Detection of Branching on Poly(vinyl fluoride) by NMR and the Effect of Synthesis Conditions on Polymer Structure

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Received July 30, 1990; Revised Manuscript Received January 2, 1991

ABSTRACT: Samples of poly(vinyl fluoride) have been examined by fluorine-19 NMR at 376.5 MHz and proton NMR at 400 MHz as solutions in *N*-methylpyrrolidone and as swollen gels in dimethyl-d_6 sulfoxide. Weak peaks in the fluorine NMR spectra have been assigned to CH_2CH_2F end groups and to tertiary fluorine atoms at branch points. A differential decoupling experiment, in which the proton spectrum was observed with and without selective irradiation of the weak fluorine peaks, permitted resonances of protons in the CH_2CH_2F end groups to be observed selectively. Pressure and temperature conditions used for polymer synthesis were found to influence branching but not the number of monomer reversals in the chain leading to head-to-head units. Monomer reversals account for about 13% of the vinyl fluoride in the polymer. Chain branching varies from about one branch every 80 monomer units to one branch every 200 monomer units depending on reactor conditions. Low polymerization temperature and high pressure yield the most linear polymers. Melting point and heat of fusion measured by DSC increase with the linearity of the product.

Introduction

Investigations of the microstructure of poly(vinyl fluoride) by fluorine NMR have been reported by Weigert[1] and Bruch et al.[2] Weigart studied a laboratory sample at 100 °C in dimethyl-d_6 sulfoxide. The broadband proton-decoupled fluorine NMR spectrum at 94.1 MHz showed two groups of peaks. The major group, in the region −178 to −182 ppm, was assigned to head-to-tail monomer units, while the minor group, in the region −189 to −197 ppm, was assigned to tail-to-tail monomer units. Peaks within each group were assigned to fluorine atoms from monomer units in different tactic sequences.

Bruch et al. studied a commercial sample and also a laboratory-prepared sample containing no monomer reversals. Broadband proton-decoupled fluorine NMR spectra of solutions in *N*,*N*-dimethylformamide at 130 °C were obtained at 188.2 MHz. A two-dimensional *J*-correlated NMR experiment enabled definitive assignments of the individual peaks to different tactic sequences to be made.

Experimental Section

Poly(vinyl fluoride) (PVF) samples were prepared by high-pressure free-radical polymerization of vinyl fluoride in aqueous dispersion in batch or continuous reactors using procedures previously reported.[3,4] NMR measurements were made with a Bruker WM-400 high-resolution NMR spectrometer operating at 400 MHz for proton NMR and at 376.5 MHz for fluorine NMR.

Most of the NMR measurements were made on solutions of the polymers in *N*-methylpyrrolidinone at 130 °C to which a small amount of dimethyl-d_6 sulfoxide (Me_2SO-d_6) had been added to provide the deuterium lock. More intense, although broader, spectra were obtained from samples swollen in Me_2SO-d_6 at 130 °C. This solvent also had the advantage of giving workable proton NMR spectra.

A differential decoupling experiment was used to link the resonances in the proton and fluorine NMR spectra via *J* couplings. In this, the proton FID was collected for a complete phase cycle of 16 pulses while one of the peaks in the fluorine spectrum was selectively irradiated. The fluorine irradiation was then moved off resonance, and data from a second phase cycle were obtained and subtracted from the first data set. This process was then repeated many times to build up an adequate signal-to-noise ratio. So that the fluorine irradiation frequency could be controlled from the Bruker software, it was derived from the WM-400 console proton decoupler output at 400 MHz by mixing with the output of a frequency synthesizer set at 23.5 MHz. The 376.5 MHz lower sideband was selected and amplified with a Hewlett-Packard Model 230B tunable amplifier. The proton NMR spectra were observed via the proton decoupling coil of a 5-mm fluorine probe, and fluorine decoupling signals were applied to the fluorine observe coil.

Results and Discussion

The fluorine NMR spectrum of a PVF sample swollen in Me_2SO-d_6 is shown in Figure 1. The two main groups of peaks corresponding to head-to-tail and head-to-head monomer sequences are seen, and their relative areas indicate that in this sample about 13% of the monomer units are reversed. The spectrum was referenced by taking the chemical shift of the sharp major high-frequency head-to-tail feature as −179 ppm.[2] At high sensitivity, weak features can be seen near −220, −147, and −162 ppm. The peaks at −220 ppm are assigned to CH_2F group fluorine atoms. These almost certainly arise from hydrogen abstraction by growing polymer radicals ending in CHF•.

