(19) Cho, I.; Lee, J. Y. *Macromolecules* **1983**, *16*, 1245.

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Polymerization of Vinylidene-d_2 Fluoride. Minimal Regiosequence and Branch Defects and Assignment of Preferred Chain-Growth Direction from the Deuterium Isotope Effect

Poly(vinylidene fluoride) has attracted considerable research and technological interest, mainly due to its piezoelectric and pyroelectric behavior.[1] The properties of the polymer (commonly abbreviated as PVF_2) depend on its chemical microstructure, which could be represented as $(-CH_2-CF_2-)_n$ for an ideal, defect-free material (neglecting end groups).

It is well established that the free-radical addition polymerization of VF_2 is not regiospecific.[2] Typically 5% of monomer units enter the growing chain with a reverse orientation creating anomalous head–head ($-CF_2-CF_2-$) and tail-tail ($-CH_2-CH_2-$) junctions.[3] These anomalous structures must exert some influence on the properties of PVF_2.[4] Therefore it would be desirable to prepare a perfectly head-to-tail (isoregic) PVF_2 for comparison with commercial samples, in which the level of reversed units varies over a limited range of only 3.5–6%.[1]

However, it seems unlikely that this small range of regiosequence defects can account for the variation in properties of commercial PVF_2 materials. We postulate that the number and type of chain branches present exert an equal if not greater effect on the chemical and physical properties of PVF_2. Unfortunately this branch structure is not as easy to characterize as the regiosequence structure, so we attempt to eliminate its effect here by preparing a highly linear polymer.

The frequency of monomer reversals during VF_2 polymerization is greater at higher temperature,[5] but it is not practical to eliminate their occurrence by going to low temperatures.[6-8] We have published an alternative procedure for preparing pure isoregic PVF_2 by the reductive dechlorination of the precursor polymer poly(1,1-dichloro-2,2-difluoroethylene).[9] In practice this material could not be obtained with a molecular weight of sufficient magnitude to impart typical polymeric properties, thus obviating a meaningful comparison with commercial PVF_2 samples.

We disclose here a method for obtaining high-molecular-weight PVF_2 with only 2.84 ± 0.02% of reversed monomer units, which is the lowest value yet reported. The method involves the bulk polymerization of 1,1-dideuterio-2,2-difluoroethylene (VF_2-d_2) at 0 °C with trichloroacetyl peroxide initiator. We believe this is the first report of an isotope effect on polymer sequence distribution. Also, since deuteration of the polymer exerts a primary isotope effect on the rate of hydrogen transfer,[10] the frequency of chain branching is reduced. Thus our samples of PVF_2-d_2 are less branched than commercial materials and more stable toward dehydrofluorination. The higher stability results from fewer labile sites containing tertiary hydrogen at branch points, and the isotope effect on hydrogen fluoride elimination.

The perdeuterated monomer VF_2-d_2 was synthesized by the procedure of Edgell and Ultef.[11] Trifluoroethanol-d_3 (99 atom % D minimum) was purchased from Merck, Sharp, and Dohme and reacted with *p*-toluenesulfonic acid. The ester derivative was then treated with sodium iodide to liberate CF_3CD_2I. The purified CF_3CD_2I was dropped slowly onto Mg in ether, and the evolved $CD_2{=}CF_2$ was collected and then transferred to a vacuum line where it was freeze–thaw degassed and distilled. The overall yield was 44%. The isotopic purity of the monomer was checked by mass spectrographic analysis. The composition by mole percent was as follows: $CD_2{=}CF_2$, 99.28; $CDH{=}CF_2$, 0.68; $CH_2{=}CF_2$, less than 0.04.

Table I
Properties of PVF_2-h_2 and PVF_2-d_2 Prepared in Bulk at 0 °C with Trichloroacetyl Peroxide Initiator

sample	monomer	initiator concn, mol %	T_m,[a] °C	$[\eta]$,[b] dL/g	ρ,[c] g/mL	% reverse addition
A-h_2	$CH_2{=}CF_2$	1	180.9	0.45	1.792	3.45
B-h_2	$CH_2{=}CF_2$	0.1	179.5	2.6	1.770	3.46
C-d_2	$CD_2{=}CF_2$	1	185.1	2.8	1.840	2.86
D-d_2	$CD_2{=}CF_2$	0.1	188.3	4.1	1.860	2.83

[a] First melting point of nascent material measured by DSC. Subsequent melting temperatures were always several degrees lower. [b] Intrinsic viscosity measured at 125 °C in dimethylformamide. Under these conditions the intrinsic viscosities of commercial polymers (Kureha, Kynar, Solef, and Pennwalt) are typically around 1.0.[16] [c] Density of polymer melt pressed into 3-mm-diameter disk of 1-mm thickness and rapidly quenched to room temperature.

