

AD-A203 939

REPORT DOCUMENTATION PAGE

DTIC FILE COPY

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY ELECTED		3. DISTRIBUTION / AVAILABILITY OF REPORT Unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE JAN 19 1989			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 13		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION The University of Texas at Arlington	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, Box 19065 The University of Texas at Arlington Arlington, Texas 76019		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Defense Advanced Research Projects Agency	8b. OFFICE SYMBOL (If applicable) DARPA	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0769	
3c. ADDRESS (City, State, and ZIP Code) 1410 Wilson Boulevard Arlington, Virginia 22209		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
		TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) "New Vinylidene Fluoride Copolymers: Poly(vinyl acetate-co-vinylidene fluoride)"			
12. PERSONAL AUTHOR(S) V. Panchalingam, John R. Reynolds			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) 1989 January 9	15. PAGE COUNT 15
16. SUPPLEMENTARY NOTATION J. Polym. Sci., Polym. Lett., in press			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Vinylidene Fluoride, Vinyl Acetate Copolymers, Capacitors, Dielectrics, organic	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Copolymers of vinylidene fluoride and vinyl acetate have been prepared at varied compositions and characterized by ¹H-NMR, ¹³C-NMR, FTIR, DSC and TGA. Copolymers were obtained as both THF soluble and insoluble fractions with the former having a relatively random distribution of monomers along the chain and the latter being somewhat blocky in nature.</p>			
<div style="border: 1px solid black; padding: 5px; width: fit-content;"> <p>DISTRIBUTION STATEMENT A</p> <p>Approved for public release; Distribution Unlimited</p> </div>			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED / UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. JoAnn Millikan		22b. TELEPHONE (Include Area Code) 202-696-4410	22c. OFFICE SYMBOL

**New Vinylidene Fluoride Copolymers:
Poly(vinyl acetate-co-vinylidene fluoride)**

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INTRODUCTION

Since the discovery of piezoelectricity and pyroelectricity in the dielectric polymer poly(vinylidene fluoride), PVF₂, it has attracted widespread interest from science and industry.¹ PVF₂ and its copolymers with trifluoroethylene²⁻⁶ and tetrafluoroethylene⁷⁻¹¹ have also been extensively studied due to their strong ferroelectric behavior. The large C-F dipole moments and details of the crystal structure are considered to play an important role in determining the electrical properties associated with these fluoropolymers.

Some non-fluorinated, dipole containing polymers also have been shown to possess novel electrical characteristics. It has been shown that the alternating copolymer of vinylidene cyanide (VDCN) and vinyl acetate (VAc) possesses high piezoelectricity.^{12, 13} The origin of the piezoelectricity in the copolymer has been attributed to the ability of the vinyl acetate unit to assist in dipolar orientation of the cyanide groups under poling conditions. Unlike the highly crystalline PVF₂ and its fluoromonomer based copolymers, this copolymer is believed to be essentially amorphous with a glass transition of 160°C. Subsequently, a small number of comonomers, including methyl methacrylate, styrene and vinyl benzoate, have been copolymerized with vinylidene cyanide and their electrical properties have been investigated.^{14, 15}

Unlike the copolymers of vinylidene fluoride (VF₂) with other fluorinated comonomers, copolymerization of VF₂ with non-fluorinated comonomers has not been studied. We anticipated that, if significant copolymerization could be made to occur, the vinyl acetate unit might also assist

dipolar orientation of the CF₂ unit in a vinylidene fluoride/vinyl acetate copolymer. Here, we report on the synthesis of this copolymer and its characterization.

EXPERIMENTAL

Materials

Vinyl acetate, (VAc, Aldrich Chemicals, 99%) was stored over CaCl₂ and fractionally distilled. Vinylidene fluoride, (VF₂, SCM Chemicals) was used after degassing. Trichlorotrifluoroethane (Isotron-113, surfactant) and *t*-butyl perpivalate (initiator, 75% in mineral spirits) were kindly supplied by the Pennwalt Corporation and used as received. Acetone-d₆ (99.9% with 0.05% TMS) was used for NMR analyses of the copolymers.