Such a mechanism should result in the formation of tertiary fluorine atom sites in the backbone, as shown below. Weigert[5] has reported fluorine NMR data for monofluoro- and difluoro-substituted hydrocarbons, which indicate that the peaks near −147 ppm can be assigned to tertiary fluorine atoms originating from head-to-tail monomer units. For example, Weigert gives the fluorine-19 chemical shift of 3-methyl-3-pentyl fluoride as −149.1 ppm and that of 3-ethyl-3-pentyl fluoride as −156.2 ppm. An even weaker broad feature is seen near −163 ppm. This is probably due to tertiary fluorine atoms in branch points originating from head-to-head monomer units. On the basis of the data for the main-chain CHF resonances, these would be expected to resonate 10–16 ppm more negative than the tertiary fluoride atoms derived from head-to-tail monomer units.

The 400-MHz proton NMR spectrum of a poly(vinyl fluoride) sample swollen in Me_2SO-d_6 is shown in Figure 2. The features around 4.8 ppm are assigned to CHF protons and the features around 2.0 ppm to CH_2 protons. The feature at 2.9 ppm is from adventitious water. It was hoped it would be possible to identify in the proton spectrum weak peaks from the branched structures

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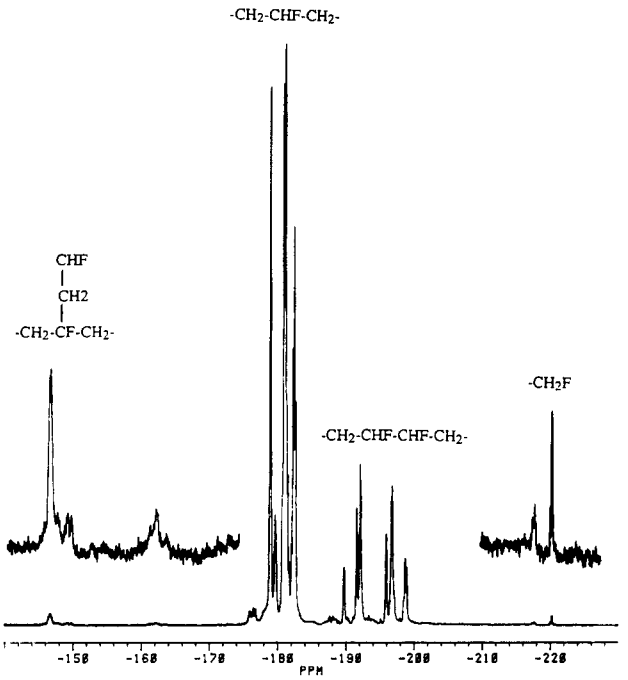


Figure 1. Proton-decoupled 376.5-MHz fluorine NMR spectrum of poly(vinyl fluoride). Inserts showing regions −140 to −170 and −212 to −228 ppm have been vertically expanded 16 times.

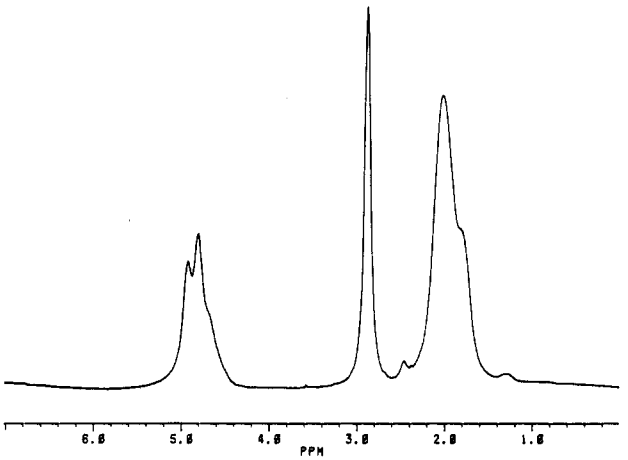
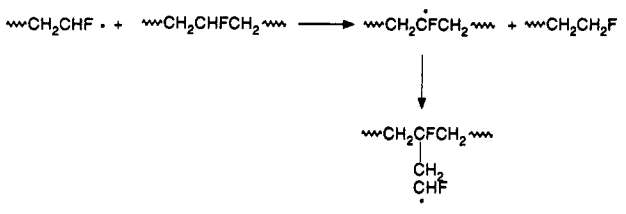