The polymerization initiator was trichloroacetyl peroxide, which was prepared from trichloroacetyl chloride and sodium peroxide according to standard procedure.[12] It was added to heavy-wall Pyrex ampules as a solution in 1,2-dichlorotetrafluoroethane, which was then evaporated to dryness at −80 °C. The monomer was then condensed into the tube at −196 °C. The tube was sealed and rapidly warmed to the polymerization temperature of 0 °C in a pressurized reactor which was held in an ice–water bath. Control samples with the protonated monomer $CH_2{=}CF_2$ were prepared in an identical manner.

After a suitable polymerization time had elapsed the tubes were frozen in liquid nitrogen and cut open. The recovered polymers were extracted with acetone to remove initiator residue and possible traces of oligomers and dried in a vacuum oven. The polymers were examined by NMR with a JEOL GX-500 spectrometer. Fluorine-19 spectra were recorded at 470.6 MHz using 5% by weight polymer solutions in dimethylformamide-d_7 at 25 °C. The spectra were analyzed according to our previously published procedure.[13]

Some properties of the PVF_2-h_2 and PVF_2-d_2 samples are compared in Table I. We note that the molecular weights of the deuterated samples, as reflected by their intrinsic viscosities, are significantly higher than their protonated analogues. This fact most likely results from the primary kinetic isotope effect on transfer and disproportionation reactions. We calculate $\bar{M}_v$ values of 11.9×10^6 and 20.1×10^6 for PVF_2 samples C-d_2 and D-d_2 using the literature Mark–Houwink–Sakurada constants.[14] The viscosity measurement overestimates molecular weights for PVF_2,[5,15] but it is clear that the deuterated samples have extremely high degrees of polymerization so that end groups will not interfere with our NMR analysis.

The densities of the deuterated polymers are higher as well, but most of the difference arises from the larger mass of deuterium. However the densities are still larger after correcting for this than those of commercial PVF_2 samples (e.g., 1.80 corrected for D-d_2 vs. 1.78 for Kureha 1100), suggesting a higher degree of crystallinity and therefore

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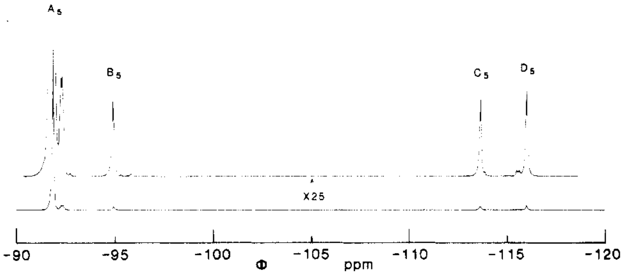

Figure 1. 470.6-MHz fluorine-19 NMR spectrum of deuterated PVF_2 sample D-d_2 dissolved in dimethylformamide at 25 °C. The internal reference is C_6F_6 at −163 ppm from $CFCl_3$. Other details are as follows: sweep width, 25 000 Hz; points, 132K; acquisition time, 2.62 s; pulse width, 14 μs (90°); pulse delay, 10.0 s; transients, 4000. The regiosequence pentads are A_5 (10101), B_5 (00101), C_5 (10110), and D_5 (00110) (0 = CH_2, 1 = CF_2).

Scheme I

	rate constant	deuterium positions in reactants
$-01 + 01 \rightarrow -01$	k_{11}	β, α
$-01 + 10 \rightarrow -10$	k_{10}	β, β
$-10 + 01 \rightarrow -01$	k_{01}	α, α
$-10 + 10 \rightarrow -10$	k_{00}	α, β

more regular chain structure in the deuterated polymers.

