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^{19}F NMR characterization of electron beam irradiated vinylidene fluoride–trifluoroethylene copolymers

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Abstract

Electron beam irradiated poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] copolymers have been recently shown to exhibit "giant" electrostrictive stains. In this work, ^{19}F nuclear magnetic resonance (NMR) spectroscopy was used to probe structure of P(VDF–TrFE) copolymers before and after irradiation in order to elucidate the chemistry associated with the development of outstanding electroactive properties. The two-dimensional solution-state ^{19}F NMR of as-synthesized copolymers reveals strong (~300 Hz) geminal indirect coupling (^2J) and the resulting assignments have some differences from the previous literature. The most frequently occurring sequence containing TrFE is –CH_2–CF_2–CHF–CF_2–CH_2–, followed by –CF_2–CH_2–CHF–CF_2–CF_2–. This reveals a strong preference for the TrFE units to be isolated and a slight preference for the head-to-tail addition. Both sequences contain VDF polymerized in the same direction around the central TrFE monomer unit. Resolution of bonding environments in the insoluble irradiated P(VDF–TrFE) required the use of fast (25 kHz) magic angle spinning (MAS) solid-state ^{19}F NMR at elevated temperature. Of the resolved peaks formed by irradiation, the side group CF_3–CH<, was present in the highest concentration. Such CF_3 pendant groups are likely to reduce crystallinity and thus impact electroactive properties. Also observed was significant formation of CF_3–CF_2–, which can be either a pendant group or a side group. Several types of CF_3 end groups were observed: CF_3–CHF, CF_3–CH_2, and CF_3–CH=. The latter, indicates the formation of some unsaturated bonds upon irradiation. Small concentrations of –CHF_2 and –CF_2H were also found. Cross-linking is indirectly evidenced by broadening of the NMR spectra of the irradiated material. In the unirradiated copolymer, two conformation; of sequence –CH_2–CF_2–CHF–CF_2–CH_2– are observed in the solid-state. In the solution-state in the post-irradiated solid-state, only one of these conformations exists.

Keywords: Magic angle spinning; Nuclear magnetic resonance; Poly(vinylidene fluoride–trifluoroethylene)

1. Introduction

Poly(vinylidene fluoride–trifluoroethylene) [P(VDF–TrFE)] copolymers have recently been shown to have unusually good electroactive properties (~4% strain) when irradiated with high energy (1–3 MeV) electrons [1–3] or gamma rays [4]. The combination of a large electrostrictive response with a large elastic energy density has been proposed to result from the formation of nanometer scale domains within the all-*trans*-β-crystalline phase of the copolymer [5]. Fundamental understanding of the chemical structure and irradiation chemistry of P(VDF–TrFE) is key for optimizing and exploiting its desirable properties, motivating research employing a variety of different characterization methods [6–9]. However, only limited use has been made of ^{19}F nuclear magnetic resonance (NMR) spectroscopy [7,10].

High resolution ^{19}F NMR spectroscopy can provide a wealth of structural and dynamical information on fluoropolymers [11,12]. The excellent detection sensitivity of ^{19}F NMR results from the 100% isotopic abundance and a high gyromagnetic ratio of the ^{19}F nucleus. Also, the isotropic chemical shift range is ~20 times broader for ^{19}F than ^{1}H, which favors the resolution of differences in chemical bonding configurations. Direct integration of the spectral intensities of the resolved peaks yields the compositional make-up of the polymer. Achievable resolution allows fluorocarbon sequences of five or more carbon bond lengths to be differentiated, thus providing knowledge of sequence distribution for determining copolymer randomness and stereochemistry. Each of these factors may be in turn affect the irradiation chemistry and products. High resolution ^{19}F NMR has been applied to the study of radiation modification in other types of fluoropolymers [13–15].

For soluble materials, such as the unirradiated P(VDF–TrFE) copolymers, solution-state NMR provides the highest

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resolution of distinct bonding environments. Also, two-dimensional (2-D) NMR techniques are commonly used in the solution-state to afford definitive chemical shift assignments of the various resonances [16,17]. However, to observe polymeric configurations which are present only in the solid-state or to acquire spectra from insoluble materials, such as the VDF–TrFE copolymers after irradiation, solid-state NMR is required. Homonuclear dipolar coupling and chemical shift anisotropy, which inherently broaden solid-state spectra, are readily reduced by magic angle spinning (MAS). Advances in NMR probe technology have enabled spinning speeds in excess of 25 kHz. At these MAS speeds, high resolution ^{19}F NMR is readily achieved [14,18]. By acquiring fast MAS spectra at higher temperatures, it is possible to increase the resolution even further [19]. The additional resolution results from increased polymeric mobility at elevated temperature, which provides further motional averaging of the intrinsic spectral broadening.

In this work, ^{19}F correlation spectroscopy (COSY), a 2-D NMR method, is employed to assign the isotropic chemical shifts for the dissolved unirradiated VDF–TrFE copolymer. The resulting assignments of CF_2 region show some differences from the previous literature [10]. There are two important factors which lead to these differences. First, the two F nuclei in a CF_2 group are not necessarily chemically equivalent [20]. Second, these two fluorines display strong (~300 Hz) geminal *J*-couplings [20]. The combination of these two factors results in a multiplet of peaks corresponding to single type of CF_2 group The 2-D NMR also permits assignment of parts of the CHF region for the first time. The assignments from the solution-state NMR are then applied to interpret the fast MAS spectra acquired at elevated temperature. This solid-state method is then used to study the irradiation chemistry of the P(VDF–TrFE) copolymer.

