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Poly(1,3-cyclohexadiene-*alt*-α-fluoroacrylonitrile) [poly(1,3-CHD/α-FAN)], an alternating copolymer of α-fluoroacrylonitrile and 1,3-cyclohexadiene has been prepared in bulk using varying monomer feed ratios and AIBN as initiator at 65°C. Elemental and ^{1}H-NMR analyses indicate that the copolymer contains an equimolar composition of α-FAN and 1,3-CHD as observed for alternating copolymers with donor-acceptor polymerizations. A 2-D ^{1}H-COSY NMR experiment indicates that the copolymer contains 1,4-linkages across the cyclohexene unit while more reliable ^{13}C-NMR spectra suggests the copolymer to contain both 1,2- and 1,4-linkages. Poly(1,3-CHD/α-FAN) exhibits improved thermal stability relative to the alternating copolymer of 1,3-CHD and α-chloroacrylonitrile due to a higher resistance to HF elimination relative to HCl elimination.

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Electronic and Ionic Transport in Processable Conducting Polymers

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POLY(1,3-CYCLOHEXADIENE-*ALT*-α-FLUOROACRYLONITRILE): SYNTHESIS AND STRUCTURAL ANALYSIS OF A NEW ALTERNATING COPOLYMER

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Poly(1,3-cyclohexadiene-*alt*-α-fluoroacrylonitrile): Synthesis and Structural Analysis of a New Alternating Copolymer

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A Contribution from the

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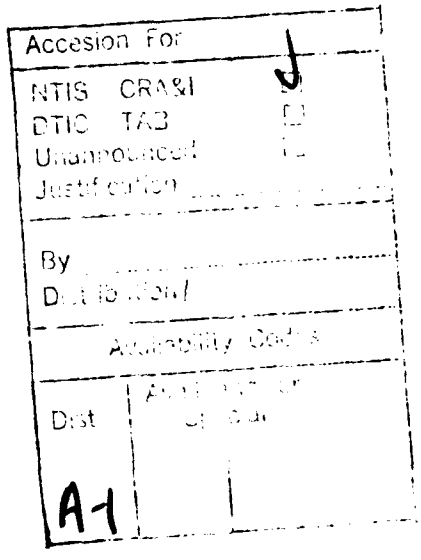

SYNOPSIS

Poly(1,3-cyclohexadiene-*alt*-α-fluoroacrylonitrile) [poly(1,3-CHD/α-FAN)], an alternating copolymer of α-fluoroacrylonitrile and 1,3-cyclohexadiene has been prepared in bulk using varying monomer feed ratios and AIBN as initiator at 65°C. Elemental and ^{1}H-NMR analyses indicate that the copolymer contains an equimolar composition of α-FAN and 1,3-CHD as observed for alternating copolymers with donor-acceptor polymerizations. A 2-D ^{1}H-COSY NMR experiment indicates that the copolymer contains 1,4-linkages across the cyclohexene unit while more reliable ^{13}C-NMR spectra suggests the copolymer to contain both 1,2- and 1,4-linkages. Poly(1,3-CHD/α-FAN) exhibits improved thermal stability relative to the alternating copolymer of 1,3-CHD and α-chloroacrylonitrile due to a higher resistance to HF elimination relative to HCl elimination.

INTRODUCTION

Donor-acceptor polymerizations present a unique method of controlling polymer chain microstructure due to their ability to form perfectly alternating structures.[1,2] The determination of the mechanisms of these polymerizations has been extremely controversial and a significant basic research effort has been devoted to this area.[3-9] In addition, the alternating polymers formed can exhibit unexpected properties that can be directly correlated with the alternating structure of the polymer formed. An example of this is poly(vinyl acetate-*alt*-vinylidene cyanide) which exhibits significant piezoelectricity at room temperature while being completely amorphous.[10,11] This is attributed to the ability of the dicyano dipole to be oriented under an applied electric field at a temperature above the glass transition (T_g=175°C). Dipole orientation is assisted by adjacent vinyl acetate groups and subsequent cooling under an applied electric field leads to a highly polarized material.

One of the interesting donor molecules that exhibits a tendency to undergo donor-acceptor polymerizations is 1,3-cyclohexadiene (1,3-CHD). In reaction with electron accepting olefins, three major reaction pathways are found; cycloaddition (Diels-Alder), 1,2-alternating

copolymerization and 1,4-alternating copolymerization. [12,13] The resultant cyclohexene ring on the main chain provides a unit which, under severe conditions, may be converted to a phenylene ring.[14] As such, it is of importance to obtain a detailed understanding of the structure of 1,3-CHD/acceptor olefin alternating polymers. We have been interested in examining the effect of localized dipoles on the dielectric properties of polymer films. Polymers having high dielectric permittivities, while simultaneously having low dielectric loss factors, could prove useful in high energy density capacitors with fast discharge characteristics.

In previous work[13], we described the structure of poly(α-chloroacrylonitrile-*alt*-1,3-cyclohexadiene) [poly(α-CAN/1,3-CHD)]. Here we report on the structure of a copolymer of α-fluoroacrylonitrile (α-FAN) and 1,3-CHD. We find that this alternating copolymer is significantly more thermally stable than poly(α-CAN/1,3-CHD) as the facility for HF elimination is significantly smaller than that for HCl elimination.

EXPERIMENTAL

Materials and Methods.

1,3-CHD (98%, Aldrich Chemicals) was distilled over CaH_2. Diethyl oxalate (99%, Sigma Chemicals) was distilled under reduced pressure. Ethyl fluoroacetate (98%, Sigma Chemicals) was dried over 5Å molecular sieves. α,α'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol.

Thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses were performed under a 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 10°C/min to 175°C and cooling back to room temperature at a rate of 10°C/min. Gel permeation chromatography (GPC) was carried out on a Waters Associates GPC System containing 100 Å, 500Å, and 10,000Å ultrastyragel columns in series using tetrahydrofuran (THF) as eluting solvent. Molecular weights were calibrated with respect to polystyrene standards. Mass spectral analysis was carried out on a Finnigan Mat model TSQ 70 instrument. Diffuse reflectance

FT-IR spectra were recorded on a Digilab FTS-40 spectrometer on 1% sample dispersed in KBr. UV-vis spectra were run on a Varian 2300 spectrophotometer.

^{1}H-NMR (300.13 MHz), ^{13}C-NMR (75.47 MHz), and ^{19}F-NMR (282.36 MHz) spectra were recorded on a Bruker 300 MSL NMR spectrometer at room temperature. Typically ~ 10% (W/W) solution in $CDCl_3$ were used for NMR analyses. Chemical shifts were referenced to $CDCl_3$ (77.00 ppm for ^{13}C) and tetramethylsilane (TMS) for ^{1}H spectra. ^{19}F-NMR chemical shifts were referenced to C_6F_6(-163 ppm) as an external standard. A sweep width of 13.16 kHz was used for the ^{13}C-NMR spectra with a digital resolution of 1.61 Hz/point. A total of 5000 transients were obtained with a delay time of 3s. The multiplicities of each carbon resonanace was determined by a DEPT (distorsionless enhancement by polarization transfer) experiment using a standard pulse sequence.[15]

COSY spectra were obtained to identify protons coupled to the olefinic protons of the cyclohexene unit in the copolymer. The homonuclear COSY was performed using the standard pulse sequence RD-90°-t-90°-acquire.[16] A total of 256 blocks of 512W data points in the F1 dimension and 1024W data points in the F2 dimension were used. The sweep width was 1100 Hz in the F1 dimension (-SW1 to +SW1) and 2200 Hz in the F2 dimension. A total of 128 scans were obtained for the polymer and 32 scans for the model compound, 3-methylcyclohexene, with a 3s delay between scans. The raw FID's were zero-filled once in the F1 dimension and both dimensions were conditioned by a sine bell squared function prior to Fourier transformation to obtain a 512 x 512 data matrix.

The copolymer composition was determined by ^{1}H-NMR spectroscopy as well as elemental analyses carried out by Robertson Laboratory and Texas Analytical Laboratory.

Monomer and Polymer Synthesis

1. Ethyl α-Fluoroacrylate (EFAc). EFAc was prepared by a modified version of a reported procedure.[17] In a typical experiment, to a 1L three neck flask equipped with a mechanical stirrer, condenser, and a dropping funnel were added sodium hydride (10.5g, 0.44 mol) and

freshly distilled diethyl oxalate (61.3g, 0.42 mol) under a nitrogen atmosphere. A solution of ethyl α-fluoroacetate (2g, 0.02 mol) and anhydrous ethanol (8.3g, 0.18 mol) was added to the stirred mixture over a period of 3h. The mixture became faint yellow with the evolution of hydrogen. The mixture was slowly refluxed and more ethyl α-fluoroacetate (36g, 0.34 mol) was added over a period of 3h. Reflux was maintained for an additional 3h and cooled to 0-5°C. Paraformaldehyde (12g, 0.41 mol) was added to the gelatinous mixture and slowly brought to reflux for 0.5h. The mixture became a light yellow solution with the formation of an insoluble salt. After cooling, the solution was decanted into a mixture of diethyl ether (100 ml) and water (400 ml). The ether layer was separated and washed with 5% $NaHCO_3$ and a saturated NaCl solution. The ether layer was then dried over anhydrous $MgSO_4$ and concentrated on a rotary evaporator at room temperature. The concentrated solution was fractionally distilled under reduced pressure with a small amount (~0.5g) of hydroquinone to avoid polymerization of the EFAc during distillation. The fraction boiling at 51-53°C/80 mm Hg was collected: yield 26.0g (60%); ^{13}C-NMR ($CDCl_3$): δ = 159.85 and 159.36 (O=<u>C</u>-CF), 154.77 and 151.30) (<u>C</u>-F), 101.65 and 101.44 (<u>C</u>H_2=C-F), 13.13 (OCH_2-<u>C</u>H_3), 62.16 (O<u>C</u>H_2CH_3). ^{19}F-NMR ($CDCl_3$): δ = -233.98, -234.12 and -237.27. The EFAc was stored at -5°C with hydroquinone as an inhibitor to avoid its facile polymerization.

2. α-Fluoroacrylamide (α-FAA). α-FAA was prepared in 75% yield according to a reported procedure.[17] ^{13}C-NMR (DMSO-d_6): δ = 163.06 and 162.62 (O=<u>C</u>-CF), 159.17 and 155.57 (<u>C</u>-F), 98.81 and 98.62 (<u>C</u>H_2-CF). ^{19}F-NMR (DMSO-d_6): δ = -114.03, -114.08, -114.21 and -114.26.

3. α-Fluoroacrylonitrile (α-FAN). α-FAN was prepared in 10% yield, according to a reported procedure.[18] ^{13}C-NMR : δ = 146.48 and 143.21 (=<u>C</u>(F)CN), 119.28 and 119.64 (CH_2=), 116.31 and 116.09 (CN). ^{19}F-NMR: δ = -112.6 and -112.8 (doublet).

Copolymerization. The required amounts of α-FAN and 1,3-CHD, as noted below, were charged into a glass ampule along with AIBN (0.011g, 0.07 mmol). The contents were deoxygenated by freeze-pump-thaw cycles and the ampule was sealed under vacuum. The polymerization was carried out at 65°C for 72 hours. The copolymers were purified by

precipitating a chloroform solution into pentane and the powder was vacuum dried at 50°C for 24 hours. The copolymers are very soluble in chloroform, dichloromethane and THF.

Elemental analyses were obtained for copolymers using the following monomer feed compositions.