The melting temperatures of PVF_2-d_2 are higher than those of PVF_2-h_2. Deuteration would be expected to *lower* the melting temperature, as observed for polyethylene where the isotopic species exhibit a 6 °C difference.[17] This interesting result is likewise suggestive of enhanced crystallinity arising from a more perfect chain structure. Likewise the relative thermal stabilities show that the deuterated polymers have fewer labile sites and are more resistant to dehydrofluorination than commercial polymers. Our preliminary study by thermal gravimetric analysis gave the following temperatures for 10% loss of initial weight: D-d_2, 490 °C; A-h_2, 474 °C; commercial Kynar 900, 476 °C; commercial Kureha 1100, 474 °C.

Our primary concern here is the isotope effect on the frequency of monomer reversals during VF_2 polymerization. The data in Table I show that only 2.84 ± 0.02 out of every 100 monomer units are reversed in the PVF_2-d_2 samples (calculated from NMR peak probabilities as described below). This level of head–head:tail–tail defects is the lowest yet reported for PVF_2 made directly by addition polymerization of VF_2. The frequency of monomer reversals in PVF_2-h_2 prepared under identical conditions is some 21% higher than this at 3.45 per 100 monomer units. We have also reexamined here the defect levels in commercial PVF_2 samples by 470.6-MHz fluorine-19 NMR. The lowest level of regiosequence defects we have observed for these materials is 3.8% for Kureha 1100, followed by 4.1% for Solef 1008 and 5.2% for Kynar 900.

Figure 1 shows the fluorine-19 NMR spectrum of sample D-d_2. The four groups of resonances are labeled A_5–D_5 in order of increasing field, in keeping with our previous convention.[13] The relative areas of these peaks were determined by numerical integration and gave the observed regiosequence pentad (five-carbon sequence) probabilities, from which the appropriate reactivity ratios r_0 and r_1 may be determined.[13] The percent of reversed units is simply $100P_{\text{obsd}}(C_5 + D_5)$. First-order Markov statistics are assumed as shown by Scheme I, which treats the system as a binary copolymerization (0 = CH_2, 1 = CF_2). Thus the regiosequence statistics is fully defined by the two reactivity ratios $r_0 = k_{00}/k_{01}$ and $r_1 = k_{11}/k_{10}$.

Table II
Observed Probabilities for the Four Nonequivalent Regiosequence Pentads (0 = CH_2, 1 = CF_2) Determined from 470.6-MHz Fluorine-19 NMR Spectra and the Derived Reactivity Ratios

	$P_{\text{obsd}}(S_5)$					
sample	A_5 10101	B_5 00101	C_5 10110	D_5 00110	r_0	r_1
A-h_2	0.4492	0.0164	0.0164	0.0181	0.003	27
B-h_2	0.4489	0.0164	0.0164	0.0182	0.003	27
C-d_2	0.4576	0.0136	0.0136	0.0150	0.003	33
D-d_2	0.4585	0.0133	0.0133	0.0149	0.003	33

The NMR method determines only the relative orientation of monomer units and cannot discern the absolute direction of chain growth, so that the preferred structure of the propagating radical is unknown. There are two possibilities, $-CH_2CF_2\cdot$ or $-CF_2CH_2\cdot$, so there must be two solutions for r_0 and r_1 consistent with the regiosequence probabilities. If $-CH_2CF_2\cdot$ is preferred, then $r_1 > r_0$; conversely if $-CF_2CH_2\cdot$ is preferred, then $r_1 < r_0$.[13]

It has been generally accepted in the field that the $-CH_2CF_2\cdot$ propagating radical is more likely; i.e., the VF_2 monomer is attacked more often at the $CH_2{=}$carbon. Maksimov and Zotikov[18] have attempted to prove this in vinylidene fluoride–tetrafluoroethylene copolymers by following the change in NMR peak intensities with composition. Prior to the present work the only direct evidence reported was from gas-phase kinetic data on the addition of trifluoromethyl radicals to VF_2.[19]

The isotope effect we have observed provides an independent and convincing test of the preferred direction of propagation.[20] The positions of deuterium (hydrogen) with respect to the reacting carbon centers are indicated in Scheme I. It has been shown for methyl and trifluoromethyl radical addition to selected olefins that the α kinetic isotope effect (k_D/k_H) is typically 1.1–1.2, whereas the β effect is insignificant.[21] Therefore we can reasonably assume a positive α effect with no β effect and deduce that $(r_0)_D < (r_0)_H$ and $(r_1)_D > (r_1)_H$.