2. Experimental

Polytetrafluoroethylene (PTFE) homopolymer, PTrFE homopolymers and P(VDF–TrFE) copolymer samples were supplied by Solvay SA, Belgium, in powder and pellet forms [21]. Three different copolymer compositions were studied: 86/14, 65/35, 50/50. The numbers in these ratios denote the weight percentages of VDF–TrFE as reported by the supplier. Additional 86/14 copolymer samples were obtained from Measurement Specialities Inc., Norristown, PA. At the Naval Undersea Warfare Center (NUWC, Newport, RI), films were solvent-cast methyl ethyl ketone solutions and then annealed at 140 °C for 1 h. The films were irradiated at MIT's High Voltage Research Laboratory under a nitrogen purge. Irradiation at electron beam energies of 1.2 MeV was carried out at 100 °C. High energy, 2.55 MeV irradiation was performed at 120 °C. Doses of up to 1.25 MJ kg^{-1} (SI) were used.

High resolution variable temperature magic angle spinning (VTMAS) solid-state ^{19}F NMR experiments were performed on a home-built spectrometer at a ^{19}F Larmor frequency of 254.0 MHz using a Chemagnetics probe with spinning capabilities up to 25 kHz. Between 10 and 15 mg of copolymer was packed into the 3.2 mm diameter zirconia MAS rotor. A duration of 1.1 μs was used for the 90° pulse and the MAS peed was set to 23 kHz. Spectra were referenced versus PTFE at −123.2 ppm. The sample temperature was controlled by running VT nitrogen through the probe while the drive and bearing MAS gases remained at room temperature. $^{207}Pb(NO_3)_2$ was used for temperature calibration [22]. An increase of 30 °C in the rotor temperature was observed upon spinning to 2.3 kHz. The sample temperature was maintained at 170 °C during experiments well above the melting point of the unirradiated fluorinated polymers of approximately 150 °C.

For the ^{19}F COSY NMR spectra, approximately 15 mg of the 65/35 copolymer sample was dissolved in D-acetone to give a 10 wt.% solution. Liquid-state ^{19}F NMR spectra without proton decoupling were acquired on a Bruker Avance DPX400 spectrometer at a ^{19}F Larmor frequency of 376 MHz. The peaks on the 1-D NMR liquid state spectra had a half-height line-width of approximately 150 Hz regardless of the concentration. For the 2-D COSY experiments, 1024 slices of 2054 points were recorded with increments of 18.4 μs in evolution time. For each slice, 16 scans were accumulated using phase cycling. The data were then multiplied by an echo window function, zero-filled, Fourier transformed, and symmetrized, resulting in 2-D spectra of 2054 by 2054 points covering 55 kHz in both dimensions.

3. Results and discussion

3.1. Unirradiated copolymer

The 1-D ^{19}F solution-state NMR spectra of the unirradiated copolymers (Fig. 1A–C) contains resonances in only two regions. As has been previously reported [10], peaks between −90 and −130 ppm are assigned to fluorine CF_2 groups, while peaks in the range from −190 to −220 ppm are assigned to fluorine in the CHF groups. The integrated area of the CF_2 region, A_{CF_2}, provides two units of fluorine intensity for each unit of VDF (–CH_2–CF_2–) and TrFE (–CHF–CF_2–). The area of CHF region, A_{CHF}, provides one unit of fluorine intensity for the TrFE units only. Thus, the mole fraction of TrFE in the copolymer is then simply calculated as $A_{CHF}/((1/2)A_{CF_2})$. The mole fraction and its conversion to weight percent are shown in Table 1, along with the nominal weight percentage specified by the supplier.

The structure within the CF_2 and CHF regions of Fig. 1 is determined by chemical shift differences for sequences of five carbon units in length. The most significant influence is the number of fluorine bonded to the two α-carbon groups.

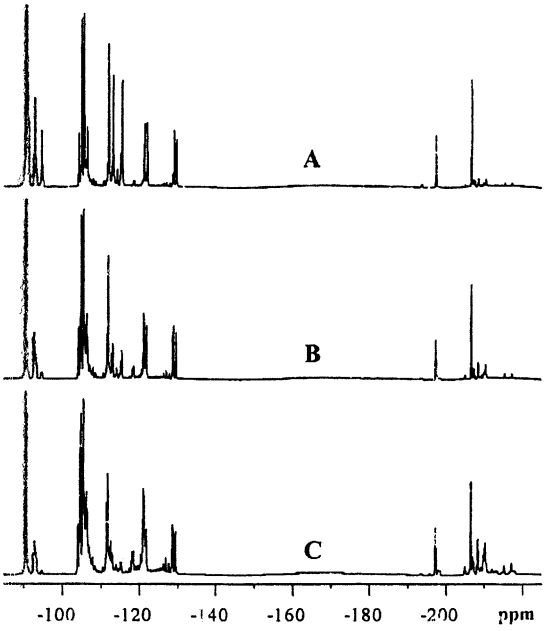

Fig. 1. ^{19}F liquid-state NMR spectra of P(VDF–TrFE) copolymer with three different compositions 86/14 (A); 65/35 (B); and 50/50 (C). The numbers in these ratios denote the weight percentages of VDF–TrFE. Copolymers were dissolved in D-acetone (10 wt.%) and spectra were referenced vs. hexafluorobenzene (−162.9 ppm).