Copolymerization

The suspension copolymerization of VF₂ and VAc was carried out using a Parr stirred high pressure reactor (300 ml capacity) equipped with temperature and speed controller. In a typical copolymerization, the reactor was charged with VAc (0.13 mol), Isotron-113 (15 ml) and *t*-butyl perpivalate (0.5ml). The reactor was closed and VF₂ (0.66 mol) was condensed into the reactor. The temperature of the reaction system was allowed to rise to ~10°C and distilled water (deareated, ~225ml) was charged into the reactor using an HPLC pump. The temperature was raised to 82°C, and the pressure raised to 2100 psi. The temperature of the system was maintained during polymerization.

The unreacted VF₂ was vented off, the water decanted and the crude product dried under vacuum. The copolymer was fractionated into two components. A THF soluble fraction was precipitated in pentane and a rubbery sample was obtained. The THF insoluble fraction was dispersed in THF and a powdery material obtained by stirring with pentane. Both fractions were dried under vacuum at 60°C.

Characterization of the Copolymer

The functionalities and different copolymer sequences were determined by IR and NMR spectroscopic analyses of the copolymer. ¹H-NMR (300.13 MHz) and ¹³C-NMR (75.47 MHz) were recorded on a Bruker, 300 MSL spectrometer at 40°C. In addition to elemental analyses,

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copolymer composition was determined by $^1\text{H-NMR}$ analysis. FT-IR (diffuse reflectance) spectra were obtained on a Digilab FTS-40 spectrometer as a 1% powder in KBr. Thermal stabilities and melting properties were determined under N_2 atmosphere using a 951 TGA module and a 910 DSC module on a model 9900 DuPont Thermal analyzer. DSC samples were thermally cycled initially by heating the sample at a rate of $10^\circ\text{C}/\text{min}$ to 190°C and cooling back to room temperature at a rate of $5^\circ\text{C}/\text{min}$. Gel permeation chromatography (GPC) was carried out on a Waters Associates GPC system containing 100Å, 500Å and 10,000Å ultrastryragel columns in series.

RESULTS AND DISCUSSION

The yield, conversion and composition results for two different initial feed ratios of VF_2/VAc are shown in Table I. The products were obtained as either THF soluble (*s*) or insoluble (*i*) fractions. It should be noted that the THF insoluble copolymer fraction $\text{VF}_2/\text{VAc-1i}$ and the THF soluble copolymer fraction $\text{VF}_2/\text{VAc-2s}$ have a VAc content of 15% as determined by $^1\text{H-NMR}$ and elemental analysis. All of these materials form free-standing films on casting from THF onto glass plates or hot pressing of the THF insoluble fractions. GPC analyses show molecular weights greater than 50,000 for vinyl acetate rich, THF soluble, copolymers. Comparison of the structural results on these polymers show the differences in their microstructures.

The $^1\text{H-NMR}$ spectra of three copolymer fractions ($\text{VF}_2/\text{VAc-1s}$, $\text{VF}_2/\text{VAc-1i}$, and $\text{VF}_2/\text{VAc-2s}$) along with poly(vinyl acetate) are shown in Figure 1. Peak assignments were made by comparing the two homopolymers' spectra to those for the copolymers. The results, summarized in Table II, show specific peak groupings that can be assigned as the triad structures in the copolymer. For example, the lone vinyl acetate methine resonance at 4.9 ppm in poly(vinyl acetate) becomes three resonances at 5.6, 5.2, and 4.9 ppm (peaks 1, 2 and 3) in the copolymers. Comparison of these peak in Figures 1c and 1d show their intensities to be different though the overall copolymer compositions are equivalent. This indicates that the microstructure of the two polymers is different and offers a possibility for their varied solubility. The dominance of the VAc-VAc-VAc triad, seen at 4.9 ppm, in the insoluble copolymer containing a high content (85 mol %) VF_2 units is most easily explained if the copolymer is blocky in nature. The methine

region of the soluble copolymer having the same composition is, on the other hand, dominated by the VF₂-VAc-VF₂ sequence. This is as expected if the VAc units are more randomly distributed along what is mainly a PVF₂ chain. The small peaks between 1.5 and 0.7 ppm are probably due to end groups or defect structures.

