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Syntheses and characterizations of new copolymers of vinylidene cyanide with para substituted α acetoxystyrenes

Jean-Pierre Montheard[1,]*, Bernard Boinon[1], Ahmed Belfkira[2], Abderahim Sadel[2], and Quang-Tho Pham[3]

[1]Faculté des Sciences et Techniques, Université de Saint-Etienne, F-42023 Saint-Etienne Cedex, France
[2]Faculté des Sciences, El Jadida, Maroc
[3]Service Central d'Analyse CNRS BP 22, Vernaison, France

Summary

Vinylidene cyanide has been copolymerized in solution by radical reaction with equal initial mole fraction of para substituted α acetoxystyrenes. The copolymers have been characterized by means of DSC, TGA and GPC. These products are stable up to 220° and have no visible glass transition temperature. The microstructure of these new copolymers has been studied by ^{13}CNMR; they have an alternating structure and monomers units are arranged in head-to-tail placements.

Introduction

An alternating copolymer of vinylidene cyanide (VCN) and vinyl acetate (VA) has been widely studied since high piezoelectric activity has been observed[1)]. This copolymer has the following characteristics : a) perfect alternating structure b) amorphous with high glass transition temperature c) High dielectric relaxation[2)].Various copolymerizations of VCN with methyl methacrylate[3)], isopropenylacetate[4)], α methyl styrene[4)], vinyl esters of fatty acids[5)], vinyl benzoate[6)], have also been studied. These products have in majority an alternating structure and piezoelectric properties. In order to find new materials with piezoelectric properties the copolymerizations of VCN with α acetoxystyrenes (ACS) have been carried out. The properties of poly ACS, dielectrical studies, thermal stability have been previously studied[7-8)] .First, these polymers or copolymers have relatively high dielectric permittivity and no glass transition temperature has been observed before the thermal decomposition with loss of acetic acid close to 160-180°C. Then, as the Alfrey-Price parameters of VCN and ACS are known[9)], the calculation of their reactivity ratios is easy and the prediction of an alternating structure is possible.

In this paper , the preparation of a new kind of copolymers of VCN and of 3 para substituted ACS is reported.

Experimental *Characterizations and measurements :*

Molecular masses of copolymers were measured with a Knauer apparatus and Ultrastyragel columns in the tetrahydrofuran as a solvent. Polystyrene standards

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*Corresponding author

were used for the calibration. Elemental analyses were performed at the Service Central d'Analyse CNRS Vernaison (France).

Glass transition temperature were investigated with a D.S.C 101 Setaram, mass sample : 10-15 mg, heating rate : 10°C/min . ^{13}C NMR spectra were recorded on a Brucker AC200 at frequency of 50,3 MHz (^{13}C) in deuterated tetrachloro 1,1,2,2 ethane at 120° C. Chemical shifts were referenced to internal tetramethylsilane and indicated as p.p.m.Infra-red spectra were measured with a Perkin-Elemer 737 apparatus (thin films). Thermal behaviour of copolymers was studied with a Setaram G 70 thermal analyser ; the weights of samples were about 20 mg.

Materials

VCN has been synthesized according to a modification of the procedure described by Russian Chemists$^{10)}$ by a pyrolysis reaction of 1,1,3,3 tetracyanopropane$^{11)}$. ACS and para substituted ACS have been synthesized by heating acetophenone or para substituted acetophenones with isopropenylacetate and with para toluenesulfonic acid as a catalyst$^{12)}$. The detailed procedures have been published elsewhere$^{13-14)}$ .Copolymers are synthesized as follows : VCN (0,0256 Mole) and para substituted ACS (0,0256 Mole) (fig 1) with 2 ‰ in weight of 2,4 dichlorobenzoyl peroxide, dissolved in 20 ml of benzene, are heated in a sealed tube during 24 hours at 45 °C,then,the content of the tube has been dissolved in the tetrahydrofuran and precipitated with methanol. The yield of copolymers III a,b,c, are close to 50 % . The molecular masses of copolymers III are given in tab 1. The elemental analyses are in good agreement with an alternating structure. The three copolymers have no visible glass transition temperature between 253°K and 500°K.

