClAcOCMS)
VCN	X = CH₂OCOCH₃	P(VCN-AcOCMS)
	X = CH₂CN	p(VCN-CNCMS)

Copolymers (B)

VCN	Y = F	p(VCN-FS)
	Y = Cl	p(VCN-ClS)
	Y = CH₂Cl	P(VCN-pCMS)
	Y = OCOCH₃	p(VCN-ACOS)

Physico-chemical analysis

The molecular masses of the copolymers, except for p(VCN–CNCMS) and p(VCN–ACOS), were measured with a Knauer apparatus and Ultra Styragel columns, using THF as a solvent. Polystyrene standards were used for the calibration. Elemental analyses were performed at the Service Central d'Analyse, Vernaison, France.

Thermal and dielectric studies were carried out on film samples of about 20–30 μm thickness. These films were prepared by casting a 10% solution in THF on a glass plate, except for p(VCN–CNCMS). The films were thermally dried at 100°C for casting in THF for materials with T_g below 100°C. The drying temperature was 160°C for other polymers; drying was performed under vacuum for 1 week. The films were then metallized with aluminium for the dielectric measurements.

Glass transition temperatures were measured with a DSC 92 Setaram using film samples of 10–15 mg and a heating rate of 10°C min⁻¹.

Dielectric measurements were carried out on metallized films under nitrogen over a large range of temperature (20–240°C) and frequencies (20 Hz–100 kHz) with a Hewlett-Packard 4284 A LCR bridge monitored by an Apple II computer and a dielectric cell supplied by Polymer Laboratory.

RESULTS AND DISCUSSION

Elemental analyses of all the copolymers are in good agreement with an alternating structure (*Tables 1* and *2*). As the reactivities of *meta-* and *para-*CMS in the

copolymerization reactions are similar[16], and knowing the Alfrey–Price parameters, the reactivity ratios in the copolymerization of VCN with *meta-* and *para-*CMS can be calculated and were found to be close to zero. These calculations are also possible with ClS[17] and ACOCMS[18] with values of the product $r_1 \times r_2 = 0$ ($r_1 = 0$ and $r_2 = 0$).

The microstructures of the copolymers have been studied by ¹³C n.m.r. and these studies have confirmed the perfect alternating structure of the copolymers of VCN with substituted styrenes. The molecular masses of these products are in the range 76×10^3 to 164×10^3 for $\bar{M}_n$ (*Tables 3* and *4*). The low polydispersity of some of these samples is due to the several reprecipitations which have withdrawn the low molecular masses. These copolymers are new except for p(VCN–ACOS)[13–19] and p(VCN–*p*CMS)[20] which were recently synthesized and

Table 1 Elemental analyses^a for copolymers (A)

X		C	H	N	O	Cl
CH₂Cl	Calc.	67.67	4.77	12.15	–	15.40
	Found	68.38	4.75	12.44	–	15.41
CH₂OCOCH₂Cl	Calc.	62.39	4.50	9.70	11.09	12.30
	Found	58.57	4.31	9.61	16.95	10.46
CH₂OCOCH₃	Calc.	70.86	5.5	11.02	12.6	–
	Found	70.57	5.44	11.49	12.5	–
CH₂CN	Calc.	75.36	4.35	20.28	–	–
	Found	75.38	5.47	19.05	–	–

^{a} The theoretical values are calculated for a perfect alternating structure

Table 2 Elemental analyses^a for copolymers (B)

Y		C	H	N	O	F	Cl
F	Calc.	72.00	4.5	14.0	–	9.5	–
	Found	72.57	4.67	13.32	–	9.45	–
Cl	Calc.	66.51	4.16	12.93	–	–	16.40
	Found	66.2	4.33	12.76	–	–	16.50
CH₂Cl	Calc.	–	67.8	4.77	12.15	–	15.40
	Found	67.72	4.61	12.06	–	–	15.53
OCOCH₃	Calc.	70	5	11.66	13.33	–	–
	Found	70.07	5.01	11.62	13.31	–	–

^{a} The theoretical values are calculated for a perfect alternating structure

Table 3 Molecular masses of copolymers (A)

X	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$
CH₂Cl	160	350	2.20
CH₂OCOCH₂Cl	150	280	1.86
CH₂OCOCH₃	130	220	1.70
CH₂CN^a	–	270	–

^{a} Values obtained by static light scattering measurements in DMF with a Wyatt apparatus

Table 4 Molecular masses of copolymers (B)

| Y	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$
F	76	120	1.6
Cl	90	120	1.4
CH₂Cl	164	292	1.8
OCOCH₃^a	–	134	–