The ¹³C-NMR spectra of the same copolymer fractions and poly(vinyl acetate) are shown in Figure 2 for the carbonyl, methine and methylene resonances. Peak assignments are summarized in Table III. The fine structure within each set of resonances arise from different stereosequences of the VAc unit and splitting by the fluorine nuclei. The assignments of the resonances for the C=O and CH carbons in different sequences can be explained by the shielding effects of the different γ -substituents for these carbons. Thus a VAc unit inserted between two VF₂ units is found upfield from a VAc with only one or zero VF₂ neighbors. The small peaks in the upfield position of the CH₂ carbon region are due to head to head linkages. A direct comparison of the intensities of the carbonyl peaks for the copolymer fractions VF₂/VAc-1i (Fig. 2c) and VF₂/VAc-2s (Fig. 2d) indicates that the insoluble copolymer fraction contains a higher content of VAc triads (peak 1) in the polymer main chain. In line with the ¹H-NMR results, the ¹³C-NMR results lead us to conclude that the insoluble copolymer is blocky in nature.

The FT-IR spectra of the same two copolymer fractions, and of poly(vinylidene fluoride), are shown in Figure 3. The peaks at 1743 cm⁻¹ (C=O) and 1237 cm⁻¹ are characteristic of the vinyl acetate unit in the copolymer. The comparison of the IR-spectra of VF₂/VAc-1i (Fig. 3b) and VF₂/VAc-2s (Fig. 3c) show them to be almost identical and confirm they have the same overall composition. Since infrared spectroscopy is generally insensitive to subtle changes in microstructure we expected no difference here.

The DSC of poly(vinylidene fluoride), copolymer fraction VF₂/VAc-1i, and VF₂/VAc-2s are shown in Figure 4. PVF₂ exhibits a higher melting temperature and higher content of crystallinity (Fig. 4a) than the copolymers. Significant recrystallization is seen on cooling (Fig. 4a) in the homopolymer with a peak at 142°C. The copolymer fraction VF₂/VAc-1i (Fig. 4b) shows a lower melting temperature and lower crystalline content than the homopolymer, while

VF₂/VAc-2s (Fig. 4c) shows only a trace amount of crystallinity. This is exemplified by the small exothermic peak for recrystallization (Fig. 4c') at about 95°C. These DSC results are expected again if the THF insoluble fraction contains blocks of vinylidene fluoride units allowing significant crystallization. On the other hand, the amorphous nature of the VF₂/VAc-2s fraction is likely caused by a more random placement of VF₂ and VAc units along the chain.

TGA thermograms of the homopolymers, copolymers of varying composition and a mixture of the homopolymers are shown in Figure 5. It is interesting to note that the copolymers exhibit thermal stabilities intermediate between PVF₂ and PVAc. In fact, the thermal behavior of the copolymers is similar to the 55/45 blend of PVF₂ and PVAc (Fig. 5c). This is worth noting in that it is well known that almost all copolymers are less thermally stable than their homopolymers. This has been reported specifically for the vinyl acetate/vinyl fluoride copolymer.¹⁶

Conclusion

Vinyl acetate and vinylidene fluoride undergo copolymerization resulting in a rubbery THF soluble fraction and a powdery THF insoluble fraction. ¹H-NMR, ¹³C-NMR, FT-IR and DSC analyses of copolymers having the same composition lead us to conclude that the THF insoluble fraction contains blocks of VF₂ and VAc units while the THF soluble fraction shows a more random placement of the comonomer units. TGA of the copolymers show them to have a thermal stability intermediate to the two homopolymers. We are investigating the copolymer structure in detail with varying monomer feed composition and will report on this in the near future.