Table 1
Compositions of P(VDF–TrFE) copolymers as measured by ^{19}F NMR

Weight fraction from supplier	Molar fraction measured	Weight fraction measured
50/50	61/39	55/45
65/35	72/28	67/33
86/14	88/12	85/15

Smaller shifts result from the two β-carbon groups. In PVDF homopolymers, the replacement of CF_2 by CH_2 at one α-position gives a +9.5 ppm change in chemical shift. Substitution by two α-CH_2 gives +28.4 ppm difference. Similar substitution at the β-position results in −3 and −4 ppm differences for one and two β-CH_2, respectively [23,24]. All the sequences of carbon pentads that were positively assigned in the P(TrFE) homopolymer and P(VDF–TrFE) copolymers studied are displayed in Table 2. For simplicity, the CF_2, CHF, and CH_2 groups are denoted only by their number of fluorine: 2, 1 and 0, respectively. The pentads resolved by NMR can be directly related to five of the six carbons of a trimer sequence. There are 16 distinct triads with 20 as the central unit and another 16 having 21 as the central unit. Relationships between pentads can be used to infer the order of up to five two-carbon monomer units.

The solution-state 2-D ^{19}F NMR of the unirradiated copolymers (Figs. 2 and 3) display off diagonal peaks as a result of homonuclear *J*-couplings. Strong (∼300 Hz) geminal couplings (^2J) occur through two bonds (e.g. F–C–F) [20]. For ^2J-coupling, the two fluorine on a single CF_2 group must be chemically inequivalent to display off-diagonal peaks. Thus, asymmetric sequences with two different α-carbon groups such as CHF–CF_2–CH_2 and CHF–CF_2–CF_2 can exhibit ^2J-couplings, while the symmetric sequences CH_2–CF_2–CF_2 or CH_2–CF_2–CH_2 do not. The symmetry of the CHF–CF_2–CHF sequence depends on the *cis* or *trans* configuration of the hydrogen and fluorine atoms on the α-carbons. The symmetric configuration gives rise to a singlet, while asymmetric configuration appears as a quartet. A clear signature of ^2J-coupled peaks will also be observed in the COSY spectrum as a square set of off diagonal peaks. The vicinal (^3J and ^4J) couplings are on the order of 10 Hz [20]. These smaller couplings occur through three or four bonds

Table 2
^{19}F NMR chemical shift assignments referenced vs. hexafluorobenzene (−162.9 ppm)[a]

Sample	Peak	α-carbon	β-carbon	Chemical shift (ppm)	^2J-coupling (Hz)	Reference
TrFE	CF_2	1$\underline{2}$1	21$\underline{2}$12^t	−121.2		[33]
			21$\underline{2}$12^c	−117.4, −119.9	300	
Copolymers P(VDF–TrFE)	CF_2	0$\underline{2}$0	20$\underline{2}$02	−90.7		[34,35]
			20$\underline{2}$01	−92.7		[10]
			20$\underline{2}$00	−94.4		[10]
		0$\underline{2}$1	20$\underline{2}$12	−104.5, −106.0	280	
		0$\underline{2}$2	120$\underline{2}$21	−111.6		[10]
			020$\underline{2}$21	−111.8		[10]
			120$\underline{2}$20	112.6		
			020$\underline{2}$20	−113.0		[34,35]
			00$\underline{2}$20	−115.2		[10,11]
		1$\underline{2}$1	21$\underline{2}$12^t	−121.2		[33]
			21$\underline{2}$12	−118.0, −118.6	300	
		1$\underline{2}$2	02$\underline{2}$10	−121.5, −129.1	280	
	CHF	0$\underline{1}$2	20$\underline{1}$22	−197.3		
		2$\underline{1}$2	020$\underline{1}$20	−206.6		
			02$\underline{1}$21	−208.4, −210.3	NA	

[a] Superscripts *t* and *c* denote the *trans* and *cis* configurations of the α-carbons, respectively.