α-FAN (0.50g, 7 mmol) and 1,3-CHD (1.13g, 14 mmol) ANAL. Calcd for $[(C_6H_8)_{.54}(C_3H_2NF)_{.46}]_x$: C, 73.08%, H, 6.91%, N, 8.49%, F, 11.52%. Found: C, 71.52%, H, 7.22%, N, 8.40%, F, 11.51%.

α-FAN (0.50g, 7 mmol) and 1,3-CHD (0.56g, 7 mmol) ANAL. Calcd for $[(C_6H_8)_{.57}(C_3H_2NF)_{.43}]_x$: C, 74.24%, H, 7.12%, N, 7.91%, F, 10.73%. Found: C, 73.31%, H, 7.49%, N, 7.99%, F, 10.24%.

α-FAN (1.00g, 14 mmol) and 1,3-CHD (0.56g, 7 mmol) ANAL. Calcd for $[(C_6H_8)_{.54}(C_3H_2NF)_{.46}]_x$: C, 73.08%, H, 6.91%, N, 8.49%, F, 11.52%. Found: C, 70.27%, H, 6.91%, N, 8.45%, F, 10.89%.

RESULTS AND DISCUSSION

The copolymerization results of 1,3-CHD and α-FAN are shown in Table I. The copolymers contain nearly equimolar composition of 1,3-CHD and α-FAN irrespective of initial comonomer feed ratios. As 1,3-CHD is a typical electron donor and α-FAN an acceptor, the possibility exists for polymerization through an electron donor-acceptor (EDA) complex to form an alternating copolymer. A further complexity arises when using 1,3-CHD with the possibility of both 1,2- and 1,4- linkages through the cyclohexene ring as outlined in reaction (1). We have utilized 2:1, 1:1, and 1:2 ratios of 1,3-CHD: α-FAN in the monomer feed in order to determine if, indeed, an alternating copolymer will form as was observed for the copolymerization of α-CAN and 1,3-CHD.[13]

Insert reaction (1)

Relatively low overall yields of 20-40% were obtained after 72 h as the copolymerization proceeds quite slowly. This is in contrast to the α-CAN/1,3-CHD copolymer which formed in higher yields

over the same amount of time using similar feed ratios.[13] It has been reported that 1,3-CHD does not undergo radical homopolymerization, most likely due to chain transfer processes.[19] The facile copolymerization between 1,3-CHD and α-CAN to form an alternating copolymer, irrespective of the comonomer feed ratios, has been attributed to the formation of a 1:1 EDA complex between the monomer pair. Given the structural similarity between α-FAN and α-CAN it seems likely that the copolymers being studied here will form with a similar mechanism.

It should be pointed out that a significant controversy exists concerning the participation of EDA complexes in alternating copolymerizations. As an example of this controversy, Olsen *et al*.[6,7] have reported stereochemical evidence for the participation of EDA complexes for the alternating copolymerizations in the N-phenylmaleimide (NPM)/2-chloroethyl vinyl ether and NPM/styrene comonomer systems. On the other hand, Jones *et al* .[8,9] reported results arguing against the formation of EDA complexes between the above donor-acceptor pairs by radical trapping techniques. They attempted to trap the EDA complex using 1-butyl radicals derived from 1-butylmercuric bromide and sodium borohydride in an aqueous medium. The experiment resulted in the reaction of the 1-butyl radical with NPM followed by a termination reaction with hydrogen and failed to produce any product derived from a complex. The results can be best explained by assuming that the EDA complex exists in very low concentration and is in equilibrium with the comonomers. In a UV-vis analysis a distinct charge transfer type absorption is observed when mixing α-CAN with 1,3-CHD.[12] α-FAN mixed with 1,3-CHD in chloroform does not exhibit any change in the electronic spectrum relative to the monomers suggesting that, if an EDA complex does exist, it is only present in very small amounts.

The slower copolymerization behavior of α-FAN with 1,3-CHD, relative to α-CAN with 1,3-CHD, can be understood by considering the copolymerization parameters Q and e. The Q-e values of a series of monomers including 1,3-CHD, α-CAN, and α-FAN are presented in Table II. The tendency toward alternation is greatest for monomers having the same Q values and high e values of opposite sign. For example, α-CAN and methyl α-chloroacrylate undergo facile alternating copolymerization[12] with 1,3-CHD due to their high Q-values of 2.16 and 2.02,

respectively. The slow copolymeriztion of the α-FAN/1,3-CHD system can be attributed to the smaller α-FAN Q-value of 0.43.[18] We have also observed this for the copolymerization of 1,3-CHD and ethyl α-fluoroacrylate.

FT-IR Spectroscopy.

The FT-IR spectrum of poly(1,3-CHD/α-FAN) is given in Figure 1 and is compared to poly(α-CAN/1,3-CHD).[13] As expected the spectra are essentially identical except for three peaks. A strong C-F stretch of poly(1,3-CHD/α-FAN) is visible at 1020 cm^{-1} while the poly(α-CAN/1,3-CHD) exhibits 2 strong C-Cl stretching absorbances at 736 and 490 cm^{-1}. The close correlation of the absorbance due to the aliphatic C-H stretching (3028, 2938 and 2868 cm^{-1}), the C≡N stretching, (2241 cm^{-1}), the CH=CH stretching (1652 cm^{-1}), and the CH_2 bending (1451 cm^{-1}) in poly(1,3-CHD/α-FAN) to those in poly(α-CAN/1,3-CHD) indicate the copolymers to be quite similar in structure. The low intensity of the C≡N absorbance in both copolymers is expected due to the electron withdrawing ability of the F and Cl substituents on the α carbon.

^{1}H-NMR Spectroscopy.

