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Structural Characterization of Poly(α-Fluoroacrylonitrile) and Poly(Ethyl α-Fluoroacrylate)

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STRUCTURAL CHARACTERIZATION OF POLY(α-FLUOROACRYLONITRILE) AND POLY(ETHYL α-FLUOROACRYLATE)

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ABSTRACT

Monomers α-fluoroacrylonitrile (FAN) and ethyl α-fluoroacrylate (EFA) and homopolymers poly(α-fluoroacrylonitrile) (PFAN) and poly(ethyl α-fluoroacrylate) (PEFA) have been synthesized and spectroscopically characterized in detail for the first time. The ^{13}C- and ^{19}F-NMR spectroscopic results are reported, and the results are correlated to the tacticity and microstructure of both homopolymers. The major portion of the polymers is atactic. TGA analysis of PFAN indicates that the polymer is stable to about 200°C with subsequent loss of HF. PEFA is stable to 300°C. Molecular weights determined by intrinsic viscosity (M_v) are found to be about 130,000 for PFAN, and GPC analysis of PEFA indicates a molecular weight (M_n) of about 36,000. Dielectric permittivities (ϵ) for PFAN and PEFA were determined to be 8.9 and 4.0, respectively, at 50 Hz.

INTRODUCTION

Previously, we reported the synthesis of poly(vinyl acetate-*co*-vinylidene fluoride), a polymer which has potential applications as a dielectric material [2]. During our studies of potential high dielectric constant polymers, we became interested in the synthesis of poly(α-fluoroacrylonitrile) (PFAN) which contains an electronegative fluorine and polarizable cyano group in a geminal position. Polarizable and electronegative substituents yield permanent dipoles along the main chain which can contribute both high permittivity and piezoelectricity to a material. This is especially evident for polyvinylidene fluoride [3] and poly(vinylidene cyanide-*alt*-vinyl acetate) [4].

PFAN has been reported previously [5]; only the work of Ueda and Yazawa [5a] provided information regarding some of the physical and spectroscopic properties. However, attempts in our laboratory to repeat their synthesis of α-fluoroacrylonitrile (FAN) resulted in inconsistent results. Another synthesis of FAN by Tolman et al. [6] was used which also allowed us to generate ethyl α-fluoroacrylate (EFA) for synthesis of poly(ethyl α-fluoroacrylate) (PEFA). PEFA has been synthesized previously [7], but a complete spectroscopic analysis was not provided.

We report here the first complete (^{1}H, ^{13}C, ^{19}F) NMR spectroscopic study of the intermediates involved in the synthesis of FAN and EFA [6]. As well, we will discuss the properties of PFAN and PEFA along with the implications of the NMR results with regards to the microstructure of each polymer.

EXPERIMENTAL

Materials

NMR spectra were obtained on a Bruker MSL 300 operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, and 282.36 MHz for ^{19}F. Proton chemical shifts were referenced to either internal TMS (δ = 0.00 ppm) or H_2O (δ = 4.6 ppm), and the carbon chemical shifts were referenced to internal $CDCl_3$ (δ = 77.0 ppm), external benzene (δ = 128.0 ppm), or internal acetone-d_6 (δ = 29.6 ppm for the methyl carbons). Fluorine chemical shifts were referenced to external C_6F_6 (δ = -163.0 ppm). Infrared spectra were obtained on a Biorad-Digilab FTS-40 Fourier transform spectrometer by the diffuse reflectance method or between salt plates. TGA experiments were performed on a DuPont 9900 thermal analysis system fitted with a Model 951 thermogravimetric analyzer. All TGA experiments were performed with nitrogen flushing through the cell at ~40 mL/min and a heating rate of 20°C/min to 900°C. Viscosity measurements were performed in a Ubbelohde viscometer, and dilutions were performed to give 0.980, 0.765, 0.574, and 0.430 g/dL PFAN in DMF. Dry solvents were freshly distilled from sodium-benzophenone ketyl before use. Reagent-grade DMF was filtered and deaerated before viscosity measurements were performed. Other reagents were used as supplied. Elemental analyses were performed in-house on a Perkin-Elmer 2400 CHN analyzer, or by Texas Analytical Laboratories.

Ethyl monofluorooxalacetate sodium salt **1**. A previously reported procedure [19] was modified. In 200 mL of freshly distilled ethyl ether, alcohol-free NaOEt was generated from 23 g sodium and 0.95 equivalent of dry ethanol. The reaction was stirred overnight. To the reaction was added dropwise one equivalent (146 g) of diethyl oxalate in 200 mL ether. The reaction was stirred until a brown homogeneous reaction mixture formed. To the reaction was added dropwise 100 g (less than one equivalent) of ethyl monofluoroacetate in 100 mL ether. A yellow precipitate began to form after about 30 minutes, and the reaction was stirred overnight. The yellow solid was filtered and rinsed several times with ether to yield 108 g (61%) of **1**. NMR (ppm) ^1H: $\delta = 4.22$ (q) $-OC\underline{H}_2CH_3$, 4.10 (q) $-OC\underline{H}_2CH_3$, 1.26 (t) $-OCH_2C\underline{H}_3$, 1.75 (t) $-OCH_2C\underline{H}_3$; ^{13}C: $\delta = 173.7$ (s) $EtO_2\underline{C}$, 169.98 (d) $EtO_2C{-}\underline{C}O$ ($^2J_{C,F} = 10.6$ Hz), 165.62 (d) $EtO_2C{-}\underline{C}{-}CF$ ($^2J_{C,F} = 24.4$ Hz), 132.76 (d) $\underline{C}F$ ($^1J_{C,F} = 211.0$ Hz), 62.58 (s), 60.85 (s) $\underline{C}H_2$, 13.22 (s), 13.13 (s) $\underline{C}H_3$; FTIR 2977, 2936, 2902 cm^{-1} C—H, 1736, 1671 cm^{-1} C=O, 1126 cm^{-1} C—F.