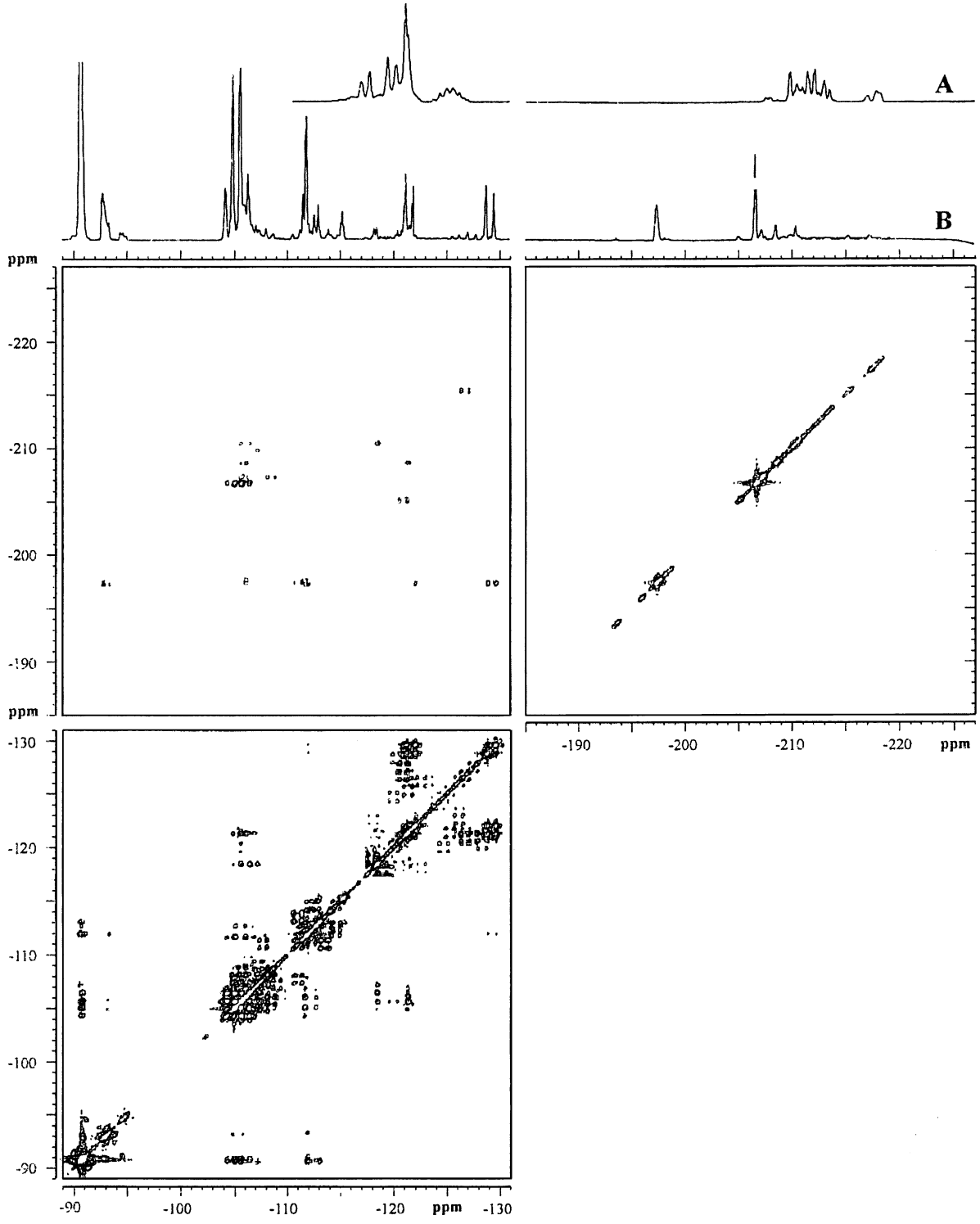

Fig. 2. ^{19}F COSY NMR spectrum of unirradiated 65/35 wt.% P(VDF–TrFE) copolymer with the 1-D projections shown across the top (B). Also displayed along the top for purposes of comparison is the 1-D spectra of the PTrFE homopolymer (A).

(e.g. F–C–C–F or F–C–C–C–F) and thus allow the connectivity between α- and β-carbon groups to be established.

Fig. 2 presents the *J*-correlated spectrum of the 65/35 copolymer in three pieces. The lower left portion of Fig. 2, shows correlations between pairs of CF_2 groups. This same section is shown in Fig. 3, where the cut-off intensity has been increased in order to retain the most intense ^2J-correlated cross-peaks. The off diagonal signatures of the four peaks at −104.1, −104.9, −105.6 and −106.3 ppm indicate the strong ^2J-coupling of an asymmetric CF_2 group. The

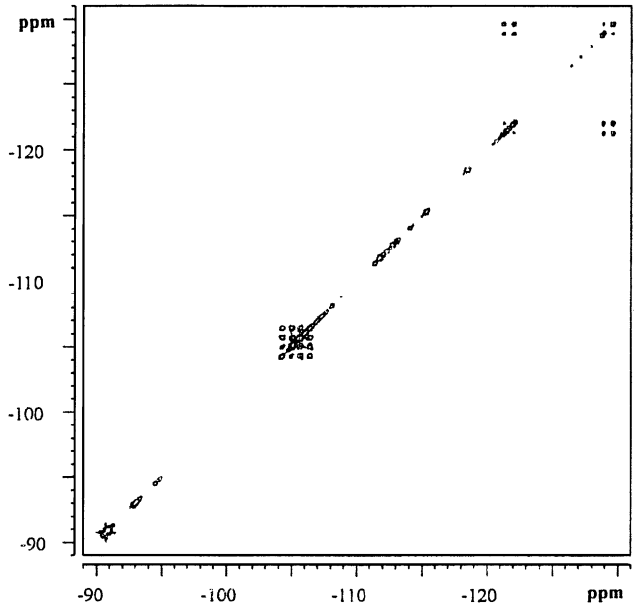

Fig. 3. The cut-off intensity for the lower left part of Fig. 2 has been increased in order to display only the most intense peaks.

same conclusion can be drawn for the quartet at −121.2, −121.9, −128.8, and −129.5 ppm.

^3J- and ^4J-couplings allow the connectivity between α- and β-carbon groups to be established and are useful in assigning the structure of the polymer chain prior to irradiation. Knowledge of the backbone structure is critical for predicting the structure of products formed by irradiation. Although not shown, 2-D COSY spectra for the 50/50 and 86/14 copolymer were also obtained. The variation in composition proved valuable to the assignment process, as the 50/50 copolymer provided more intensity in some cross peaks while the 86/14 providing fewer total peaks helped to confirm the main assignments.

The upper right portion of Fig. 2, where ^3J-coupling between adjacent CHF groups would be observed, shows no detectable off-diagonal peaks, suggesting few linkages between CHF units. Additionally, the two most intense peaks in the CHF region, do not appear in the P(TrFE) spectrum (Fig. 2A, top). This supports the hypothesis that there are relative few adjacent TrFE units. Thus, the two most intense peaks in the CHF region of the ^{19}F NMR spectrum are hypothesized to represent therefore only two trimers. For the 86/14 copolymer, these two peaks are clearly dominate (Fig. 1A). The reactivity ratios for the polymerization of VDF with TrFE, $r_{\mathrm{VDF}} = 0.7$, $r_{\mathrm{TrFE}} = 0.5$ indicate that TrFE is more likely to be adjacent to VDF than itself [25]. Thus, at low fractions of TrFE, such as the 86/14 copolymer, the population of sequences with a single isolated TrFE unit in a PVDF chain (VDF:TrFE:VDF) is likely to be much larger than for chains which have dimers of adjacent TrFE units (e.g. VDF:TrFE:TrFE). Chains containing three or more successive TrFE units are even less probable. Thus, only the four distinct trimers having one central TrFE unit will be considered: 20:21:20, 02:21:20, 02:21:02, and 20:21:02.