The results from the regiosequence analyses are given in Table II, where we have chosen the solution with $r_1 > r_0$. The r_0 values are vanishingly small, and the difference between $(r_0)_D$ and $(r_0)_H$ for the polymerizations of VF_2-d_2 and VF_2-h_2 cannot be measured reliably from pentad sequence data. We will consider this point in a subsequent publication which will deal with higher order regiosequences. For the present it is sufficient to note that $(r_1)_D > (r_1)_H$ as predicted above, so that our solution with $r_1 > r_0$ is correct. The alternative solution with $(r_0)_D = 33$, $(r_0)_H = 27$, and $r_1 < r_0$ can be ruled out. Therefore the preferred direction of VF_2 propagation results in the $-CH_2CF_2\cdot$ radical structure.

We can argue more simply that if $-CF_2CH_2\cdot$ is the preferred propagating radical, then the α effect favors reverse addition in the deuterated polymer which should contain *more* regiosequence defects. On the other hand, if $-CH_2CF_2\cdot$ is the preferred structure, then the α effect favors forward addition so the deuterated polymer should have *less* defects as observed. We can calculate the magnitude of the α effect from the $(r_1)_D/(r_1)_H$ ratio in Table II by assuming $(k_{10})_D = (k_{10})_H$ (i.e., no β effect), whence $(k_{11})_D/(k_{11})_H = 1.22$. This value is consistent with literature data for similar radical additions.[21] Its magnitude shows that there is little deviation from planarity in the transition state and that the incipient CF_2---CH_2 bond is relatively long.[22]

The spectrum in Figure 1 is the highest field fluorine-19 NMR spectrum yet reported for PVF_2. Close inspection

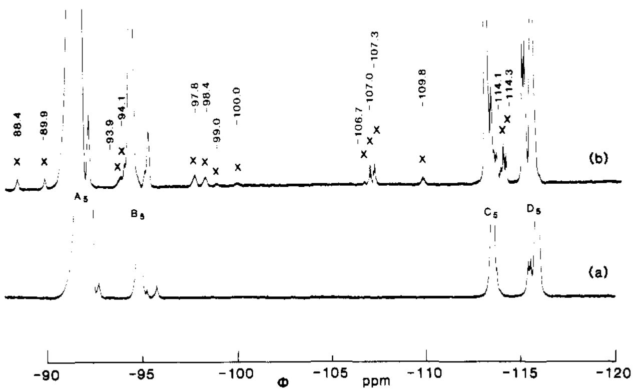

Figure 2. Comparison of 470.6-MHz fluorine-19 NMR spectra of (a) deuterated PVF_2 sample D-d_2 with (b) commercial PVF_2 (Kynar 900 from Pennwalt) at equally high sensitivity. The spectra were obtained under identical conditions (caption to Figure 1) and the detection limit is approximately 1 part in 10000. Note the deuterium isotope effect on chemical shift which is responsible for the 0.35 ppm displacement of the PVF_2-d_2 spectrum to higher field. The peaks marked × (with appropriate chemical shifts) in commercial PVF_2 are not due to higher order regiosequences and reflect mainly the increased chain branching in the commercial material.

of the fine structure shows that 11-carbon regiosequences are resolved, as has been noted by Lovchikov et al.[23] and Ferguson and Ovenall.[24] The intensities of many of the 11-carbon regiosequences S_{11} are exceedingly small[24] and are comparable to peaks often observed in commercial PVF_2 samples which are not due to regiosequence isomerism. This makes the complete assignment of all 32 S_{11} sequences ambiguous for these polymers.

We believe that most of the interfering peaks seen in typical PVF_2 spectra are due to branch structures. Short branches can arise from a back-biting mechanism like that for polyethylene,[25] and hydrogen abstraction at a site remote from the growing chain end will lead to long branches. These mechanisms will be subject to the primary deuterium kinetic isotope effect[10] so that their likelihood is reduced substantially for the polymerization of VF_2-d_2. The possibility of chain transfer to solvent or emulsifier is also eliminated by the bulk polymerizations as carried out here.