The authors gratefully acknowledge the financial support given by The Center for Energy Conversion Research Power Conditioning Laboratory, of The University of Texas at Arlington and a grant from the Defense Advanced Research Project Agency, monitored by the Office of Naval Research. Discussions with Dennis Mulvey of the Pennwalt Corporation concerning the copolymerization of VF₂ are greatly appreciated.

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Table I

Yield and Composition of VF₂/VAc Copolymers Prepared at 82°C

	Molar Monomer Feed Ratio (VF ₂ /VAc)	Polymerization Time (h)	% Yield ^a		% Conversion		% VAc Composition ^b	
			THF soluble polymer	THF insoluble polymer	VF ₂	VAc	THF soluble polymer	THF insoluble polymer
VF ₂ /VAc-1	5:1	1.5	30.8	4.0	21	87	50	15
VF ₂ /VAc-2	40:1	0.5	2.5	23.0	25	34	15	~2 ^c

^a Based on initial feed^b Determined by ¹H-NMR^c Determined by elemental analysis

Table II
¹H-NMR Assignments for VF₂/VAc Copolymers

Peak Number	Proton Type	Chemical shift (ppm)	Sequence
1	methine	5.6	VF ₂ -VAc-VF ₂
2	methine	5.2	VAc-VAc-VF ₂
3	methine	4.9	VAc-VAc-VAc
4	methylene	2.9	VF ₂ -VF ₂
5	?	2.7	—
6	methylene	2.3	VF ₂ -VAc + irregular linkages ^a
7	methylene + methyl	~2.0	VAc-VAc

^a Irregular linkages include head to head and tail to tail linkages.

Table III¹³C-NMR Assignments for VF₂/VAc Copolymers

Peak Number	Carbon Type	Chemical shift (ppm)	Sequence
1	C=O	170.6	VAc-VAc-VAc
2	C=O	170.4	VAc-VAc-VF ₂
3	C=O	170.1	VF ₂ -VAc-VF ₂
4	CH	~70 - 67	VAc-VAc-VAc
5	CH	~67 - 65	VAc-VAc-VF ₂
6	CH	~65 - 63	VF ₂ -VAc-VF ₂
7	CH ₂	~45 - 43	VF ₂ -VF ₂
8	CH ₂	~43 - 41	VAc-VF ₂
9	CH ₂	~41 - 39	VAc-VAc

Figure Captions

Figure 1. ^1H -NMR spectra (300.13 MHz) of poly(vinyl acetate) and VF₂/VAc copolymers: a) poly(vinyl acetate); b) 50/50 (VF₂/VAc-1s); c) 85/15 (VF₂/VAc-1i); d) 85/15 (VF₂/VAc-2s).