Ethyl 2-fluoro-3-hydroxy-propanate **2** [6]. Sodium salt **1** (one equivalent) was slowly added to a solution of 37% formaldehyde (slight excess) in 400 mL water and 300 mL ether at 0°C. The reaction was allowed to warm to room temperature and was stirred overnight. The two layers were separated, and the aqueous layer was washed with 4 × 100 mL ether. The ether layer was dried over Molecular Sieves. The ether was filtered and evaporated in vacuo to give a crude yellow product. Short-path vacuum distillation gave 66.5 g (66%) of clear colorless liquid **2** (65–68°C at 2 mm) [lit. 6, 95–96°C, 12 mm]. NMR (ppm) ^1H: $\delta = 4.50$ (br, s) $\underline{H}O-$, 4.11, 4.02 (ddd) $-OC\underline{H}_2CHF-$ methylene protons are nonequivalent ($^1J = 12.9$ Hz, $^2J = 4.5$ Hz, $^2J_{H,F} = 23.5$ Hz), 5.16 (dt) $-C\underline{H}F-$ one coupling unresolved ($^1J_{H,F} = 50.7$ Hz, $^2J = 4.5$ Hz), 4.36 (q) $-OC\underline{H}_2CH_3$, 1.39 (t) $-OCH_2C\underline{H}_3$; ^{13}C: $\delta = 168.76$ (d) $\underline{C}{=}O$ ($^2J_{C,F} = 24.3$ Hz), 61.94 (d) $-H_2\underline{C}OH$ ($^2J_{C,F} = 24.0$ Hz), 89.91 (d) $-\underline{C}HF-$ ($^1J_{C,F} = 182.0$ Hz), 65.53 (s) $-\underline{C}H_2-$, 13.22 (s) $-\underline{C}H_3$.

2-Fluoro-3-hydroxy-propanamide **3** [6]. A solution of 55 g of **2** in 200 mL dry ethanol was cooled at 0°C and slowly bubbled with ammonia gas for 2 hours. The reaction mixture was then placed in a refrigerator for 3 days. The ethanol was removed in vacuo at <40°C. The resulting solid was recrystallized from acetone to yield 40.6 g (78%) of **3**, mp 114–116°C [lit. 6, 114–116°C]. NMR (ppm) ^1H: $\underline{H}O$ not found, exchanged with the D_2O, $\delta = 3.84$, 3.75 (ddd) $HOC\underline{H}_2CHF-$ methylene protons are nonequivalent ($^1J = 13.3$ Hz, $^2J = 3.5$ Hz, $^2J_{H,F} = 22.9$ Hz), $-CON\underline{H}_2$ not observed, 4.89 (ddd) $-C\underline{H}F-$ ($^1J_{H,F} = 47.4$ Hz, $^2J = 3.5$ Hz); ^{13}C: $\delta = 172.90$ (d) $\underline{C}{=}O$ ($^2J_{C,F} = 19.5$ Hz), 60.97 (d) $-H_2\underline{C}OH$ ($^2J_{C,F} = 19.5$ Hz), 91.17 (d) $-\underline{C}HF-$ ($^1J_{C,F} = 188.0$ Hz); FTIR: 3375, 3192 cm^{-1} N—H, 2996, 2882, 2783 cm^{-1} C—H, 1652 cm^{-1} amide I, 1624 cm^{-1} amide II, 1088 cm^{-1} C—F.

2-Fluoro-3-(4-toluenesulfonyloxy)propanamide **4** [6]. In a solution of water-free pyridine was placed 25.5 g (0.236 moles) of **3**. The reaction was cooled to −8 to −10°C in a dry ice/acetone bath. To the reaction mix was added 1.5 equivalents of tosyl chloride over 15 minutes. The reaction was allowed to warm to room temperature. The reaction was recooled in the dry ice/acetone bath and a solution of 10% H_2SO_4 (usually 4–5 times the volume of the reaction mixture) was slowly added. NOTE: A violent exotherm can take place, so extreme caution is needed. A precipitate formed and was filtered. The resulting solid was recrystallized from acetone, yield 78%, mp 112–116°C [lit. 6, 114–116°C]. NMR (ppm) ^1H: aryl protons 7.77 (d) ($^2J = 6.1$ Hz), 7.40 (d) ($^2J = 8.1$ Hz), 7.26, 7.04 (br, two peaks split by 66 Hz) NH_2, 4.42, 4.34 (ddd) $-OC\underline{H}_2CHF$ methylene protons are nonequivalent ($^1J = 11.6$ Hz, $^2J = 4.9$ Hz, $^2J_{H,F} = 22.2$ Hz), 5.12 (ddd) $-C\underline{H}F-$ ($^1J_{H,F} = 48.3$

Hz, ^2J = 4.9 Hz), 2.41 (s) $-C\underline{H}_3$; ^{13}C: δ = 168.47 (d) $\underline{C}{=}O$ ($^2J_{C,F}$ = 19.5 Hz), 69.80 (d) $-H_2\underline{C}O-$ ($^2J_{C,F}$ = 19.5 Hz), 89.25 (d) $-\underline{CHF}-$ ($^1J_{C,F}$ = 192.9 Hz), 146.05 (s) $-\underline{C}-$ SO_3, 133.40 (s) $-\underline{C}-CH_3$, aryl carbons 130.78, 128.60 (s), 21.37 (s) $-\underline{C}H_3$; FTIR: 3384, 3261 cm^{-1} N$-$H, 3187 cm^{-1} aryl C$-$H, 2921, 2799 cm^{-1} C$-$H, 1649 cm^{-1} amide I, 1598 cm^{-1} amide II, 1097 cm^{-1} C$-$F.

Ethyl 2-fluoro-3-(4-toluenesulfonyloxy)propanoate **5** [6]. In a solution of water-free pyridine was placed a measured amount of compound **2**. The reaction was cooled to −20°C in a dry ice/acetone bath. To the reaction mixture was slowly added 1.5 equivalents of tosyl chloride over 10–15 minutes. The reaction was warmed to 0°C. The reaction was placed in a refrigerator overnight (the mixture turned brown-black). The reaction mixture was placed in an ice/H_2O bath and a solution of 10% H_2SO_4 was slowly added. An oil formed and the reaction mixture was extracted 4 times with ether. The ether was dried over Molecular Sieves, removed in vacuo, and the resulting solid recrystallized from ethanol, mp 48–51°C [lit. 6, 53–54°C], yield 58%.