^{a} Values obtained by static light scattering measurements in DMF with a Wyatt apparatus

Table 5 Glass transition temperature (T_g), $\Delta\varepsilon$ and activation energy (E_a) for copolymers (A)

X	T_g (°C)	$\Delta\varepsilon$	E_a (kJ mol^{-1})
CH_2Cl	102	20.5	167
CH_2CN	130	22.5	123
CH_2OCOCH_3	72	18.8	166
CH_2OCOCH_2Cl	64	14.5	143

Table 6 Glass transition temperature (T_g), $\Delta\varepsilon$ and activation energy (E_a) for copolymers (B)

Y	T_g (°C)	$\Delta\varepsilon$	E_a (kJ mol^{-1})
Cl	160	13.1	332
F	157	23.4	344
$OCOCH_3$	180	22.7	240
CH_2Cl	122	18.3	297
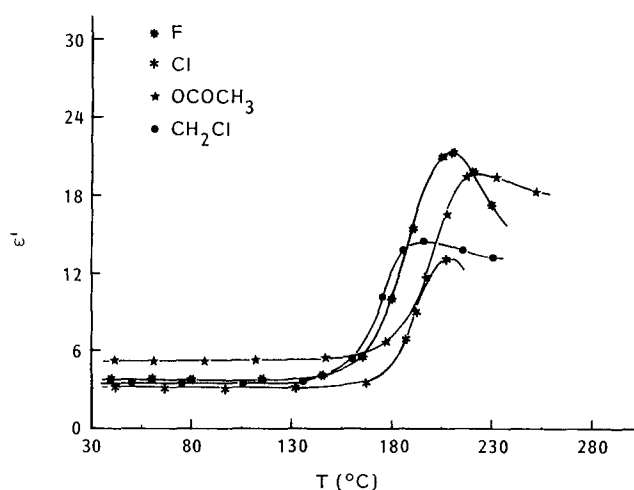
Figure 1 Comparative permittivities *versus* temperature at 1 kHz for copolymers (B)

grafted with dyes to study their properties in the field of non-linear optics.

The glass transition temperatures of the copolymers have been investigated and the results can be divided as follows:

(i) *Copolymers* (*A*). Copolymers with substituted (chloromethyl)styrenes: (VCN–CMS); (VCN–AcOCMS); (VCN–ClAcOCMS); (VCN–CNCMS). The measured glass transition temperatures are in the range 64–130°C. Similar values have been recorded for the poly(acetoxymethyl)styrenes[16] prepared from CMS (mixture of *meta* and *para*) (*Table 5*).

(ii) *Copolymers* (*B*). Copolymers with 4-substituted styrenes: (VCN–ClS); (VCN–FS); (VCN–ACOS); (VCN–pCMS). The observed values of T_g (*Table 6*) are in the range 122–180°C.

Comparing the values of T_g for these two series, we observe a large influence of the nature and position of the substituents; the introduction of a methylene group and the use of a *meta* and *para* position decrease the T_g. For example, in the case of (chloromethyl)styrene

copolymers, the combined effect of *meta* and *para* substitution decreases the T_g value of 20°C compared to that of *para* substitution alone. The influence of the methylene group as a spacer is more important at about 60 and 100°C for the chloro and acetoxy substituents. In the same way, for an identical series, the steric and polar effects of the substituents modify the values of the T_g in accordance with the general rules found for polymers[21]. For all the copolymers the d.s.c. spectra do not show any melting transition, so we assume that these materials are very poorly crystalline.

Dielectric spectra of the two series of materials are presented in *Figures 1–4*, which show the permittivities ε' and the dielectric losses tan δ *versus* temperature at a frequency of 1 kHz. More detailed spectra are given in *Figures 5* and *6* for p(VCN–CMS) at different frequencies.