The ^{1}H-NMR spectrum of poly(1,3-CHD/α-FAN) is shown in comparison to poly(α-CAN/1,3-CHD) in Figure 2. Again the spectra are quite similar with the peaks between 5.4-6.2 ppm assigned to the olefinic protons, and the peak at 2.7 ppm assigned to the methine protons of the cyclohexene unit on the copolymer. While the two methine protons are not equivalent, only one resonance is observed for these in poly(α-CAN/1,3-CHD). A close analysis of the methine proton resonance for poly(1,3-CHD/α-FAN) at 2.7 ppm shows a shoulder on the upfield portion of the signal suggesting partial separation of the two resonances. Integration of the ^{1}H-NMR spectrum and comparison of the olefinic and aliphatic regions indicates that the copolymer contains approximately a 50:50 ratio of 1,3-CHD:α-FAN in agreement with the elemental analysis. The region between 1.0 - 2.45 ppm is assigned to the methylenic protons of the 1,3-CHD and α-FAN units. Comparison of the spectra for the two copolymers show distinct differences in the intensities of the various methylenic resonances. These differences suggests that there are some

differences in the polymer backbone structure which may be 1,4- or 1,2-linkages across the cyclohexene unit.

^{13}C and ^{19}F-NMR Spectroscopy.

The ^{13}C-NMR spectrum (DEPT- a, regular-b) of poly(1,3-CHD/α-FAN) is shown in Figure 3. The specific DEPT pulse sequence used yields positive intensities for carbons containing a single attached proton while all other resonances exhibit zero intensity. Comparing these spectra, and examining the general copolymer structures in reaction (1), we assign the peaks between 120-140 ppm to the olefinic carbons of the cyclohexene unit, the peaks at ca. 116 ppm to the cyano carbon of the α-FAN unit, and the peaks between 92-98 ppm to the quaternary carbon of the α-FAN unit that contains both a fluorine and a cyano substituent. The splitting of this signal is due to the adjacent fluorine and exhibits a coupling constant, J, of 190 Hz. It should be noted that the related quaternary carbon in poly(α-CAN/1,3-CHD) appears at 64 ppm and is not split. Though the peaks observed between 20-45 ppm (Figure 3b) in the regular ^{13}C-NMR spectrum are quite complicated, the assignments are simplified using the DEPT experiment. Due to the loss of signal in the DEPT spectrum, the peaks between 40-42 ppm and 20-28 ppm are assigned to the methylene carbons. The downfield set of peaks are due to the CH_2 units of the α-FAN which are adjacent to a highly electron withdrawing, F and CN substituted, carbon, while the remaining upfield methylene resonances are from the cyclohexene ring. The remaining peaks in this region, those visible in the DEPT spectrum, are assigned to the methine carbons on the cyclohexene ring. The complexity here is not surprising considering structures **1-3** shown in reaction (1).

Several important features become evident in comparing the ^{13}C-NMR spectrum of poly(1,3-CHD/α-FAN) to poly(α-CAN/1,3-CHD).[13] Specifically, a downfield shift (~30 ppm) is observed for the quarternary carbon, substituted with both CN and F, which is due to the higher electron withdrawing ability of F relative to Cl. The ^{19}F-NMR spectrum of poly(1,3-CHD/α-FAN), shown in Figure 4, exhibits one distinct resonance centered at *ca* . -160 ppm. The cyclohexene ring olefinic region of poly(1,3-CHD/α-FAN) is more complicated than the chlorine substituted analogue. Poly(α-CAN/1,3-CHD) exhibits only two sets of olefinic carbon resonances

assignable to two distinct 1,4-linked olefinic carbons. The more complicated olefinic region in poly(1,3-CHD/α-FAN) suggests both 1,2- and 1,4-linkages. These complications are not due to end groups as, with M_n ~ 5,000, these contributions are minimal and cannot be explained by the expected small splitting by the β-fluorine substituent. It is more likely that the bonding pattern through the ring is more complicated.

Two Dimensional ^{1}H-COSY Spectroscopy.

We have previously reported that poly(α-CAN/1,3-CHD) contains essentially all 1,4-linkages across the cyclohexene unit based on a combination of derivatization, FT-IR and NMR experiments.[13] Examining reaction (1), it can be seen that the presence of 1,2- and 1,4-linkages can be identified by the coupling of the olefinic protons on the cyclohexene ring to adjacent methylene and methine protons respectively. The highly complicated ^{13}C-NMR spectrum of poly(1,3-CHD/α-FAN) suggests multiple linkages across the cyclohexene ring and led us to carry out a two dimensional (2D) ^{1}H-COSY experiment in an attempt to identify these structural linkages. Figure 5 shows the 2D ^{1}H-COSY spectrum of poly(1,3-CHD/α-FAN) to only exhibit visible strong couplings (circled regions) between the olefinic protons (regions a) and methine protons (region b) of the cyclohexene ring. The lack of olefinic-methylenic (region c) proton couplings suggests a low number of 1,2-linkages. Unfortunately, this is not consistent with the ^{13}C-NMR spectrum. Another possibility is that short spin-spin relaxation times for the methylenic protons would result in substantial signal loss during the COSY experiment; a problem previously addressed in NMR studies of poly(vinyl chloride),[20] or that the coupling constants for the olefinic and methylenic protons may be too small for detection under the conditions of this COSY experiment.

In order to address this lack of visible 1,2-linkages, we have examined the 2D ^{1}H-COSYspectrum of a model compound, 3-methylcyclohexene (**4**), which contains both methylenic

INSERT STRUCTURE 4

(H_1) and methine (H_2) protons adjacent to the olefinic protons.