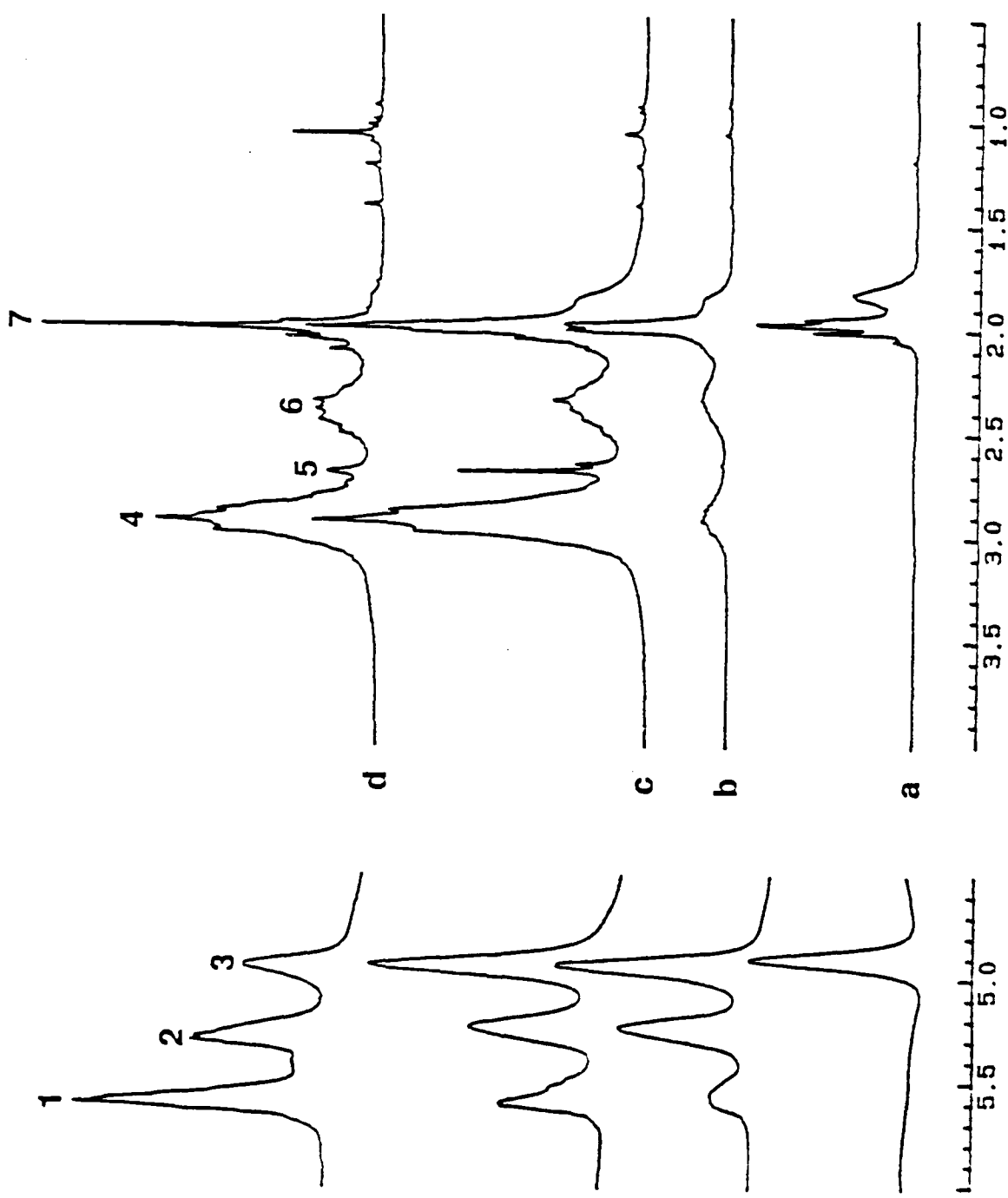
Figure 2. ^{13}C -NMR spectra (75.47 MHz) of poly(vinyl acetate) and VF₂/VAc copolymers for the C=O, CH and CH₂ carbon region: a) poly(vinyl acetate); b) 50/50 (VF₂/VAc-1s); c) 85/15 (VF₂/VAc-1i); d) 85/15 (VF₂/VAc-2s). Ref. (CD₃), CO: 29.8 ppm.

Figure 3. FT-IR spectra (Diffuse reflectance 1% in KBr) of poly(vinylidene fluoride) and VF₂/VAc copolymers: a) poly(vinylidene fluoride); b) 85/15 (VF₂/VAc-1i); c) 85/15 (VF₂/VAc-2s).

Figure 4. DSC scans of poly(vinylidene fluoride) and VF₂/VAc copolymers under nitrogen at a heating rate of 10°C/min. and a cooling rate of 5°C/min.: a) poly(vinylidene fluoride); b) 85/15 (VF₂/VAc-1i); c) 85/15 (VF₂/VAc-2s).