Results and discussion

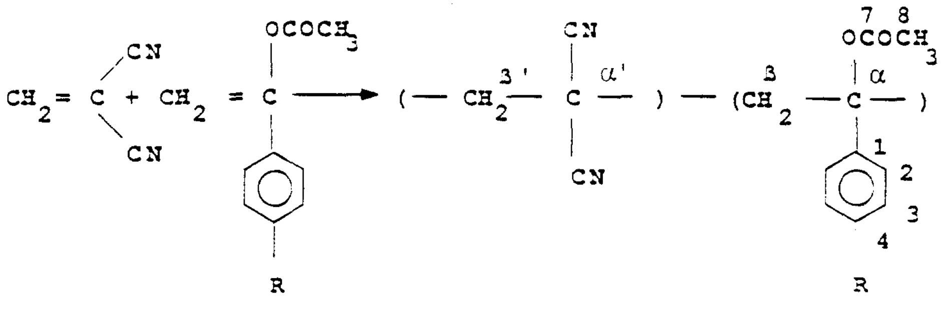
Due to the piezoelectric properties of the amorphous copolymer of VCN and VA, many works have been devoted to this product : synthesis$^{15)}$, dielectrical and piezoelectric studies$^{5)}$, microstructure by means of ^{13}C NMR$^{15)}$. The copolymerization reactions of VCN with other enol esters have scarcely been carried out.VCN copolymerizes with isopropenylacetate$^{4)}$ and with vinyl ester of fatty acids$^{5)}$. A recent patent describes a terpolymerization reaction between VCN and various aliphatic enol esters$^{16)}$. The synthesized terpolymers have good piezoelectric properties.First attempts of copolymerization of VCN with ACS have given a mixture of organic compound and copolymer with a poor yield ; similar reaction has been observed with para methyl ACS . The reaction of styrene with VCN has also given a mixture of organic and macromolecular compound$^{17)}$.The organic compound is the 1,1,3,3 tetracyano-4-phenylcyclohexane resulting from the addition of 2 moles of VCN with one mole of styrene, through a cycloaddition reaction on the double bond of the styrene.When a styrenic enol ester, with an electron donating group is used, a similar organic product is immediatly observed after mixing VCN and ACS. But when the enol ester has in the para position an electro withdrawing group,no organic reaction has been observed Therefore we have employed three enol esters with $OCOCH_3$, $OCOOCH_3$ and $OCOCH_2Cl$ as electro withdrawing group.

Three copolymers III a,b,c have been studied : Molecular masses of copolymers are relatively high and the products are soluble in all the organic solvents except alcohols and petroleum ether (Tab 1).Infra-red spectra of the three copolymers show absorption at 2230 cm^{-1} (CN group; weak) and at 1740 cm^{-1} (carbonyl group; strong).The thermogravimetric analyses in programming heating runs indicates that the thermal degradation of these copolymers occurs in a single step .This degradation ,which begins at about 210°C for IIIa and 230°C for IIIb and IIIc shows a sharp loss of 58 % of the starting copolymers IIIa and IIIb and of 46 % of IIIc. The mechanism seems to be more complex than a simple elimination of one molecule of acetic acid and hydrogen cyanide per block (VCN-ACS). Thermal stability of these copolymers is better than that of homopolymers poly para substituted ACS which loss acetic acid at about 140°C. Above 320°C, the thermal degradation continues with a fairly constant rate.The chemical shifts of ^{13}C NMR are given in tab 2.The various resonance peaks have been assigned by comparison with those of poly VCN/styrene(6) and of poly para substitued ACS(18). As each peak in the spectra of these three copolymers is very sharp and simple and as a single peak for the $CH_2\beta$ and $CH_2\beta'$is observed, it appears that all monomeric units are arranged in head-to-tail placements and that the three copolymers have an alternating structure.The configurations in the alternating sequence can be explained after observation of the resonance peak in the CN region : the three resonances can be due to the different triads of the alternating copolymers denoted m'm'-m'r'and r'r' (fig 2).