Figure 2 supports the above postulates. The fluorine-19 NMR spectra of PVF_2-d_2 and commercial PVF_2 are compared. The spectrum of the latter material has many additional peaks, marked ×, which cannot be due to regiosequence isomerism. A few of these may be due to emulsifier residue, but most can only be due to branches since we observe the same peaks in our PVF_2 sample A-h_2. A definitive assignment of these peaks to particular branch structures requires an analysis of the chemical shifts for appropriate model compounds. The branch frequency (number of branch carbons per total number of carbons) ranges between 0.3 and 3 per 1000, depending on how the peaks marked × in Figure 2 are assigned. If all these peaks are generated by just the one type of branch structure, then the lower value is appropriate. If, on the other hand, each peak × represents a different type of branch structure, then the upper value is correct. The true situation is most likely intermediate. In any case we cannot detect these peaks in our PVF_2 sample D-d_2, which therefore has an upper limit on branching of 0.1 per 1000.

We are presently characterizing additional properties of PVF_2-d_2 and assigning the 11-carbon regiosequence structure observed in the 470.6-MHz fluorine-19 NMR spectrum. The results will be the subject of a forthcoming publication.

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Registry No. PVF_2-h_2, 24937-79-9; PVF_2-d_2, 91606-88-1; A-h_2, 75-38-7; C-d_2, 563-93-9.

References and Notes

(1) Lovinger, A. J. "Developments in Crystalline Polymers"; Bassett, D. C., Ed.; Applied Science, Publishers: London, 1982; Vol. 1, pp 195–273.
(2) Bovey, F. A. "Chain Structure and Conformation of Macromolecules"; Academic Press: New York, 1982; Chapter 6.
(3) Koenig, J. L. "Chemical Microstructure of Polymer Chains"; Wiley-Interscience: New York, 1980; pp 288–292.
(4) Hopfinger, A. J. "Conformational Properties of Macromolecules"; Academic Press: New York, 1973; pp 222–233.
(5) Görlitz, M.; Minke, R.; Trautvetter, W.; Weisgerber, G. *Angew. Makromol. Chem.* **1973**, *29/30*, 137–162.
(6) Liepins, R.; Surles, J. R.; Morosoff, N.; Stannett, V. T.; Timmons, M. L.; Wortman, J. J. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 3039–3044.
(7) Duan, Y.; Yu, X.; Xue, Y.; Zeng, M.; Ji, S. *Gaofenzi Tongxun* **1983**, *2*, 93–98; *Chem. Abstr.* **1983**, *22*, 99:140482*c*.
(8) We have prepared PVF_2 at −80 °C by irradiation of the bulk monomer mixture with cobalt-60 γ rays. The level of reversed monomer units was about 3%, but a host of new anomalous structures was evident in the NMR spectrum, probably from γ-ray-induced dehydrofluorination and grafting.
(9) Cais, R. E.; Kometani, J. M. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, *48*, 216–220.
(10) Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, *93*, 5584–5586.
(11) Edgell, W. F.; Ultef, C. J. *J. Chem. Phys.* **1954**, *22*, 1983–1985.
(12) Young, D. M.; Stoops, W. N. **1957**, *U.S. Patent* 2792423.
(13) Cais, R. E.; Sloane, N. J. A. *Polymer* **1983**, *24*, 179–187.
(14) Ali, S.; Raina, A. K. *Makromol. Chem.* **1978**, *179*, 2925–2930.
(15) Stillwagon, L. E. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, *48*, 780–783.
(16) Hellman, M. Y., private communication.
(17) Stehling, F. C.; Ergos, E.; Mandelkern, L. *Macromolecules* **1971**, *4*, 672–677.
(18) Maksimov, V. L.; Zotikov, E. G. *Vysokomol. Soedin Ser. B* **1969**, *11*, 818–821.
(19) Sloan, J. P.; Tedder, J. M.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1846–1850.
(20) We are grateful to Dr. R. C. Ferguson for this suggestion.
(21) Feld, M.; Stefani, A. P.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 4451–4453.
(22) Matsuoka, M.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 1260–1261 and references therein.
(23) Lovchikov, V. A.; Shlyakov, A. M.; Dolgopolskii, I. M. *Issled. Stroeniya Makromolekul Metodom YAMR Vysok. Razresheniya, M* **1983**, 51–62.
(24) Ferguson, R. C.; Ovenall, D. W. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1984**, *25* (1), 340–341.
(25) Mattice, W. L.; Stehling, F. C. *Macromolecules* **1981**, *14*, 1479–1484 and references therein.

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