2-Fluoro-3-(toluenesulfonyloxy)propanenitrile **6** [6]. A solution of one equivalent of **4** in dioxane and 2.2 equivalents of pyridine was cooled in an ice bath. To the reaction was added dropwise 1.1 equivalents of trifluoroacetic anhydride in dioxane. The reaction was allowed to warm to room temperature and stirred overnight. A large volume (~100%) of water was added and the tosyl nitrile separated as an oil. The aqueous layer was extracted four times with ether. The ether layer was extracted one time with 10% sodium bicarbonate and one time with water. The ether was dried over Molecular Sieves, and the ether was removed in vacuo. The resulting oil was recrystallized from hexanes, yield 78%, mp 40–42°C [lit. 6, 40–42°C]. NMR (ppm) ^1H: aryl protons 7.83 (d) (^2J = 8.6 Hz), 7.29 (d) (^2J = 8.1 Hz), 4.41, 4.34 (ddd) $-OC\underline{H}_2CHF-$ methylene protons are nonequivalent (^1J = 12.7 Hz, ^2J = 5.8 Hz, $^2J_{H,F}$ = 20.6 Hz), 5.34 (ddd) $-C\underline{H}F-$ ($^1J_{H,F}$ = 48.9 Hz, ^2J = 5.8 Hz), 2.45 (s) $-C\underline{H}_3$; ^{13}C: δ = 145.97 (s) $-\underline{C}-SO_3-$, 131.52 (s) $-\underline{C}-CH_3$, aryl carbons 130.15, 128.03 (s), 112.47 (d) $-\underline{C}N$ ($^2J_{C,F}$ = 30.1 Hz), 66.70 (d) $-H_2\underline{C}O-$ ($^2J_{C,F}$ = 24.5 Hz), 76.78 (d) $-\underline{C}HF-$ ($^1J_{C,F}$ = 189.7 Hz), 21.69 (s) $\underline{C}H_3$.

Generation of α-fluoroacrylonitrile (FAN) [6]. In a short-path distillation apparatus was placed a homogenized mixture of 1 equivalent **6** and 3 equivalents potassium phthalimide. The reaction was placed under aspirator vacuum and slowly heated to 150°C and held at that temperature for 30 minutes. The reaction was allowed to cool and FAN was recovered as the distillate as a clear colorless liquid, yield 99%. NMR (ppm) ^1H: 5.59 (dd) H_{cis} (^1J = 4.6 Hz, $^1J_{H,Fcis}$ = 11.4 Hz), 5.56 (dd) H_{trans} (^1J = 4.6 Hz, $^1J_{H,Fcis}$ = 41.4 Hz); ^{13}C: δ = 108.79 (d) $H_2\underline{C}{=}$ ($^2J_{C,F}$ = 16.0 Hz), 137.34 (d) $=\underline{C}F-$ ($^1J_{C,F}$ = 250.0 Hz), 111.48 (d) $-\underline{C}N$ ($^2J_{C,F}$ = 48.1 Hz); FTIR: 3149, 3061, 3007 cm^{-1} olefinic C$-$H, 2243 cm^{-1} CN, 1655 cm^{-1} C$=$C, 1264 cm^{-1} C$-$F.

Generation of ethyl α-fluoroacrylate (EFA) [6]. The procedure was the same as for FAN, yield 61%. NMR (ppm) ^1H: 5.47 (dd) H_{cis} (^1J = 3.1 Hz, $^1J_{H,Fcis}$ = 13.5 Hz), 5.66 (dd) H_{trans} (^1J = 3.1 Hz, $^1J_{H,Fcis}$ = 43.3 Hz), 4.22 (q) $-OC\underline{H}_2CH_3$, 1.25 (t) $-OCH_2C\underline{H}_3$; ^{13}C: δ = 102.32 (d) $H_2\underline{C}{=}$ ($^2J_{C,F}$ = 17.1 Hz), 153.38 (d) $=\underline{C}F-$ ($^1J_{C,F}$ = 263.7 Hz), 160.25 (d) $\underline{C}{=}O$ ($^2J_{C,F}$ = 36.6 Hz), 61.80 (s) $-O\underline{C}H_2CH_3$, 13.95 (s) $-OCH_2\underline{C}H_3$.