The most intense CHF peak at −206.6 ppm is correlated to the (0 2 1) quartet at −104.1, −104.9, −105.6 and −106.3 ppm, eliminating two of the four possible trimes from consideration. This (0 2 1) quartet is ^4J-coupled on the left to the sequence 20:20:2 with a line of cross-peaks going from the (x, y) coordinates (−90.7, −104 ppm) to (−90.7, −106 ppm), suggesting a VDF:VDF:TrFE:VDF:VDF pentamer in which all of the units are joined head-to-tail, denoted by the shorthand 20:20:21:20:20 (or 02:02:12:02:02).

The other strong CHF peak at −197.3 ppm should correspond to one of the remaining three trimers: 02:21:20, 02:21:02, or 20:21:02. The large chemical shift from the 20:21:20 peak at −206.6 ppm suggests the presence of 221 triad, which is confirmed by ^3J-coupling to the 122 quartet at −121.2, −121.9, −128.8, and −129.5 ppm. Thus, only 02 : 21:20 and 02 : 21:02 remain as possibilities. The 20201 related cross-peak at (−92.7, −197.3 ppm) narrows the final choice to 02:21:02. It also identifies that two VDF units linked head-to-tail are adjacent to left of the TrFE unit. Cross-peaks found at coordinates of (−111.8, −128.8 ppm), (−111.8, −129.5 ppm), (−111.8, −197.3 ppm) are related to the sequences 12:20:2, 0:12:20, and 12:20:2, respectively. Thus, two VDF units are also adjacent to the right of the TrFE unit. Thus, the final assignment is a VDF:VDF:TrFE:VDF:VDF pentamer, where the sense of the TrFE polymerization is opposite to that of both VDF units, i.e. 20:20:12:20:20 (or 02:02:21:02:02).

Considering the two primary trimer sequences with the isolated TrFE units, a quantitative comparison between peaks 02120 and 20122 shows that there is a slight preference for the head-to-tail addition.

Koenig presented three models of coplymerization in which the last one, two, or three monomer units in a propagating polymer radical affect the probability of the next monomer to be added (terminal, penultimate, penpenultimate models) [25,26]. Supposing that the copolymerization of VDF with TrFE can be described by a terminal model, one would expect to get a high concentration of sequence such as 02:21:20 or 20:12:02, where a TrFE unit is in a reverse position as compared to the first VDF group and where the second VDF unit is in a head-to-tail position with regards to the TrFE group. Such sequences were not observed in any of the spectra. On the contrary, in the two main sequences 02:12:02 and 02:21:02 described above, the two VDF units surrounding the central TrFE monomer are polymerized in the same direction. These two sequences are indeed strongly favored over trimers such as 02:21:20 and 20:12:02, which reverse the sense of the neighboring VDF units. This observation supports the fact that the VDF–TrFE copolymerization does not follow the terminal model.

The comparison between 1-D spectra for the P(TrFE) (Fig. 2A) and P(VDF–TrFE) (Fig. 2B) copolymers shows that they have a singlet peak in common at −121.2 ppm.

This peak is attributed to a *trans* 21$\underline{2}$12 sequence. For the P(TrFE) homopolymer, this sequence is the result of three TrFE units in a head–tail position. For the copolymer, this five-carbon segment comes from one VDF unit attached to two TrFE units such as 02:12:12 (or 21:21:20). The CF_2 portion of the P(TrFE) spectrum also has a quartet at −117.0, −117.8, −119.5 and −120.3 ppm attributed to a *cis* 21$\underline{2}$12 sequence. A (1 2 2) sequence resulting from two TrFE units head-to-head was ruled out because three-carbon 1$\underline{2}$2 segments all appear from −121 to −122 ppm for the first doublet and from −125 to −129 ppm for the second. The same type of peaks appears in the copolymers spectrum at −117.6, −118.4, −118.2 and −119.0 ppm also attributed to a *cis* 21$\underline{2}$12 segment. Fig. 1 shows that the intensity of these peaks increases faster from the 86/14 to the 50/50 spectrum than any of the VDF:TrFE:VDF peaks assigned previously. This supports our interpretation based on a VDF:TrFE:TrFE sequence. Finally, both ^{c}21$\underline{2}$12 and ^{t}21$\underline{2}$12 peaks are coupled to their neighboring CHF which leads to the following assignment 02:$\underline{1}$2:1 for the peaks at −208.4 and −210.3 ppm. Both ^{c}21$\underline{2}$12 and ^{t}21$\underline{2}$12 peaks are also ^{4}J-coupled to the quartet 20$\underline{2}$12 through the cross-peaks a (−118, −106 ppm) and (−121.2, −106 ppm). This correlation comes from 20:21:21 trimers although surprisingly no CHF–CHF cross-peaks were observed.

4. Irradiated copolymer

The intrinsic sensitivity of high speed MAS ^{19}F NMR at elevated temperatures has allowed resolution of multiple types of new bonding configurations resulting from irradiation of P(VDF–TrFE) copolymers. Fig. 4 compares the solid-state ^{19}F NMR spectra of the 65/35 copolymer before and after irradiation by 2.55 MeV electrons with a total dose of 1.25 MJ kg^{-1}, showing several resolvable resonances induced by irradiation. Similar peaks were formed by experiments at other dosages involving two different copolymer compositions (75/25 and 50/50) and two different electron energies (1.2 and 2.5 MeV).