The dielectric spectra of all the materials are in good agreement with the thermal properties. We observed a relaxation associated with the glass transition. This relaxation is sometimes overlapped by the d.c. conduction at low frequency and at high temperature for the tan δ curves. *Figure 7* shows plots of $\log f_m$ against reciprocal temperature for the different samples. Owing to the limited accuracy of these curves, we could not fit them
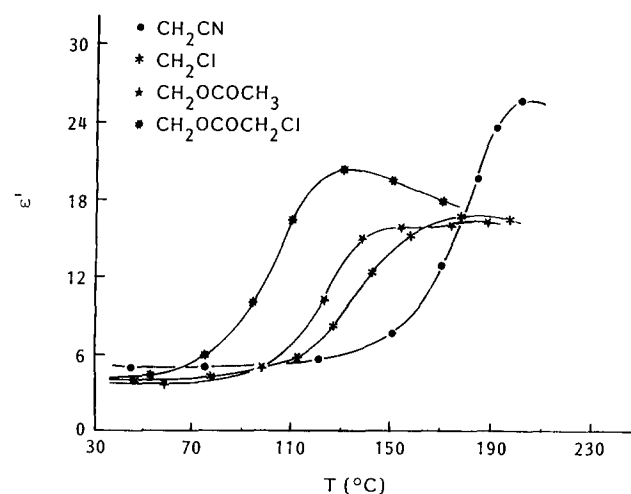
Figure 2 Comparative permittivities *versus* temperature at 1 kHz for copolymers (A)
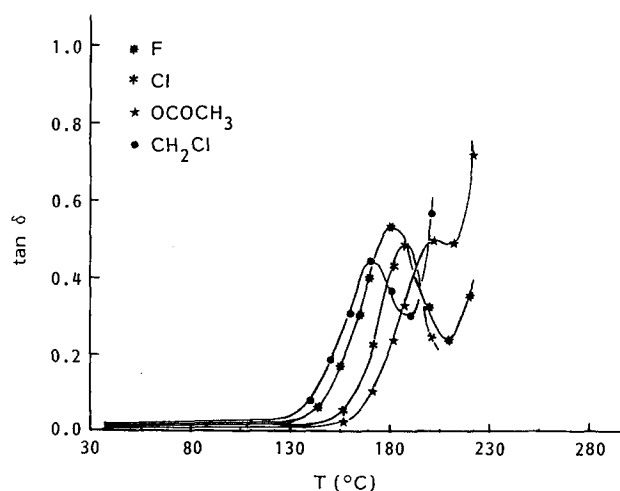
Figure 3 Variation of tan δ with temperature at 1 kHz for copolymers (B)
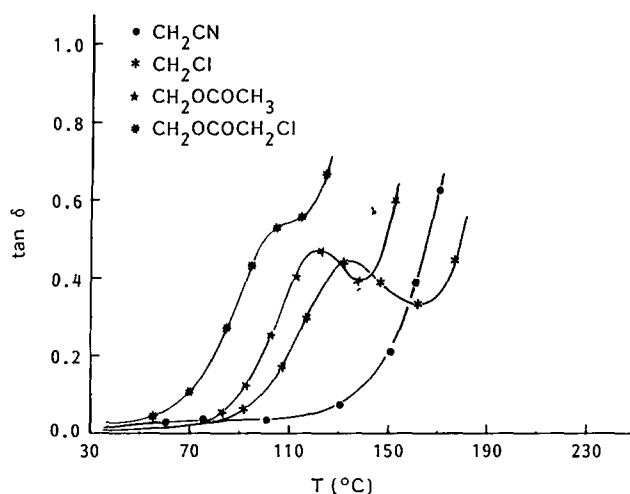
Figure 4 Variation of tan δ with temperature at 1 kHz for copolymers (A)
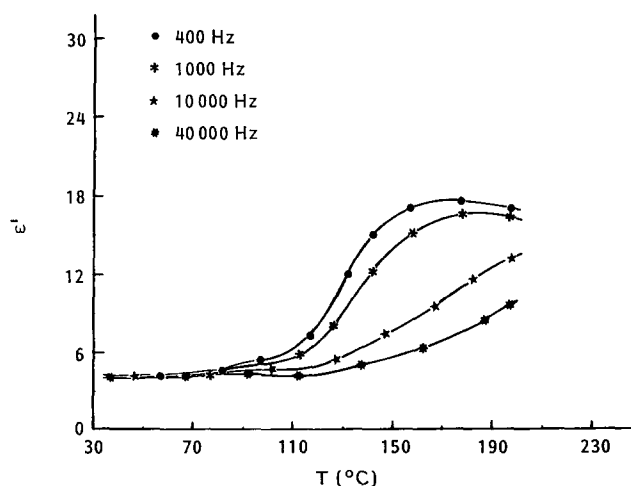

Figure 5 Dielectric spectra of the variation of permittivities with temperature at different frequencies for the copolymer p(VCN–CMS)

to a VFT-type (Vogel–Fukher–Taughman) equation. We observe an apparent activation energy (*Tables* 5 and 6) for the copolymers of VCN with 4-substituted styrenes higher than for the copolymers with *meta-* and *para-* substituted styrenes; these results are in concordance with the spacing effect of the methylene group.