Bulk Polymerization Procedure

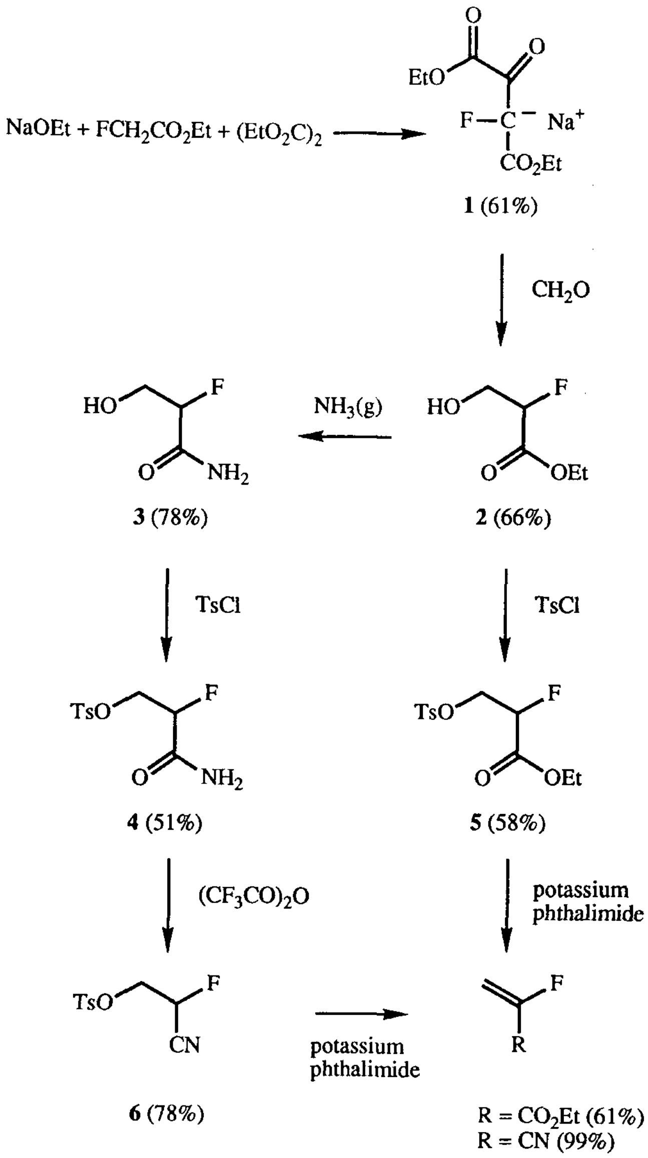
In a thick glass tube was placed an appropriate amount of monomer and about 1.0% AIBN. The tubes were sealed under vacuum after three freeze-thaw cycles. The tubes were heated at 65°C. For PFAN, heating was for 24 hours. The polymer was dissolved in acetone and precipitated into ether, resulting in 90% yield. NMR not previously discussed: ^{1}H: $-C\underline{H}_2-$ 3.43 ppm broad; ^{13}C: 46.2 ppm broad multiplet $-\underline{C}H_2-$. Elemental analysis: Calculated C 50.71, H 2.84, N 19.71, F 26.74%; found C 50.77, H 2.78, N 19.75, F 26.63%. For PEFA, heating was for 45 minutes. The polymer was dissolved in acetonitrile and precipitated into methanol, resulting in 80% yield. NMR not previously discussed: ^{1}H: 4.18 ppm broad $-OC\underline{H}_2CH_3$, 1.28 ppm broad $-OCH_2C\underline{H}_3$; ^{13}C: 169.2 ppm multiplet $\underline{C}=O$, 45.2 ppm broad multiplet $-\underline{C}H_2-$. Elemental analysis: Calculated C 50.80, H 5.97%; found C 56.88, H 6.21%.

RESULTS AND DISCUSSION

The synthesis of FAN and EFA was accomplished as indicated in Scheme 1 with a slight modification of the procedure of Tolman et al. [6]. The first step was the generation of the oxalacetic ester salt **1** from the condensation of ethyl monofluoroacetate and diethyl oxalate.

Condensation of **1** with formaldehyde was used to give ethyl 2-fluoro-3-hydroxypropanoate **2**. Compound **2** was reacted with ammonia to generate 2-fluoro-3-hydroxypropanamide **3** which was subsequently reacted with tosyl chloride to generate 2-fluoro-3-(4-toluenesulphonyloxy)propanamide **4**. Compound **2** was also reacted with tosyl chloride to give ethyl 2-fluoro-3-(4-toluenesulfonyloxy)-propanoate **5**, the immediate precursor to EFA. The formation of these two tosyl derivatives (**4** and **5**) provides an excellent means of storing a stable precursor to the FAN and EFA monomers. Compound **4** was dehydrated with trifluoroacetic anhydride to yield 2-fluoro-3-(4-toluene-sulfonyloxy)propanenitrile **6**, the precursor to FAN. The generation of FAN or EFA was accomplished by reacting either **5** or **6** with three equivalents of potassium phthalimide. Compounds **1–4**, **6**, FAN, and EFA were further characterized by their physical properties: ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy; and in some cases FTIR spectroscopy (see Experimental Section). The ^{19}F-NMR spectroscopic results provide interesting insights into the structure of the synthetic intermediates that is not easily provided in some cases by the ^{1}H- or ^{13}C-NMR spectroscopic results as illustrated in Table 1.

The ^{19}F-NMR spectrum of compound **1** is a singlet. This indicates that in D_2O there is no exchange between the deuteron and the salt [8]. If exchange were taking place, splitting of the ^{19}F-NMR signal would be evident. Compounds **2** and **3** have very similar ^{19}F-NMR spectra, as expected. The spectra clearly indicate that the methylene protons are diastereotopic, resulting in a doublet of doublet of doublets pattern [9]. If the protons were equivalent, each spectrum would appear as a doublet of triplets. The diastereotopic nature of the methylene protons is also indicated by the complex pattern observed in the proton spectrum of **2** and **3** (see Experimental Section).



SCHEME 1.

Compound **4** is the precursor to the monomer α-fluoroacrylamide which can be polymerized to yield poly(α-fluoroacrylamide). The ^{19}F-NMR spectrum of compound **4** (Fig. 1) contains 13 peaks instead of the eight peaks that one would expect as a result of the nonequivalence of the methylene protons. In 1971, Ouchi and coworkers [10] showed that one amide proton of trifluoroacetamide (CF_3CONH_2) couples to the fluorines ($J_{(F,NH)} = 1.8$ Hz) and that the other proton has a coupling constant of <0.3 Hz. In compound **4** a $J_{(F,NH)}$ of about 3.7 Hz is observed. Interest-

TABLE 1. ^{19}F-NMR Chemical Shifts and Coupling Constants

Compound	δ, ppm	$^1J_{F\text{-}H}$, Hz	$^2J_{F\text{-}Ha}$, Hz	$^2J_{F\text{-}Hb}$, Hz
1	−181.6 (s)			
2	−196.8 (ddd)	50.7	23.5	23.5
3	−193.7 (ddd)	47.4	22.9	22.9
4	−193.4[a]	48.3	22.2	22.2
6	−195.3 (dt)	48.9	20.6[b]	
FAN[c]	−107.7		11.4 (*cis*)	41.4 (*trans*)
FEA[c]	−118.6		13.5 (*cis*)	43.3 (*trans*)

[a] Complex pattern, see Results and Discussion Section.
[b] Only one coupling apparent.
[c] *cis* and *trans* coupling constants.

ingly, there was no apparent coupling observed between the fluorine and amide protons of compound **3**.