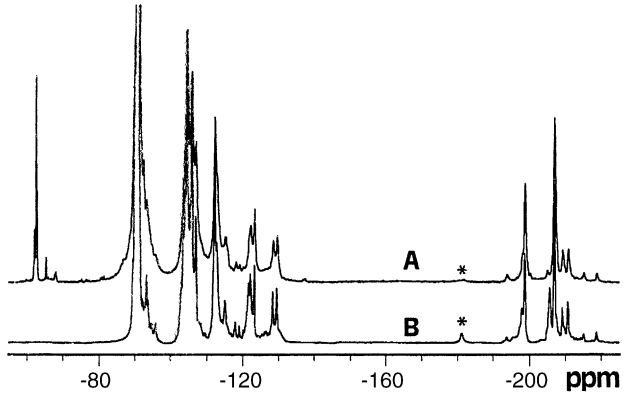

Fig. 4. ^{19}F NMR spectra of a 65/35 wt.% P(VDF–TrFE) copolymer before (B) and after (A) irradiation (1.25 MJ kg^{-1} at 2.55 MeV). Spectra referenced vs. PTFE (−123.2 ppm); (∗) denotes a side-band.

One of the main changes determined by NMR is associated with the disappearance of the CHF peak at −205.3 ppm upon irradiation (Fig. 4). Furthermore, a comparison between the liquid state NMR spectrum (Fig. 2B) and the unirradiated solid-state spectrum (Fig. 4B) reveals that the peak also disappears when the polymer is dissolved. Thus, it is believed that the 02$\underline{1}$20 configuration can adopt two different local conformations. The primary one gives a peak at −206.6 ppm. The secondary conformation with a signature peak at −205.3 ppm exits only in the unirradiated polymer and is lost in solution or upon irradiation. The intensity of the peak at −205.3 ppm is undetectable at all irradiation doses examined. Thus, the associated conformational change is fully induced by irradiation at the lowest dosage or its associated heating.

Two low intensity peaks are seen at −137.1 and −235.9 ppm, corresponding to –CF_2H and –CFH_2 groups, respectively (Table 3). A third set of low intensity peaks is observed between −75 and −80 ppm and are assigned to CF_3 end groups. Similar peaks were observed in radiation modified PTFE examined in this study and in previous work [13].

Irradiation also results in a set of intense peaks in the region from −60 to −70 ppm. This chemical shift range is associated with –CF_3 groups with varying nearest neighbor substituents. These CF_3 groups can form either end groups or side groups on the polymeric chains. The concentration of CF_3 groups increases linearly with irradiation (Fig. 5a) with a corresponding *G*-value of 3 mol J^{-1}. At the highest dosage investigated, 1.25 MJ kg^{-1}, 0.4 mol kg^{-1} of CF_3 (2 mol CF_3) is formed. Note that this represents the minimum concentration of the species in the copolymer which must be susceptible to irradiation. Thus, defects present at low concentrations cannot be entirely responsible for the formation of CF_3 groups. Additionally, if all of the CF_3 were end groups for linear chains, the irradiated samples would have only an average of 100 carbons per chain. However, the material becomes insoluble with irradiation, so cross-links and branches terminating in CF_3 must also be forming. Fig. 5 shows no significant difference between the two different copolymers compositions, 65/35 and 50/50. As the CF_3

Table 3
List of peaks formed or destroyed upon irradiation

Species	Shift (ppm)
CF_3–CH<	−62.5
CF_3–CH=	−64.3
CF_3–CH_2	−67.7
CF_3–CHF–[a]	−75.1
CF_3–CHF–[a]	−76.5
CF_3–CF_2–	−81.0
–CF_2H	−137.1
–CH_2–CF_2–CHF–CF_2–CH_2–	−205.3
–CFH_2	−235.9

[a] Conformational differences.

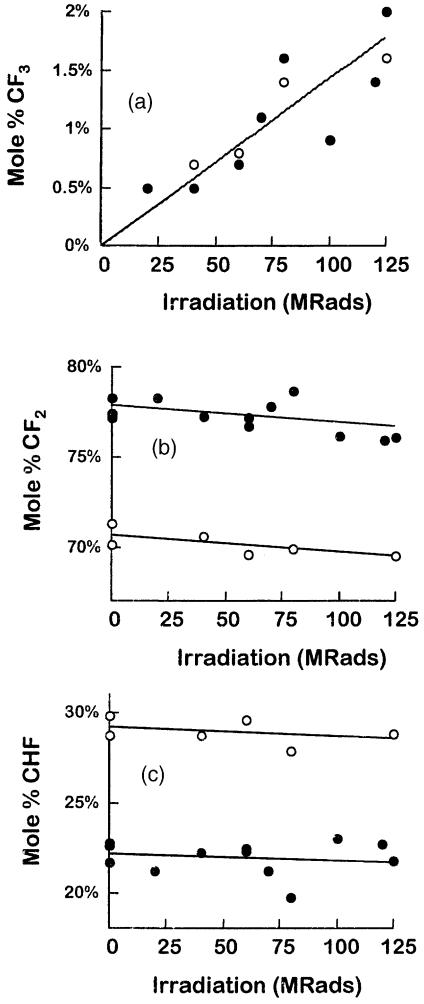

Fig. 5. Mole percentages of (a) CF_3; (b) CF_2; and (c) CHF as a function of electron beam dose for the 65/35 (filled circles) and the 50/50 (open circles) P(VDF–TrFE) copolymers.

concentrations increases with dose, the concentrations of both CHF and CF_2 units drop off linearly.

In order of decreasing intensity, the most clearly resolved peaks produced upon irradiation of the PVDF–TrFE copolymer (Fig. 6, top) are located at −62.5, −64.3, and −67.7 ppm. These three peaks do not appear in ^{19}F NMR spectrum of electron beam irradiated PTFE [13]. Thus, these three peaks must correspond to the irradiation products of polymeric segments containing hydrogen. The peaks at −62.5 and −67.7 ppm are also observed in the irradiated PVDF homopolymer spectrum (Fig. 6, bottom) and thus are most likely formed from $–CH_2–CF_2–$ segments. The peak at −64.3 ppm is absent from the spectrum of irradiated PVDF homopolymer and is most likely formed from segments containing CHF.