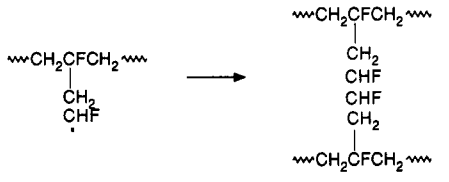
Figure 2. 400-MHz proton NMR spectrum of poly(vinyl fluoride).

detected by fluorine NMR. However, the proton spectrum was too broad for this to be done directly. Attempts at improving the resolution by Gaussian to Lorentzian resolution enhancement were unsuccessful. A weak peak visible at about 1.2 ppm may be due to methyl protons in end groups with structures $CHFCH_3$, originating from hydrogen abstraction by growing polymer chains ending in reversed monomer units.

For detecting the resonances of hydrogen atoms in chain ends and near branch points, the differential selective fluorine irradiation experiment was used to link the two spectra via H–F couplings.



branching



radical coupling

Irradiation of a particular fluorine peak should result in narrowing of the resonances of any protons coupled to the corresponding fluorine atom. These will then appear in a differential mode as sharpened features with the original broad peaks subtracted. The experiment was tested by irradiating one of the major fluorine resonances and gave a positive response. When both fluorine irradiation frequencies were in an empty part of the spectrum, little or no response was given in the proton spectrum, even at the positions of the major peaks. Figure 3 shows the differential proton spectrum obtained when the fluorine NMR spectrum was irradiated at −220 ppm, corresponding to the weak CH_2F resonances. A positive response from the CH_2F protons is seen at 4.5 ppm. No distinct peak is visible at this point in the normal proton spectrum. A weaker response from the CH_2 protons in the CH_2CH_2F end groups is seen at 2.0 ppm. No responses were obtained in the proton spectrum when the weak features at −147 ppm were irradiated. These are assigned to tertiary fluorine atoms which have the closest hydrogen atoms three bonds away, and the H–F couplings are presumably too weak to give a detectable response.

Pressure and Temperature Effects on PVF Structure

Using the NMR techniques described above, we have studied the effect of synthesis conditions on the structure of PVF.

Table I shows the results obtained for polymer made in a batch reactor at various pressures and temperatures. We find the number of head-to-head units to be invariant, within the precision of the NMR measurement, over the range of polymerization conditions examined. This result is consistent with observations made by earlier researchers.[6] Trends showing a decrease in the number of CH_2F end groups and tertiary fluorine atoms as the reactor temperature decreases and the reactor pressure increases seem evident.

Similar responses to changes in conditions are seen in the data in Table II for polymers made by continuous polymerization. As found for polymers made in the batch reactor, the samples produced in the continuous reactor show no significant variation in the number of head-to-head reversals. A regular decrease is observed in the number of CH_2F and tertiary fluorine atoms as the reactor temperature decreases from 103 to 80 °C. Higher pressures also reduce the number of CH_2F groups and tertiary fluorine atoms as can be seen from a comparison of the data for PVF made at 97 °C and 4000 psi to those for PVF made at 97 °C and 8000 psi.

The tertiary fluorine atoms are primary evidence for branching in PVF, and we conclude that more linear polymers are made as reactor pressure increases and reactor temperature decreases. This would be expected since such changes in conditions should favor chain propagation rather than chain transfer. It is interesting to note that the tertiary fluorine content of polymer made in the continuous reactor is much lower than that for polymer made under similar conditions in the batch

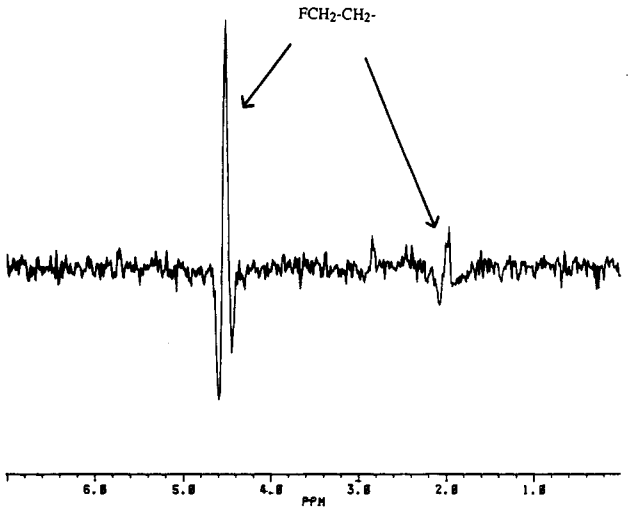


Figure 3. 400-MHz proton NMR spectrum of poly(vinyl fluoride) with differential fluorine decoupling at −220 ppm.