Tab 1 : Molecular masses of copolymers III a,b,c*

	Mn	Mw	Mw/Mn
IIIa	138000	200000	1,45
IIIb	170000	318000	1,87
IIIc	230000	420000	1,82

* The molecular masses have been measured after three reprecipitations.

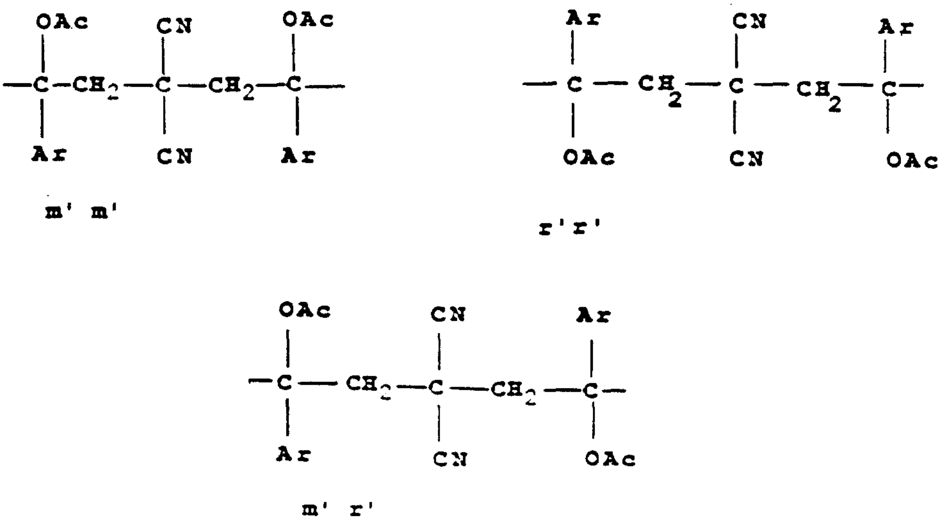


I II III

VCN ACS

	R = H	α acetoxystyrene
	$R = CH_3$	4 methyl α acetoxystyrene
a	$R = OC\overset{5}{O}C\overset{6}{H}_3$	4 acetoxy α acetoxystyrene
b	$R = OCO\overset{5}{O}C\overset{6}{H}_3$	4 methylcarbonyloxy α acetoxystyrene
c	$R = OC\overset{5}{O}C\overset{6}{H}_2Cl$	4 chloroacetoxy α acetoxystyrene

Fig 1 : preparations of the copolymers (VCN-ACS)



m' m'

r'r'

m' r'

Fig 2 : triads of poly (VCN-ACS) : (OAc = $OCOCH_3$; Ar = aromatic nucleus)

Tab 2 : Chemical shifts assignments of copolymers III

Carbon	IIIa	IIIb	IIIc
CO (7)	171,81	171,84	172,32
CO (5)	169,59-169,13	154,17-153,87	166,57
C_4	151,85	152,32	152,44
C_1	133,89	134,19	135,08
C_2	127,68	127,67	128,63
C_3	122,72	122,32	122,80
CN	114,67-112,96	114,59-112,86	115,17-113,91
	111,35	111,3	112,67
$C\alpha'$	81,26	81,16	82,30
$C_B+C_{B'}$	44,69	44,57	46,39
$C\alpha$	27,45	27,47	28,34
CH_2 Cl			41,64
CH_3 (6)	21,17	55,82	
CH_3 (8)	22,77	22,73	23,20

Conclusion

Three new copolymers of vinylidene cyanide were synthetized. The characterizations of these products by physical methods such as ^{13}C NMR were in good agreement with a perfect alternating structure. These products were stable up to 220°C and no glass transition temperature was observed. As many copolymers of vinylidene cyanide have interesting dielectrical and piezo- electric properties studies, of these materials will be carried out in a near future.

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