The ^{19}F-NMR spectrum of compound **6** appears as a doublet of triplets as would be expected for equivalent methylene protons. However, the methylene region in the proton spectrum is more complex and indicates that the methylene protons are in fact nonequivalent. The complexity of the methylene region in the proton spectrum indicates that the central peak of the triplets in the fluorine spectrum is composed of two unresolved peaks.

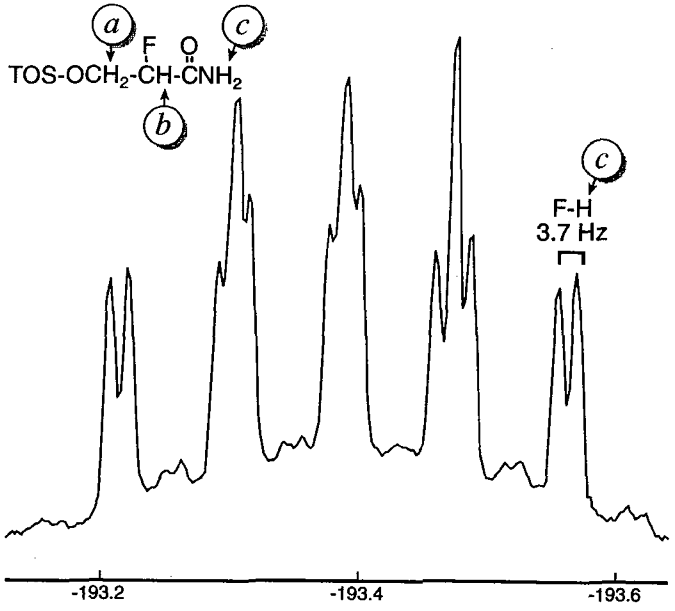
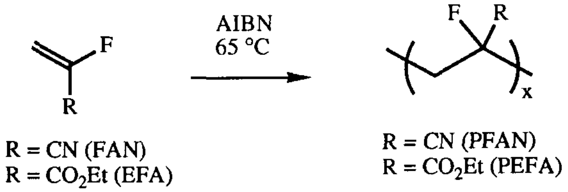


FIG. 1. ^{19}F-NMR spectrum of 2-fluoro-3-(4-toluenesulfonyloxy)propanamide (**4**).



SCHEME 2.

Both of the ^{19}F-NMR spectra of FAN and EFA contain a doublet of doublets. The fluorine is coupled to the cis and trans protons. In FAN, the cis proton coupling is 11.4 Hz and the trans proton coupling is 41.4 Hz. In EFA, the cis proton coupling is 13.5 Hz and the trans proton coupling is 43.3 Hz. In both FAN and EFA the spectral results are different from previous literature reports [5a, 6]. However, in the previous work a 60-MHz NMR was used and the coupling determined from the proton spectra was probably not as well resolved as in this study.

Polymerization to generate the homopolymers was accomplished in bulk polymerization using AIBN as the initiator (see Scheme 2 and the Experimental Section). The polymers were purified by reprecipitation as reported in the Experimental Section.

Both PFAN and PEFA were characterized by FTIR, and ^{1}H-, ^{13}C-, and ^{19}F-NMR spectroscopy. The FTIR results contain the appropriate features as shown in Table 2, whereby both polymers contain aliphatic C—H and C—F stretching vibrations. PFAN contains a CN stretching vibration and PEFA contains the C=O stretching vibration.

The proton NMR spectrum of PEFA was similar to the proton spectrum of poly(methyl α-fluoroacrylate) (PMFA) as reported by Majumdar and Harwood in 1981 [11]. In the 1981 report, the methylene region was used to determine the ratio of meso:racemic diads. From the meso:racemic ratio the authors determined that PMFA follows Bernoullian statistics [11] with a $P(m) = 0.41$ [$P(m)$ is the probability that addition to the end of the polymer chain is in the meso configuration for the distribution of diads]. For a completely random distribution, $P(m) = 0.50$ [12]. Using a similar analysis for PEFA, the meso diad is observed centered about 2.7 ppm. The racemic diad is centered at 2.4 ppm. The integral ratios of these areas is about 1:1.5 (meso:racemic). This result indicates that the $P(m) = 0.40$, assuming Bernoullian statistics, and that the diad distribution in PEFA is similar to the diad distribution observed in PMFA. From the proton spectral results one can conclude

TABLE 2. Major IR bands of PEFA and PFAN (in cm^{-1})

Assignment	PEFA	PFAN
C—H stretch	2995, 2944, 2908	2995, 2965
CN stretch	–	2258
C=O stretch	1788	–
C—F stretch	1194	1189

that PEFA is atactic. Confirmation of this result can be found in the ^{13}C- and ^{19}F-NMR spectra of PEFA. Of particular note is the fluorine spectrum as shown in Fig. 2. The spectrum contains 9 peaks of a possible 10, indicating that pentad stereosequences are being observed with one peak unresolved. A previous report of the ^{19}F-NMR spectrum of PEFA showed only three poorly resolved peaks [13]. Based on a *P*(*m*) = 0.40, we conclude that the peaks correlate to the pentad stereosequences as shown in Table 3.

The ^{13}C-NMR spectrum of PEFA clearly shows that the backbone methylene, quaternary, and carbonyl carbons are all multiple peaks due to the atactic nature of PEFA (see the Experimental Section for assignments). The C—F coupling is observed in the quaternary carbon region (Fig. 3) with a coupling constant of 194 Hz. The triad assignments for the peaks are given in Table 3 based on *P*(*m*) = 0.40. The assignment of the peak stereosequences are similar to the peak assignments of the quaternary carbon in poly(methyl methacrylate) [14, 15].

From the NMR spectral results one can conclude that PEFA is atactic, the stereosequences follow Bernoullian statistics, and that one can correlate proton, carbon, and fluorine spectral data to the diad, triad, and pentad stereosequence distribution, respectively.