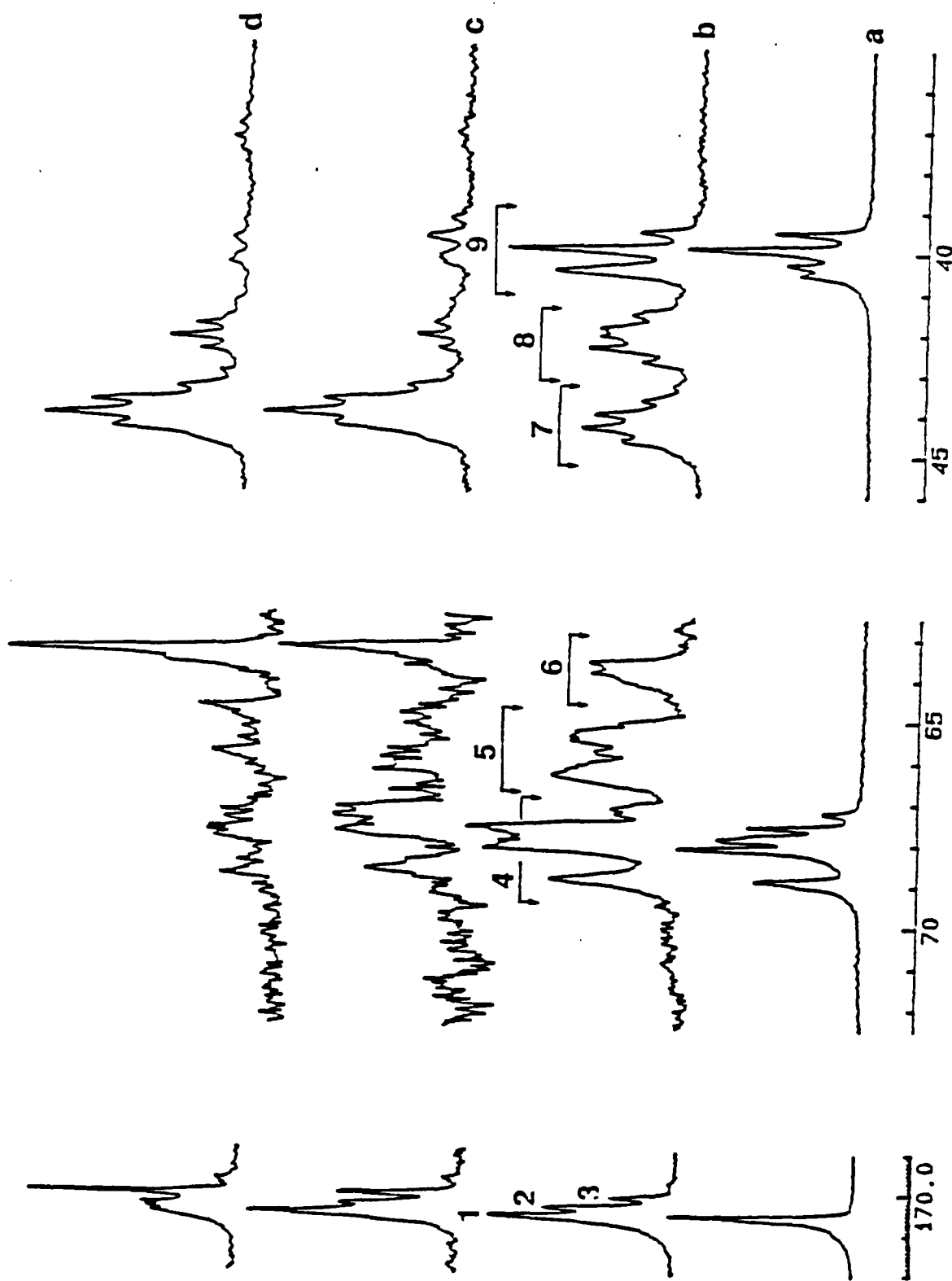
Figure 5. Thermogravimetric traces of homopolymers, VF₂/VAc copolymers and blends under nitrogen atmosphere. Heating rate = 20°C/min.: a) poly(vinylidene fluoride); b) 85/15 (VF₂/VAc-1s); c) 55/45 PVF₂/PVAc blend; d) 50/50 (VF₂/VAc-1s); e) poly(vinyl acetate).