For further discussion of dielectric data, we have examined the effect of relaxation on the value of ε' by looking at the value of the dielectric strength Δε determined by Cole–Cole analyses at high temperatures. In the low-temperature region, it is difficult to determine Δε from Cole–Cole plots because of the influence of the d.c. conduction. *Figure 8* shows an example of a Cole–Cole plot and the different values are reported in *Tables 5* and *6*. We observe that the dielectric relaxation strength Δε is large compared to most non-crystalline polymers for which Δε is generally about 5–10. However, the Δε values obtained in this study are much lower than in a vinylidene cyanide–vinyl acetate (VDCN–VAC) copolymer[22–24]. In this copolymer the extremely large relaxation strength of a cooperative motion implies the presence of a cooperative motion of cyano dipoles even at temperatures above the transitions. In our samples, these lower values of Δε (13.1–23.4) can be explained by

the higher molecular volume of the comonomer units, inducing a trivial density effect. It is difficult at this level of the study to conclude any more about the influence of the nature of the comonomer units. Undoubtedly, a more quantitative consideration, including units of cooperative motion and modes of motion of the cyano dipoles in relaxation with chain flexibility, should be performed[25]. Nevertheless, it appears that the substituted phenyl ring restricts the dynamic of the chain compared to the VDCN–VAC copolymers.

CONCLUSIONS

Only a few copolymerization reactions of VCN with substituted styrenes have been previously studied and
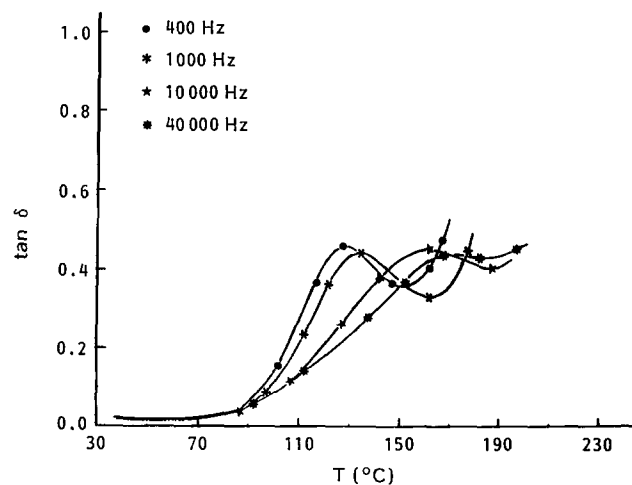

Figure 6 Dielectric spectra of the variation of tan δ with temperature at different frequencies for the copolymer p(VCN–CMS)
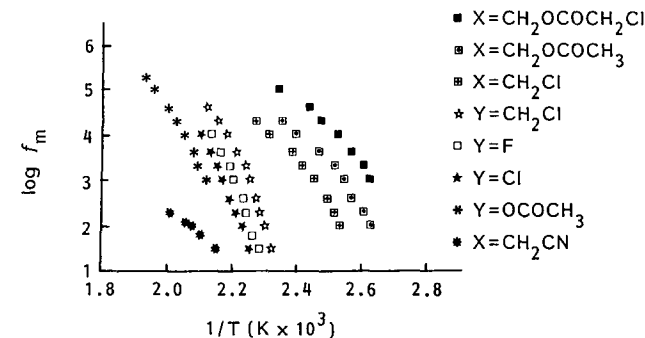

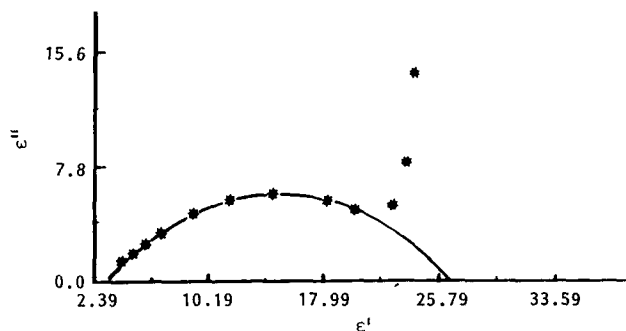**Figure 7** Plots of log f_m against reciprocal temperature for different copolymer samples

Figure 8 Cole–Cole diagram at 209.6°C for the copolymer p(VCN–FS)

this work shows that the reactivity of substituted styrenes with VCN seems to be independent of the nature and position of the substituent because perfect alternating products are obtained.

The dielectric properties of eight VCN alternating copolymers were investigated. An ordinary primary relaxation was evidenced with a large relaxation strength, although lower than the value found for the VDCN–VAC copolymer. This was interpreted in terms of the lower flexibility of the chains due to the hindrance of the phenyl group of the comonomers, limiting the reorientation of the CN group and masking the expected effect of the nature of the lateral substituents.

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