In a similar manner we have used the NMR results to determine the stereosequence distribution of PFAN. The ^{19}F-NMR spectrum of PFAN is shown in Fig. 4. There is significantly more peak overlap in the fluorine spectrum of PFAN than in PEFA. The triad stereosequences can be identified clearly and the pentad stereosequences assignments become more tenuous. The peak at δ = −149.8 ppm

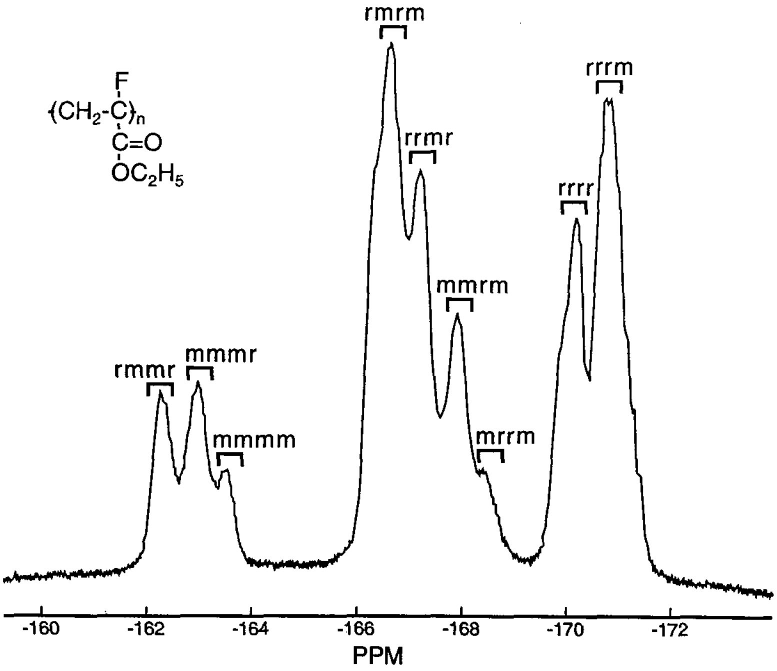


FIG. 2. ^{19}F-NMR spectrum of PEFA.

TABLE 3. Stereosequence Assignments of PFEA

	Chemical shift[a]	Assignment	Integral area	Calculated area
		^{19}F NMR		
	−162.3	rmmr	0.07	0.066
	−163.0	mmmr	0.07	0.070
	−163.6	mmmm	0.03	0.032
	−166.7	rmrm, mmrr	0.25	0.232
	−167.3	rrmr	0.12	0.119
	−168.0	mmrm	0.09	0.085
	−168.4	mrrm	0.04	0.058
	−170.2	rrrr	0.13	0.130
	−170.9	rrrm	0.21	0.211
		^{13}C NMR		
Quaternary carbon	95.0, 92.4	mm	0.16	0.16
	94.2, 91.6	mr, rm	0.51	0.48
	93.5, 90.9	rr	0.34	0.36

[a] Chemical shifts in ppm (see Experimental Section for details).

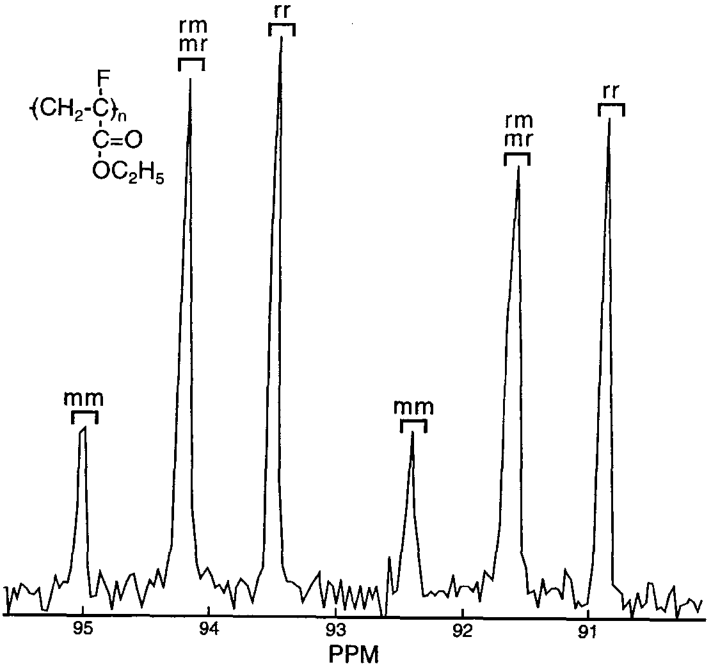


FIG. 3. ^{13}C-NMR spectrum of PEFA quaternary carbon region.

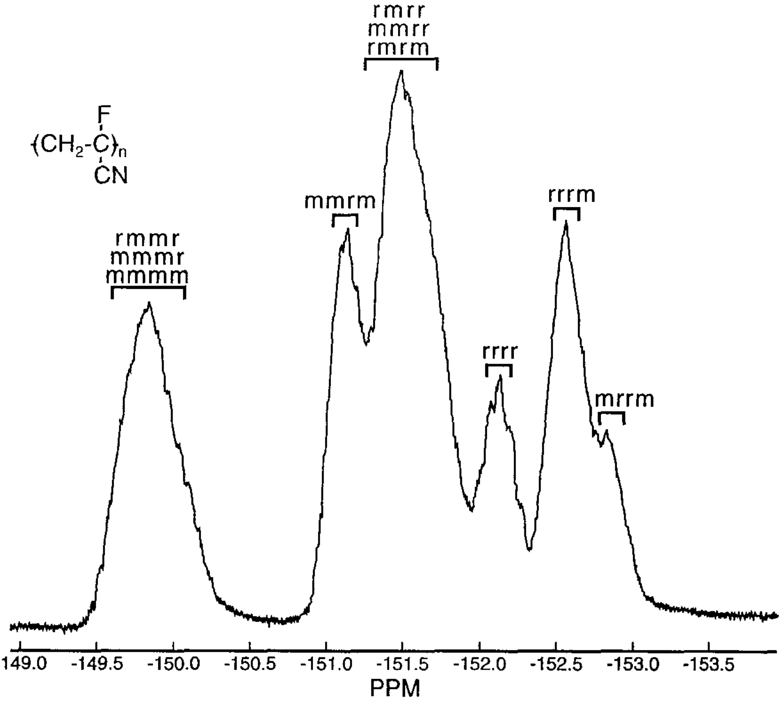


FIG. 4. ^{19}F-NMR spectrum of PFAN.