Fig. 1



δ , PPM

Fig. 2



δ , PPM

Fig. 3

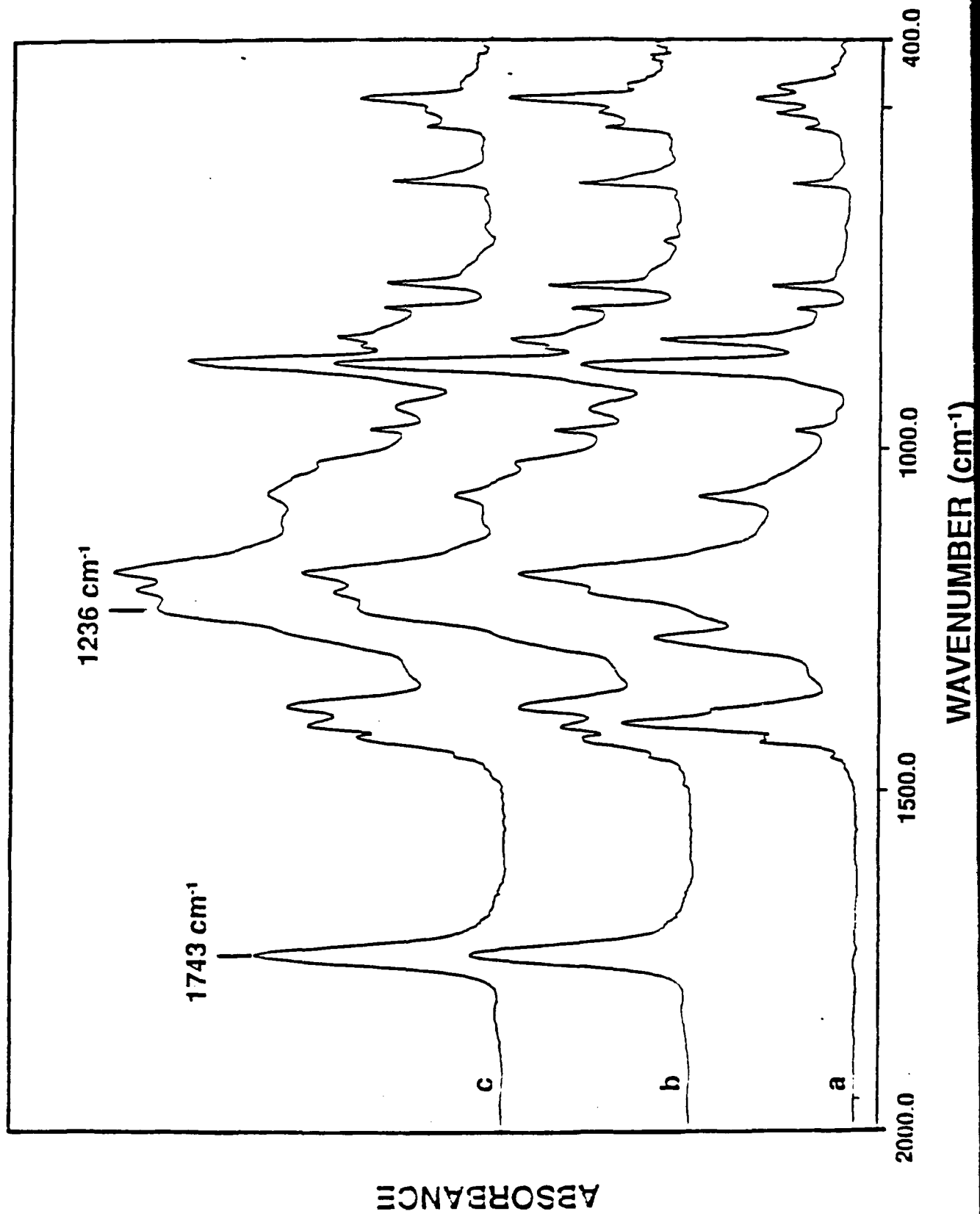