The contour plot, shown in Figure 6, indicates strong olefinic (~5.65 ppm) - adjacent methylenic (1.95 ppm) proton couplings. The contour plot also shows strong olefinic (~5.55 ppm) - methylenic (1.95 ppm) proton couplings which are separated by four bonds. In addition, we observe weak methyl (d: 0.98, 0.95 ppm) olefinic (~5.55 ppm) proton and methylenic (C4 - H, ~ 1.75 ppm) - olefinic (~5.55 ppm) proton couplings which are separated by four bonds. On the other hand, the methine (~2.20 ppm) - olefinic (~5.55 ppm) proton coupling, which is separated by three bonds, also shows only a weak coupling. These complications in the 2D-COSY of 3-methylcyclohexene indicates that the lack of an observed coupling is not sufficient evidence to rule out a proposed structure. As such, this model compound study indicates that the lack of any observable methylenic-olefinic coupling in poly(1,3-CHD/α-FAN) does not rule out the possibility of 1,2-linkages across the cyclohexene unit. It should be noted that the several peaks for the methylenic protons of the 3-methylcyclohexene are due to conformational isomerism in the molecule. The methylenic protons of C-6 are easily identifiable due its allylic nature. The assignment of other methylenic protons are difficult and will not be discussed further.

Thermal Analysis.

In our studies of poly(α-CAN/1,3-CHD) we found that the copolymers' thermal stability was limited by a dehydrochlorination that begins below 200°C. In the TGA thermograms in Figure 7 it can be seen that poly(1,3-CHD/α-FAN) is significantly more stable with an onset of degradation of about 325°C. In fact, in this copolymer, main chain cleavage to volatile products seems to be occurring first as approximately 80% of the mass is lost in one step. Mass spectral analysis of the copolymer volatilized between 300-400°C using a direct exposure probe shows multiple fragments larger than monomer residues. This indicates that main chain cleavage involves more than two repeat units and is not a simple depolymerization .

Poly(1,3-CHD/α-FAN) exhibits over a 30°C decrease in Tg to 74°C when compared to the chlorinated analogue. This is not surprising considering the smaller size of the fluorine which allows significantly easier main chain rotations.

CONCLUSIONS

An alternating copolymer of 1,3-CHD and α-FAN has been prepared and its structure characterized by the combined use of FTIR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and 2D-^{1}H COSY spectroscopic techniques. While both poly(α-CAN/1,3-CHD) and poly(1,3-CHD/α-FAN) are essentially alternating, the former contains only 1,4-linkages and the latter contains both 1,2- and 1,4-linkages and is more complex. We speculate that this may be due to a stronger EDA complex between α-CAN and 1,3-CHD, compared to α-FAN and 1,3-CHD. The replacement of Cl by F in this polymer backbone causes the fluorinated analogue to be significantly more thermally stable as expected.

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Table I. Copolymerization Results of 1,3-Cyclohexadiene and α-Fluoroacrylonitrile[a]

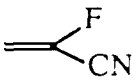
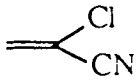
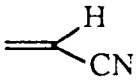
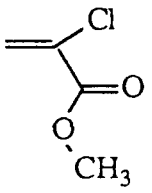
Monomer Feed Composition (1,3-CHD/α-FAN) (mmol)	Polymer Yield(%)[b]	Copolymer Composition (1,3-CHD/α-FAN)[c]	Molecular Weight M_n (MWD)
14/7	20	54/46	5000 (1.84)
7/7	25	57/43	5025 (2.07)
7/14	40	54/46	7808 (2.08)

[a]Bulk copolymerization was carried out at 65°C for 72 h using 1 mol% AIBN as initiator. Initiator concentration was based on the monomer of lowest concentration as limiting reagent.

[b]Based on the limiting reagent.

[c]Based on elemental analysis.

Table II. Q-e Values for Polar Vinyl Monomers and 1,3-CHD

	Q	e	Ref.
	1.48	-1.09	a
	0.43	1.28	b
	2.16	1.48	a
	0.60	1.20	a
	2.02	0.77	a

[a] Polymer Handbook; J. Brandrup and E.H. Immergut, Eds.; Wiley and Sons, New York (1975).

[b] Reference 18

FIGURE CAPTIONS

Figure 1: FT-IR spectra of (a) poly(1,3-CHD/α-FAN) and (b) poly(α-CAN/1,3-CHD).

Figure 2: ^{1}H-NMR spectra of (a), poly(1,3-CHD/α-FAN) (300 MHz) and (b) poly(α-CAN/1,3-CHD) (200 MHz).