is the *mm* triad signal and integrates to 0.20 of the total spectrum. Using Bernoullian statistics, this indicates that *P*(*m*) = 0.45 for PFAN is similar to the *P*(*m*)s for PEFA and PMFA. The *P*(*m*) = 0.45 indicates that the two large peaks at −151.1 and −151.5 ppm are part of the *mr* triad. The calculated area would be 0.49 and the integral area of the two peaks is 0.14 (−151.1) and 0.36 (−151.5) for a total of 0.50, indicating good correlation in the assignments. The *rr* triad would incorporate the peaks at −152.1 and −152.6 ppm. The integral area was found to be 0.29, in good agreement with the calculated area of 0.30 from the *P*(*m*) value. Probable pentad assignments are given in Table 4.

From the ^{13}C-NMR spectrum of PFAN we have correlated the cyano and quaternary carbon regions with the fluorine spectrum (Figs. 5a and 5b). As in the case of PEFA, the methylene region of PFAN was complex (see the Experimental Section). The cyano region clearly shows the C—F coupling of 34 Hz. The cyano region triad assignments are given in Table 4 with the integrated and calculated areas of the peaks. The assignments are in agreement with a *P*(*m*) = 0.45. One interesting result is the apparent shift of the peak order relative to the assignments observed in poly(acrylonitrile) [16], which may be the result of the electron-withdrawing fluorine.

In the quaternary carbon region of the spectrum there is some resolution to the pentad signals but, as in the fluorine spectrum, the assignments are tenuous. The triad assignments are given in Table 4, as well as the integral and calculated peak areas. The results are similar to the peak order assignments seen in PEFA,

TABLE 4. Stereosequence Assignments of PFAN

	Chemical shift[a]	Assignment	Integral area	Calculated area
		^{19}F NMR		
	−149.9	rmmr, mmmr, mmmm	0.20	0.203
	−151.1	mmrm	0.14	0.100
	−151.5	mmrr, rmrm, rmrr	0.36	0.369
	−152.1	rrrr	0.09	0.092
	−152.6	rrrm	0.16	0.150
	−152.8	mrrm	0.06	0.061
		^{13}C NMR		
Cyano carbon	115.5, 115.0	mr, rm	0.56	0.495
	115.4, 114.9	rr	0.30	0.303
	115.3, 114.8	mm	0.14	0.202
Quaternary carbon	86.6, 84.1	mm	0.20	0.202
	86.0, 83.5	mr, rm	0.51	0.495
	85.4, 82.9	rr	0.29	0.303

[a]Chemical shifts in ppm (see Experimental Section for details).

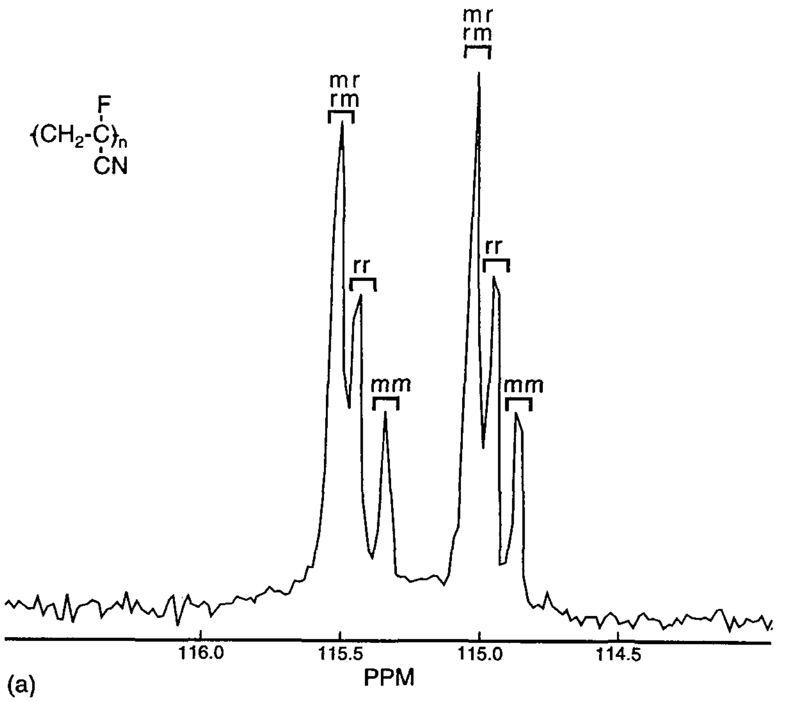


FIG. 5a. ^{13}C-NMR spectrum of PFAN cyano carbon region.

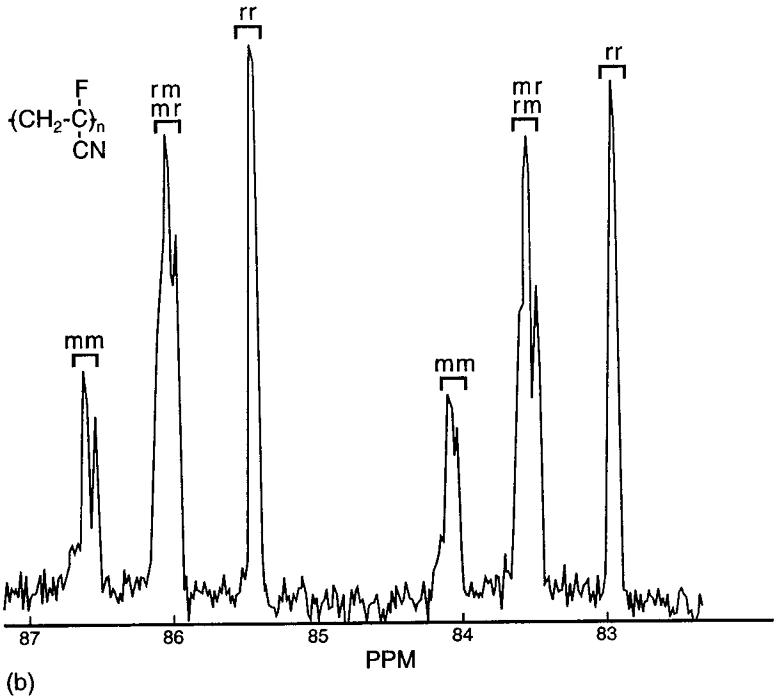


FIG. 5b. ^{13}C-NMR spectrum of PFAN quaternary carbon region.

and the calculated and integral areas show good agreement based on the *P*(*m*) value. The C—F coupling constant is found to be 189.1 Hz.