Unfortunately, the use of 2-D NMR to assign the nearest neighbor substituents of the $–CF_3$ groups was unsuccessful. The primarily limitation was the line-widths in both the high-temperature solid-state NMR and solution NMR of the swollen irradiated copolymer. The relative broadness

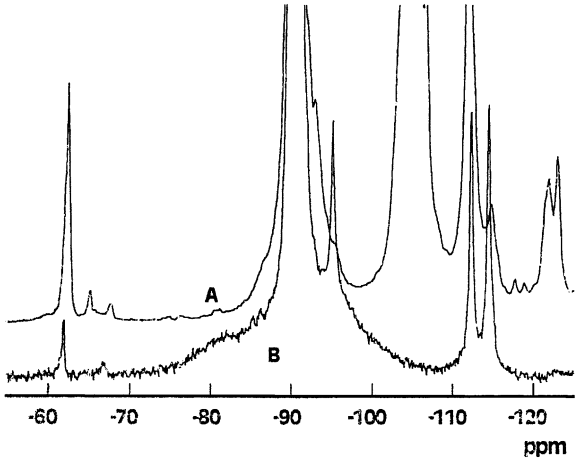

Fig. 6. Comparison between the 1.25 MJ kg^{-1} irradiated 65/35 copolymer (A) and an irradiated PVDF homopolymer (B).

of these lines reduced the maximum intensity of the off-diagonal cross peaks in the 2-D NMR spectra to below the signal-to-noise level. Thus, a more conventional assignment strategy using literature assignments of the 1-D NMR spectra will be presented.

First, α-carbon substituents with fluorine can be ruled out as the isotropic chemical shifts for $CF_2–CF_3$, CHF–CF_3, and =CF–CF_3, fall at −83.7, −74.9, and −71.5 ppm, respectively. Next, the oxygen-containing groups –(C=O)–CF_3 (−76.6 ppm) and O–CF_3 (−59.0 ppm) were ruled out on the basis of chemical shift. In addition, a relatively large amount of oxygen would be required to account for the intensity of the peaks between −60 and −70 ppm. While oxygen may not have been completely removed from the polymer before irradiation in an inert environment, it is unlikely that such a concentration remains dissolved. Also, no intensity was seen for carbonyl fluoride (COF) in the 15–30 ppm region. This is a common product of fluoropolymer irradiation if dissolved oxygen is available to react at the site of polymer scission event [27,28].

The remaining CF_3 groups to consider for assigning the peaks in the −60 to −70 ppm region have α-carbon substituents bonded to only hydrogen or they contain only carbon: $CH_2–CF_3$ (saturated end group or two-carbon side group, −67.9 ppm), =CH–CF_3 (saturated end group, 60.6, −64.7 ppm), >CH–CF_3, (saturated side group, 61.6 ppm) [29], or (=C–)CF_3 (unsaturated side group, −55.1, −59.4 ppm). Of these four possibilities, the first three fall in the appropriate chemical shift range. These assignments were determined for small molecules in solution. Small shifts are to be expected in the solid-state, as solvent effects are absent [20].

Thus, the proposed assignments for the irradiation produced peaks in the −60 to −70 ppm region are: >CH–CF_3 (−62.5 ppm), =CH–CF_3, (−64.3 ppm) and $–CH_2CF_3$ (−67.7 ppm). The predominant product, >CH–CF_3, is a pendant group, which in contrast to an end group, would not result in large scale molecular weight reduction. The

species, $–CH_2CF_3$ could represent such an end group but could also be pendant chain, two carbons in length.

The formation of high concentrations of pendant. groups (up to 2 mol%) has significant implications for the properties of the irradiated copolymers. Pendant groups decreases the ability of the chains to pack in the irradiated material. Thus, pendant groups would contribute to a loss of crystallinity and a reduction in the dimensions of the crystallite domains. The structural disruption caused by the pendant groups would be in addition to disorder induced by the formation of cross-linking sites. Small crystallite size in the irradiated copolymer has previous been postulated to result in the unusual electroactive properties of P(VDF–TrFE) [5]. Additionally, based on the known thermal decomposition pathways of branched fluoroalkanes [30], such pendant groups would be expected to reduce the thermal stability of the irradiated material. The evolution of CF_3 and CH_2CF_3 from the pendant groups would be anticipated upon heating.

To develop a mechanism for the formation of pendant groups, the most probable irradiation induced events in fluoropolymers were considered [31]. The polar nature of the CF bond renders it susceptible to homolytic cleavage by ionizing irradiation, resulting in reactive free fluorine radicals. The weaker C–C bonds also commonly scission upon irradiation. Carbon radicals formed in irradiated fluoropolymers generally do not participate in disproportionation reactions, as the high CF bond strength makes transfer of fluorine atoms is unfavorable. In contrast, hydrogen atom transfer a common reaction pathway in irradiated hydrocarbon polymers. It is unknown how the mixed chemical nature of the P(VDF–TrFE) copolymer will effect the relative ease of fluorine and hydrogen transfer reactions.

The formation of $–CF_3$ groups can easily be envisioned as the rupture of bond between a $–CF_2–$ unit and another carbon with subsequent acceptance a free fluorine radical by the $–CF_2^{\bullet}$ radical. However this CF_3 is an end group and the second carbon is still a radical. A complex pathway can be envisioned to form a $–CF_3$ pendant group which also consumes the second carbon radical. However, the NMR spectrum shows little evidence of either the intermediate reaction products or the expected products of side reactions.