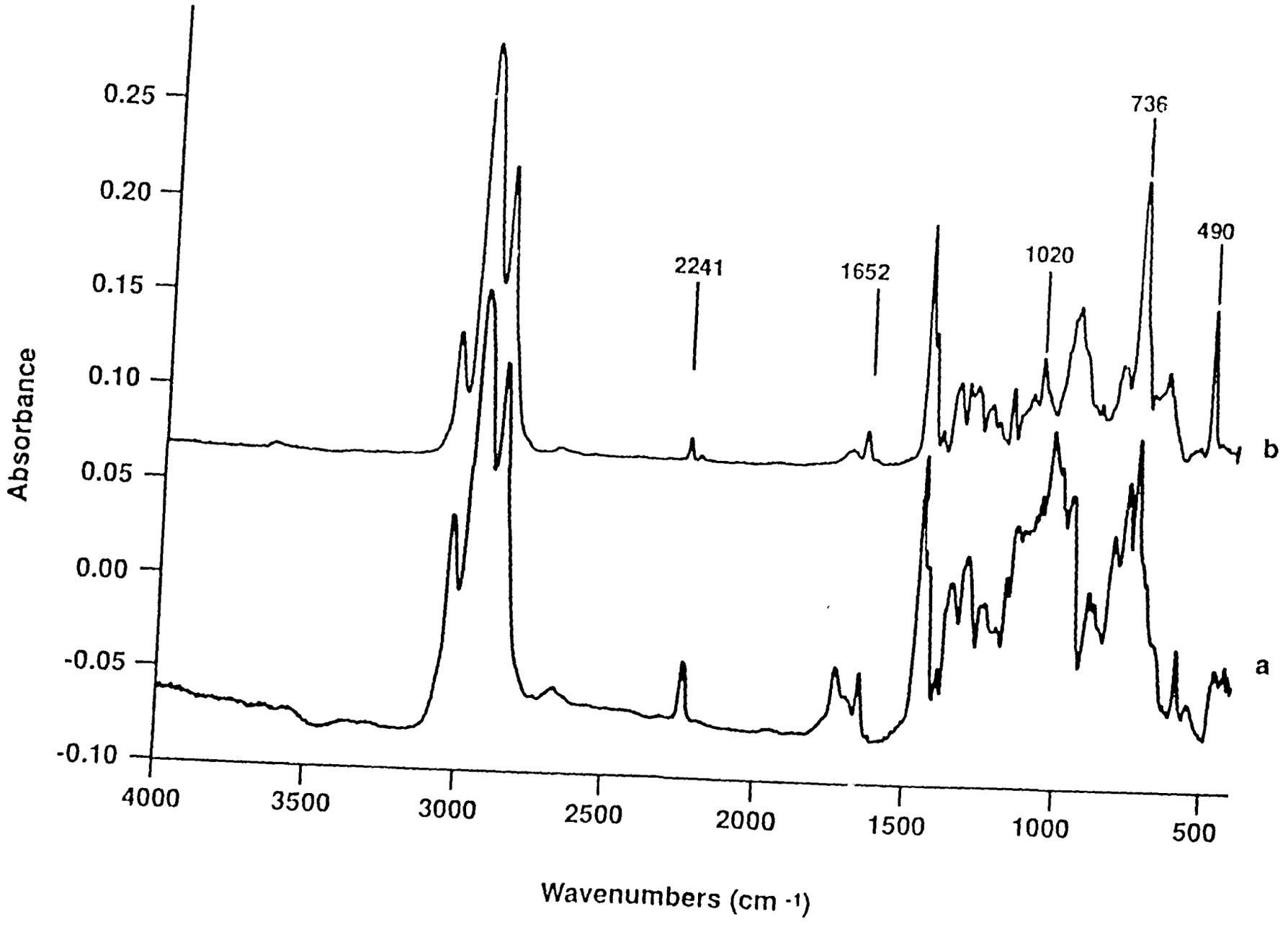
Figure 3: ^{13}C-NMR (75 MHz) spectra of poly(1,3-CHD/α-FAN) (a) DEPT spectrum and (b) normal spectrum.

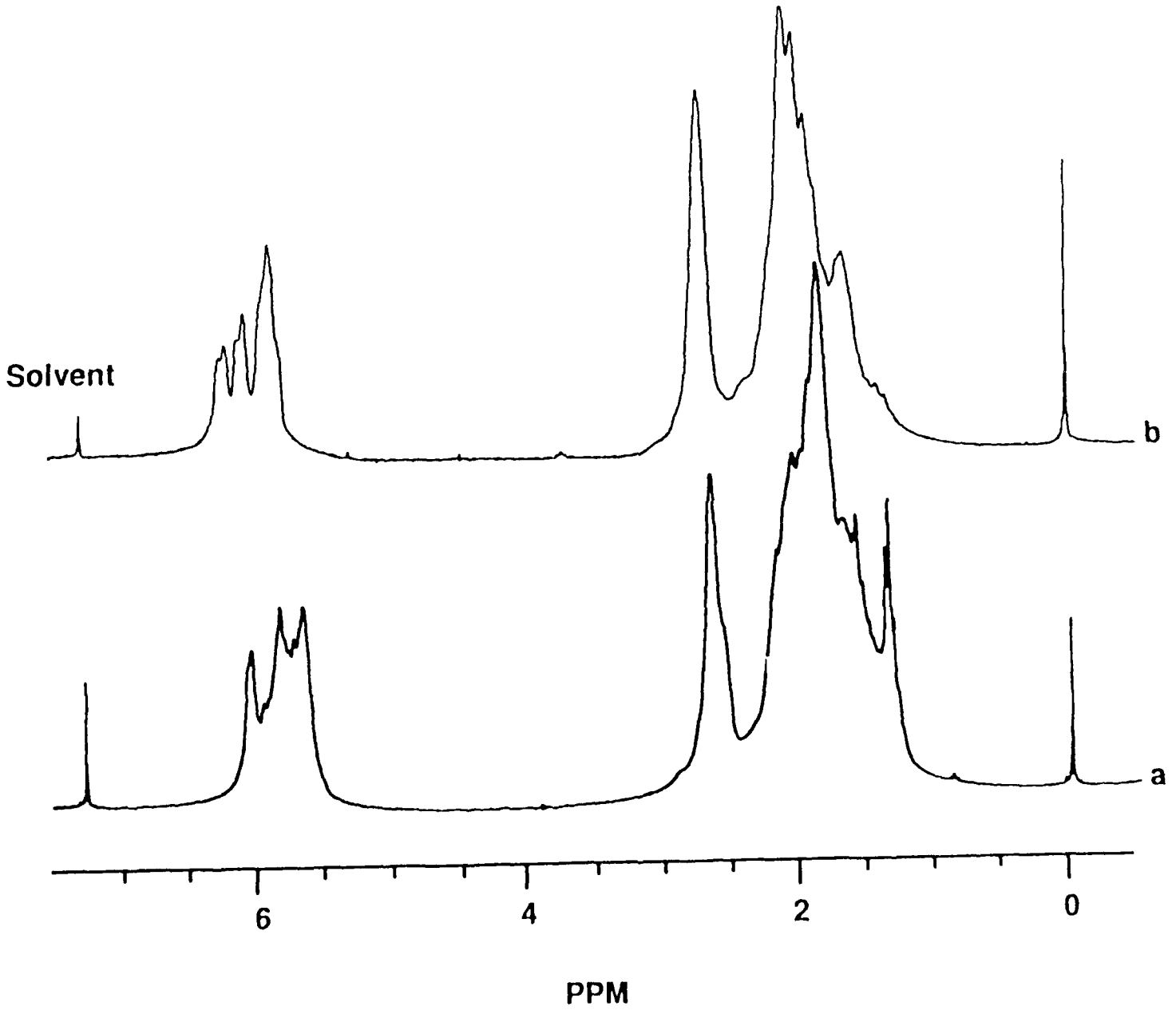
Figure 4: ^{19}F-NMR (282 MHz) spectrum of poly(1,3-CHD/α-FAN).