The above results indicate that both PFAN and PEFA are atactic. In both polymers the fluorine spectra are resolved sufficiently to allow the assignments of the pentad microstructure, and correlation can be found in some regions of the carbon spectra. Both polymers have nearly a random distribution of meso and racemic diads, with a small preference for the addition at the end of the polymer chain to be in the racemic position.

Further characterization of the two polymers was directed toward molecular weight analysis. The molecular weight (M_v) of PFAN was estimated using intrinsic viscosity measurements determined in DMF at 30°C. The intrinsic viscosity was determined from analysis of the results of experiments at four dilutions of PFAN in DMF following standard techniques [17]. The value was determined to be η = 1.67. Mark-Houwink coefficients of *K* and *a* for polyacrylonitrile in DMF at 30°C [17] were used and resulted in a molecular weight for PFAN of about 130,000 g/mol. While the polarity of the two polymers is different, which may lead to small discrepancies in the *K* and *a* values, we expect polyacrylonitrile to be a good model for PFAN. Ueda and Yazawa [5a] reported an M_n of 200,000 g/mol for PFAN in DMF at 30°C. While PFAN is THF insoluble, precluding GPC analysis, the number-average molecular weight of the THF-soluble PEFA is 36,000 g/mol (relative to polystyrene standards).

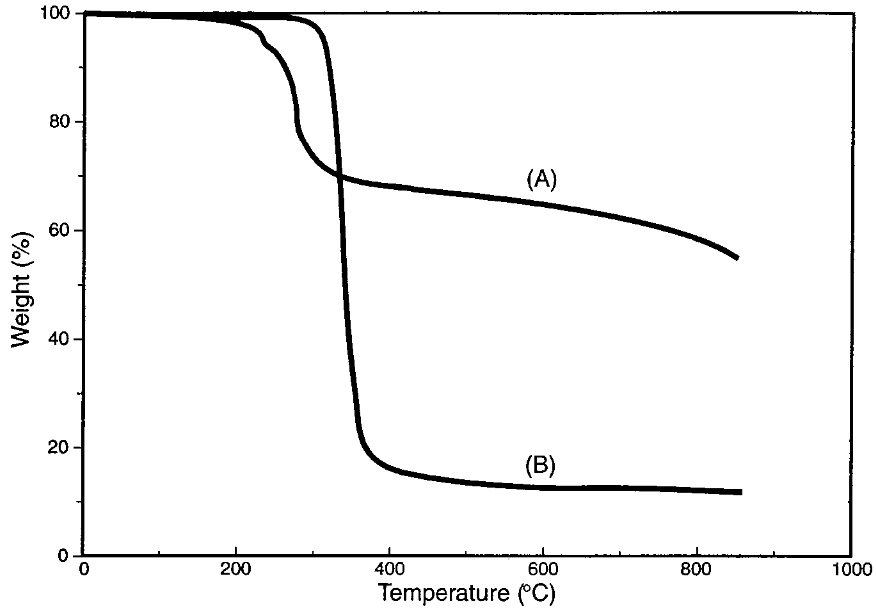


FIG. 6. TGA of PFAN (A) and PEFA (B) in an N_2 atmosphere.

The thermal stability of both polymers was analyzed by TGA in an N_2 atmosphere (Fig. 6). PFAN had no decomposition below 200°C, with subsequent HF loss (30%) between 250°C and 300°C. The remaining material likely undergoes cyclization of the cyano groups along the backbone to give a ladder-type polymer [5a, 18] as little further weight loss is observed to 800°C. The TGA of PEFA indicates thermal stability to above 300°C with almost complete degradation by 400°C.

The dielectric permittivities (ϵ) for PFAN and PEFA were determined and found to be 8.9 and 4.0, respectively, at 50 Hz. The ϵ of 8.9 for PFAN was similar to an ϵ of 11.0 for commercial polyvinylidene fluoride. Since both polymers are atactic, these values suggest that the generation of more regiocontrolled polymers might lead to higher permittivities. These very preliminary results are highly encouraging and indicate that the potential for higher dielectric permittivities with α-fluorinated polymers is possible.

CONCLUSIONS

Poly(α-fluoroacrylonitrile) has been synthesized and completely characterized spectroscopically. The results of the NMR analysis indicate that the polymer is atactic and follows Bernoullian statistics with $P(m) = 0.45$. The molecular weight was found to be about 130,000 g/mol based on intrinsic viscosity measurements. The polymer is stable to about 200°C whereupon HF is lost and the resulting material cyclizes to form a ladder polymer. The dielectric permittivity was measured and found to be 8.9 at 50 Hz, similar to the $\epsilon = 11.0$ found for commercially available polyvinylidene fluoride.

Poly(ethyl α-fluoroacrylate) has been synthesized and completely characterized spectroscopically. The NMR spectroscopic results indicate that the polymer is atactic and follows Bernoullian statistics with $P(m) = 0.40$. GPC analysis indicates that the polymer has a number-average molecular weight of 36,000 g/mol (relative to polystyrene standards). TGA analysis indicates that the polymer is stable to 300°C with almost complete degradation by 400°C. An $\epsilon = 4.0$ at 50 Hz was found for PEFA.

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