Table I
Vinyl Fluoride Batch Polymerizations

reactor temp, °C	reactor pressure, psi	% head-to-head	% CH_2F ends	% tertiary F
100	8000	13.0	0.49	0.89
100	4000	13.6	0.59	1.30
100	4000	12.5	0.52	1.20
70	4000	12.8	0.66	0.78
70	1000	12.4	0.83	1.24
60	8000	12.5	0.26	0.54

Table II
Vinyl Fluoride Continuous Polymerizations

reactor temp, °C	reactor pressure, psi	% head-to-head	% CH_2F ends	% tertiary F
103	8000	13.1	0.26	0.68
97	8000	13.2	0.27	0.69
97	4000	13.4	0.35	0.80
91	8000	12.8	0.22	0.57
86	8000	12.7	0.20	0.57
80	8000	12.5	0.18	0.51

reactor. This may be a result of the short residence times, 6–10 min, in the continuous reactor compared to the much longer residence times, ca. 60 min, in the batch experiments. The longer residence time may allow more opportunity for hydrogen atom abstraction from polymer to occur, leading to increased branching. The concentrations of tertiary fluorine observed imply that one branch occurs about every 140 monomer units, on average, for polymer made in the continuous reactor at 103 °C and 8000 psi. At 80 °C and 8000 psi, branching decreases to about one branch every 200 monomer units. In contrast, some of the polymers made in the batch reactor have branches as often as every 80 monomer units. Of course, we are only observing branching at the carbon atoms bearing fluorine. There is no reason to exclude the possibility of branching at the other carbon atoms which would lead to tertiary hydrogen atoms in the polymer.

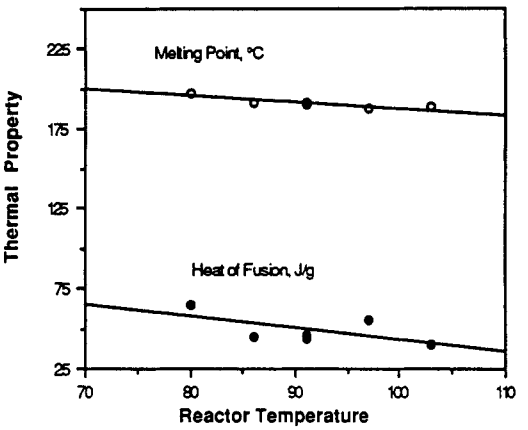


Figure 4. Data showing the relationship between reactor temperature and melting temperature or heat of fusion for poly(vinyl fluoride) made by continuous polymerization at 8000 psi reactor pressure.

We, therefore, believe that the estimates of branching given here are minimum values. Total branching may well be much higher.

One might expect these structural changes to influence the thermal properties of PVF. The plot in Figure 4 shows a shallow but definite decrease in melting point and heat of fusion for PVF as the reactor temperature increases and the polymer becomes more branched. Investigators at Bell Laboratories[7] have noted an inverse relationship of PVF melting point with the head-to-head content of the polymer. In their case, polymers with controlled amounts of the head-to-head structure were prepared by special synthetic procedures. Branching, if it exists in the Bell Laboratories polymers, was not reported. Since we find no compelling evidence of change in head-to-head content in the polymers of this study, we believe the changes in melting point and heat of fusion are attributable to variations in branching.

Finally, we note that the NMR data consistently show higher concentrations of tertiary fluorine atoms than CH_2F end groups. The significance of this is unclear at present. It may be that many of the $CHF^{\bullet}$ radical ends couple with other polymer radical species. This would eventually lead to the formation of some cross-links. Alternatively, hydrogen abstraction leading to the formation of tertiary fluorines may occur preferentially with $CH_2^{\bullet}$ to form methyl end groups. Resolution of this question awaits further research.

References and Notes

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Registry No. PVF, 24981-14-4.