Figure 5: 2D ^{1}H-COSY (300 MHz) spectrum of poly(1,3-CHD/α-FAN).

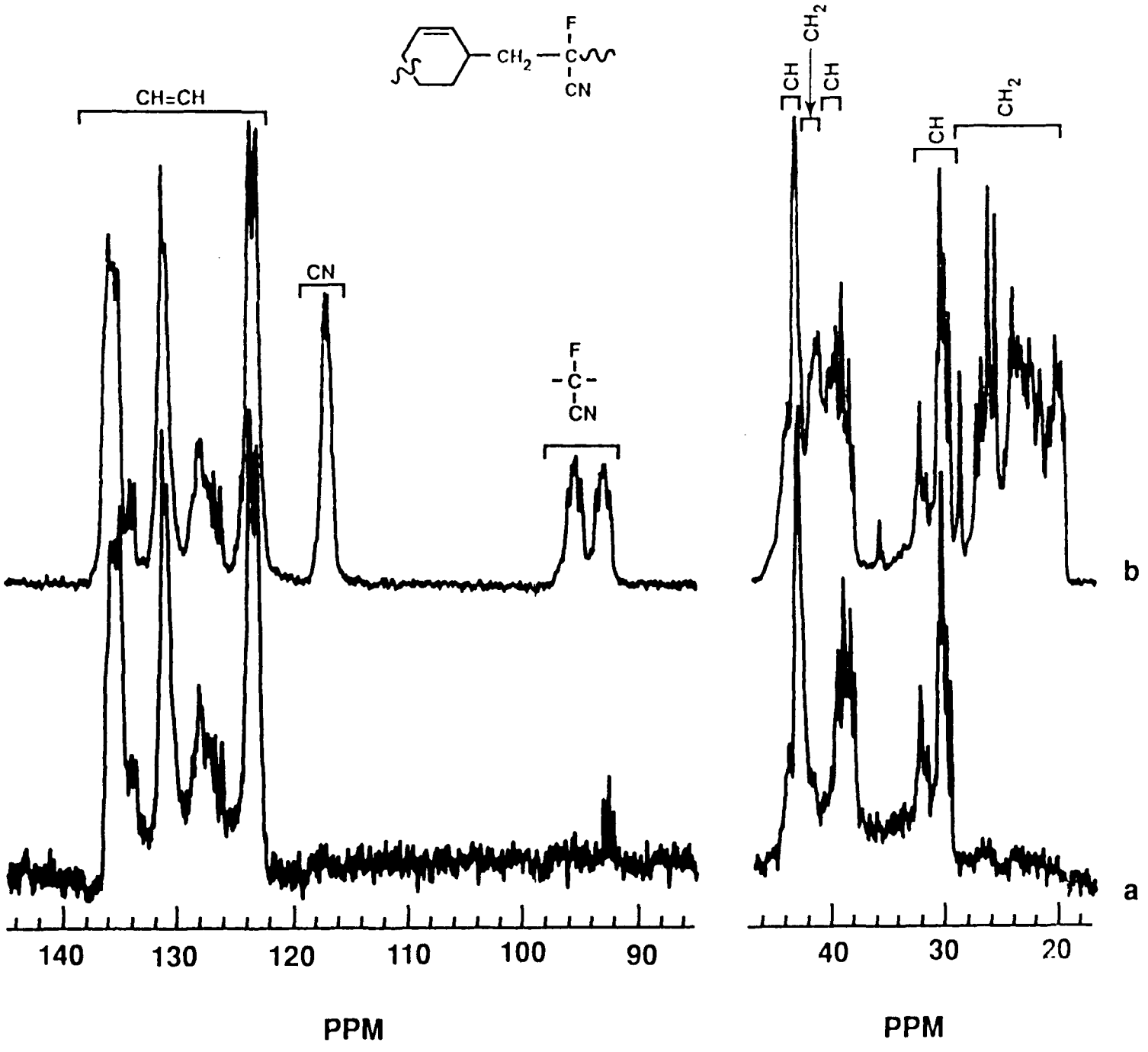
Figure 6: 2D ^{1}H-COSY (300 MHz) spectrum of 3-methylcyclohexene.

Figure 7: TGA thermograms of (a) poly(1,3-CHD/α-FAN) and (b) poly(α-CAN/1,3-CHD) under nitrogen atmosphere.


0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
Absorbance
2241
1652
1020
736
490
b
a
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm -1)