Fig. 4

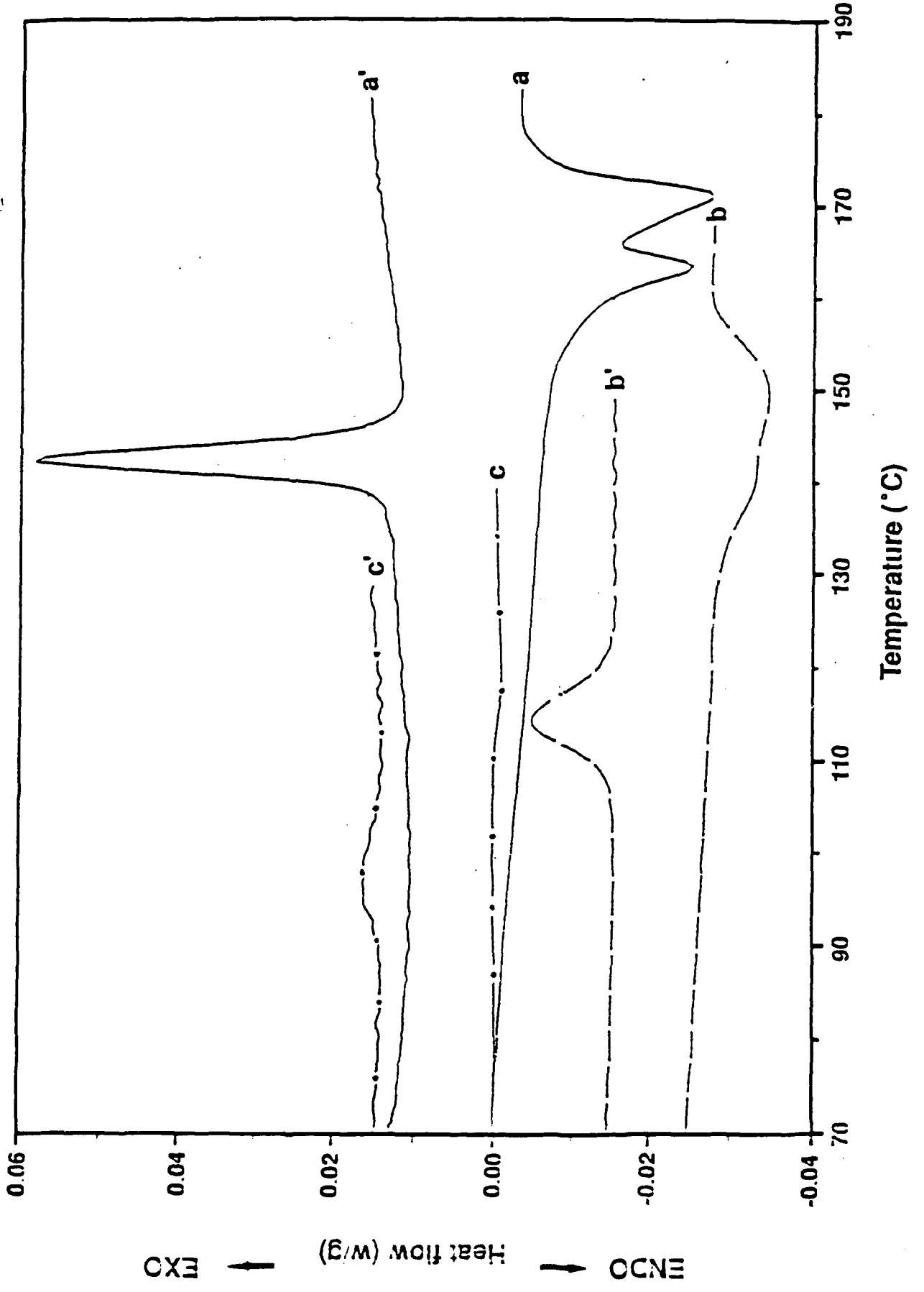


Fig 5