The packing of adjacent chains may be a driving force for the formation of $>CH–CF_3$ end groups. Recall that the predominate sequences have the same sense of polymerization for the surrounding VDF units:

$$-[CF_2-CH_2]-[CF_2-CH_2]-[CF_2-CHF]$$
$$-[CF_2-CH_2]-[CF_2-CH_2]-$$

and

$$-[CF_2-CH_2]-[CF_2-CH_2]-[CHF-CF_2]$$
$$-[CF_2-CH_2]-[CF_2-CH_2]-$$

In these two favored configurations, all of the CH_2 units are spaced apart by an even number of carbon units (i.e. CH_2 occurs every second or fourth carbon). This regularity contributes to the efficient of packing adjacent polymeric chains. When the sense of polymerization of surrounding VDF units is reversed chains such as

$$-[CF_2-CH_2]-[CF_2-CH_2]-[CF_2-CHF]$$
$$-[CH_2-CF_2]-[CH_2-CF_2]-$$

result, having some of the CH_2 units are spaced an odd numbers of carbon units apart, inhibiting optimal packing with adjacent chains. Additionally, these less favored configurations may be more susceptible to reaction upon irradiation. The net rearrangement of a TrFE unit, $–CHF–CF_2–$, to the pendant group, $>CH–CF_3$, would restore the spacing of all CH_2 groups to an even number of carbon units along the backbone:

$$-[CF_2-CH_2]-[CF_2-CH_2]-[\overset{CF_3}{CH}]-[CH_2-CF_2]-[CH_2-CF_2]-$$

The proposed net rearrangement is consistent with the results of Fig. 5, the decrease of both CHF and on CF_2 units and the appearance of CF_3 with increasing irradiation dose. This mechanism, while conceptually simple, would require the transfer of fluorine from the CHF to the adjacent CF_2 group. While such reactions are unlikely in pure fluoropolymers, the mixed chemical nature of the P(VDF–TrFE) copolymer may increase the probability of this mechanism. Additionally, the unfavorable energetics associated with the breakage of the C–F bond may be partially offset by the simultaneous formation of the new C–C backbone bond.

While ^{19}F MMR has proved useful in identifying new irradiation products, it should be noted that other species may be present but are unable to be resolved for several reasons. An example would be cross-linking sites, which are one of the principle effects of the irradiation of P(VDF–TrFE) [32]. First, the concentration could be lower than the detection limit. Note that the detection limit will depend on the line-width of the peak and species having broader resonances will be correspondingly more difficult to detect. Broad line-widths may result from groups having large numbers of combinatorial possibilities for nearest neighbors. This may be a particularly important factor for cross-links having at least three α-carbon neighbors. Finally, the isotropic chemical shift for new peak could fall into regions of the spectra already occupied by the unirradiated resonances and thus be obscured. Even though cross-links were not directly detected by ^{19}F NMR the broader line-widths of the solid-state spectra for the irradiated material (e.g. Fig. 4B) indirectly support for the existence of cross-links. The broadening in the spectra of the irradiated samples also limits the ability to identify the species lost upon irradiation.

5. Conclusions

Two-dimensional ^{19}F NMR spectroscopy was found to be an extremely useful aid for assigning the spectrum of the

soluble as-synthesized fluoropolymers. This method was particularly valuable for identifying strong ^2J-couplings which lead to multiplets in the 1-D NMR spectrum. The ^3J- and ^4J-couplings allow the connectivity between α- and β-carbon groups to be established and are useful in assigning the structure of the polymer chain prior to irradiation. Knowledge of the backbone structure is an essential starting point for understanding the reaction products formed by irradiation.

In P(VDF–TrFE) copolymers, two most common sequences containing TrFE were found to be $–CH_2–CF_2–CHF–CF_2–CH_2–$ and $–CF_2–CH_2–CHF–CF_2–CF_2–$. This reveals a strong preference for isolated TrFE units. Comparing these two intensities showed a slight preference for the head-to-tail addition. Both sequences contain VDF polymerized in the same direction around the central TrFE monomer. Thus, for P(VDF–TrFE), two or more monomers in the propagating polymer radical appear to effect the probability for direction and identity of the next monomer to be added.

High speed MAS ^{19}F NMR at elevated temperatures allowed resolution of multiple types of new bonding configurations resulting from irradiation of P(VDF–TrFE) copolymers. Clearly resolved are various types CF_3, CF_2H, and CFH_2 end groups. One type of end group, $CF_3–CF=$, is adjacent to an unsaturated bond. No cross-links were resolved, but cross-linking is indirectly suggested by the broadening in the NMR spectra of the irradiated samples. The broadening of the spectra of the irradiated samples hampered the ability to resolve specific peaks which decreased in intensity upon irradiation. One peak was shown to completely disappear with the lowest dosage of irradiation used or with dissolution of the copolymer. This peak was a signed a one confirmation of the $–CH_2–CF_2–CHF–CF_2–CH_2–$ sequence.

The most intense (up to 2 mol%) and clearly resolved product of irradiation was $CF_3–CH<$. The formation of this pendant group and was an unexpected finding. Additionally, $CF_3–CH_2–$ was a prevalent irradiation product and could represent either an end group or a two-carbon pendant group. These pendant groups would decrease the crystallinity of the copolymer and hence may directly impact the electroactive behavior. The pendant groups are also anticipated to reduce the thermal stability.

The ^{19}F NMR characterization has added to the knowledge of the complex of the irradiation chemistry of P(VDF–TrFE). This fundamental knowledge may impact the understanding and optimization of electroactive properties of these irradiated copolymers.

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