F3


CH=CH
CN
F
C
CN
CH2
CH
CH
CH2
CH
b
a
140
130
120
110
100
90
40
30
20
PPM
PPM

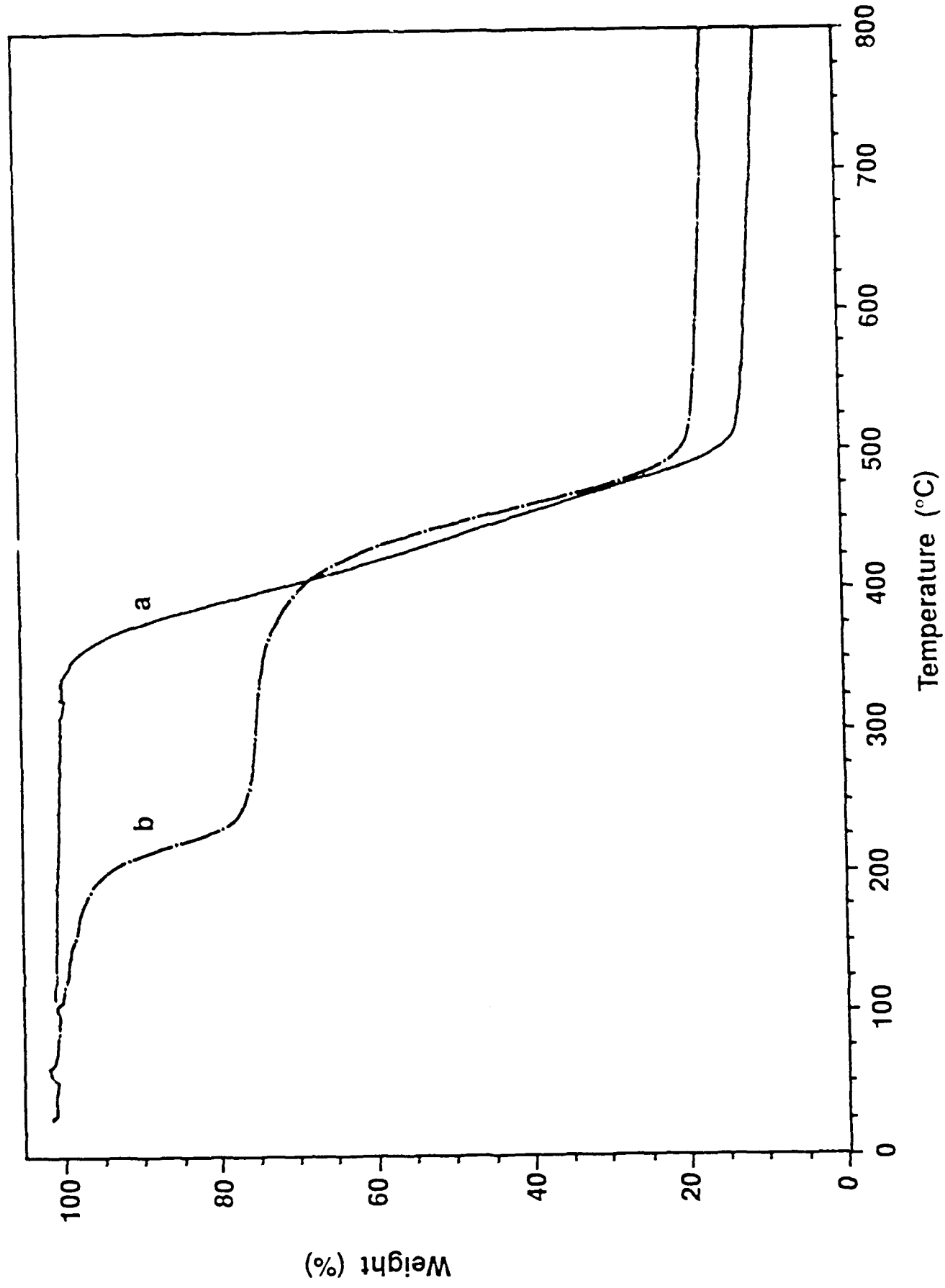
F3

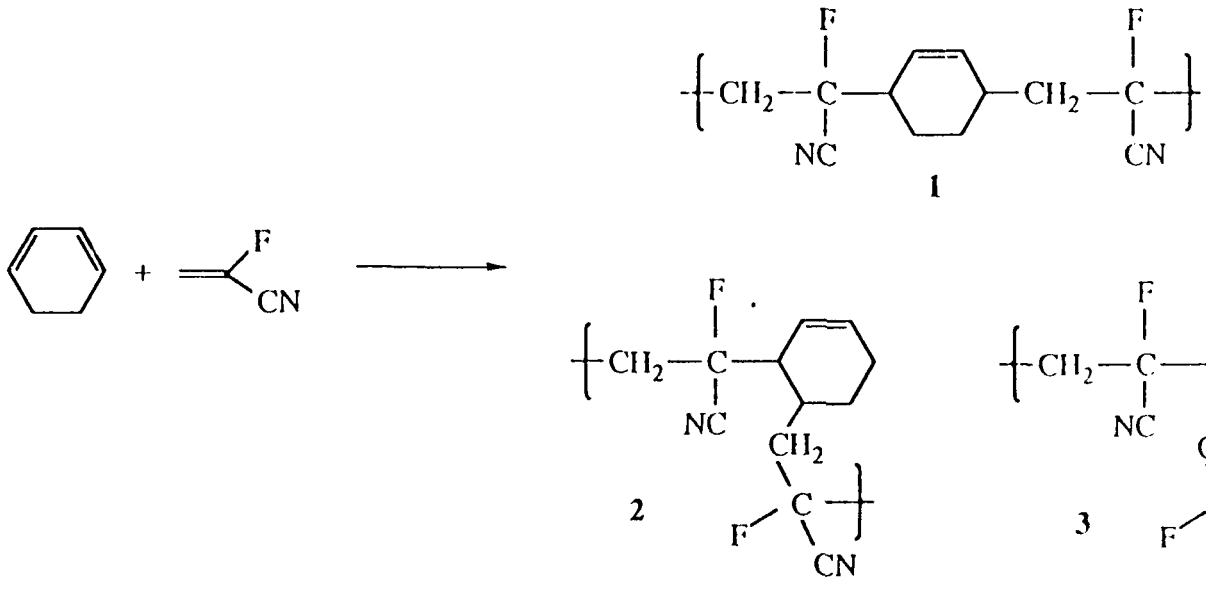
F 4

F5

F6

F7


Weight (%)
100
80
60
40
20
0
0
100
200
300
400
500
600
700
800
Temperature (°C)
a
b

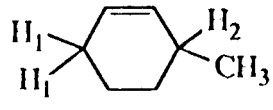


1

2

3

(1)



4