

## The Radiation-Initiated Solution Polymerization of Vinylidene Fluoride

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### Synopsis

The radiation-initiated solution polymerization of vinylidene fluoride was examined in an effort to determine the effect of polymerization conditions on the head-to-head content of the resulting poly(vinylidene fluoride). No appreciable change was observed in the head-to-head content when this new type of polymerization was utilized. However, the polymers which resulted had melting points 10–15°C higher than those of the suspension-polymerized poly(vinylidene fluoride), higher crystallinity, and, when trifluoroacetic acid was used as a solvent, a higher molecular weight.

### INTRODUCTION

Nuclear magnetic resonance spectroscopy has indicated that 5% to 6% of the monomer units in poly(vinylidene fluoride), PVF<sub>2</sub>, will add in a head-to-head fashion.<sup>1–3</sup> With suspension polymerization, it has been demonstrated that the head-to-head content found in poly(vinyl fluoride) is a function of polymerization temperature,<sup>3,4</sup> although this has never been demonstrated for PVF<sub>2</sub>. Doll and Lando<sup>5</sup> have shown that the head-to-head linkages are at least partially responsible for the polymorphic transition from phase II to phase I which occurs when PVF<sub>2</sub> is oriented at 50°C. Several attempts have been made to polymerize vinylidene fluoride using conditions under which the amount of head-to-head addition might be reduced. Solid state polymerizations using  $\gamma$ -radiation as an initiator at liquid nitrogen temperatures resulted in low yields of polymeric materials which were oils.<sup>6</sup> Polymerizations at –78°C and higher using  $\gamma$ -radiation have not indicated any major change in the head-to-head content.

Commercially, PVF<sub>2</sub> is polymerized by a suspension polymerization technique. Attempts to polymerize vinylidene fluoride in solution have not been reported in the literature. PVF<sub>2</sub> is reported to be soluble in esters, ketones, amines, and solvents such as dimethyl acetamide (DMAC), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO), which are good hydrogen-bonding solvents.<sup>7</sup> Very little has been reported on the use of fluorinated solvents such as hexafluoroacetone sesquihydrate (HFAS) or trifluoroacetic acid (TFAA). There have, however, been reports that hexafluoroacetone (HFA) will copolymerize with vinylidene fluoride.<sup>8–11</sup>

The purpose of this paper is to report some preliminary results on the solution polymerization of  $\text{VF}_2$  using  $\gamma$ -radiation as an initiator. As will be seen, the head-to-head content is not greatly reduced; however, the melting points of these solution-polymerized materials are generally higher than the melting point of suspension-polymerized  $\text{PVF}_2$ .

### EXPERIMENTAL

A 45-ml stainless-steel Parr pressure vessel was used for all the solution polymerization experiments. A Gamma cell 220 cobalt-60 source with an average dose rate of 0.33 Mrad/hr was used as the  $\gamma$ -radiation source. Debye-Scherrer powder photographs and flat-plate x-ray photographs were taken in order to determine the crystalline phases and lattice constants of the resulting polymers. Melting points were obtained by using a du Pont 900 DTA with a heating rate of  $10^\circ\text{C}/\text{min}$ . Head-to-head content of some of the samples was measured by using a 10% polymer solution in DMAC in a Varian A-56/60 NMR with a fluorine resonance cell. Integral NMR spectra were used to determine the area under the respective curves. Infrared spectra of either thin films or powdered samples in KBr pellets were obtained on a Perkin-Elmer 521-grating infrared spectrometer. Viscosity measurements were made on samples of  $\text{PVF}_2$  in a DMF solution.

After the pressure reactor had been thoroughly cleaned, the solvent to be used in the polymerization experiment was introduced. The system was then cooled to liquid nitrogen temperature, and the vinylidene fluoride gas was condensed into the bomb. The entire system was then allowed to return to room temperature and was checked for leaks around the seals. It was then placed in a Dewar at the desired polymerization temperature and irradiated in the cobalt-60 source. The resulting polymer was washed in methyl alcohol and vacuum-dried.

### RESULTS AND DISCUSSIONS

Table I indicates the samples and nonfluorinated solvent systems which were studied. As can be seen, the polymerizations were carried out between  $0^\circ$  and  $40^\circ\text{C}$  at a polymerization pressure equal to the vapor pressure of the solvent- $\text{VF}_2$  mixture.

The esters and ketones which were used as solvents appeared to act as good chain-transfer agents for vinylidene fluoride. Polymers which resulted from solution polymerization using the solvents in Table I exhibited very poor molding characteristics. Table I indicates that the intrinsic viscosity of the suspension-polymerized commercial polymer was greater than that of the sample which was polymerized in an acetone solution. These intrinsic viscosity data, therefore, would suggest that the molecular weight of the acetone solution-polymerized  $\text{PVF}_2$  is much lower than that of the suspension-polymerized  $\text{PVF}_2$ . Since the  $\text{PVF}_2$  samples resulting from solution polymerizations utilizing the remaining solvents presented in Table I also exhibited poor molding characteristics, it was assumed that

TABLE I  
Solution Polymerization Experiments for Vinylidene Fluoride

Solvent	Special polymerization conditions	Radiation dose, Mrad	Temperature of polymerization, °C	Head to Head, %	$T_m$ , °C	$[\eta]$	Moldability	Yield	Crystallinity, %
Commercial PVF <sub>2</sub>	Kynar	—	—	6.8	160	1.68	VG	—	68
None	gas phase	1.33	0	9.7	175	—	VG	G	—
None	gas phase	1.39	35	—	176	—	VG	G	—
Acetone	95-5 mole-% copolymer with VF	2	35	—	177	—	P	G	63
Acetone	—	2	35	9.0	176	0.183	G	G	75
Acetone	50% transmission lead shields	2	35	—	175	—	P	G	—
Acetone	30% transmission lead shields	2	35	—	175	—	P	F	—
Acetone	10% transmission lead shields	2	35	8.3	175	—	P	F	—
Methyl ethyl ketone	—	2	35	—	163	—	P	VP	—
Ethyl acetate	—	2	35	7.2	174	—	P	G	—
Butyl acetate	—	2	35	—	169	—	P	F	—
Amyl acetate	—	2	35	—	168	—	P	P	—
2-Butoxyethyl acetate	—	2	35	—	165	—	P	VP	—
Acetophenone	—	2	35	—	165	—	P	VVP	—
DMAC	—	2	35	—	163	—	P	VP	—
DMF	—	2	35	—	173	—	P	VP	—
DMSO	—	2	35	—	169	—	P	P	—
$\gamma$ -Butyrl lactone	—	2	35	—	149	—	P	P	—

these polymers also had relatively low molecular weights. In every experiment where ketones or esters were used, the resulting product was highly crystalline. Samples polymerized in an acetone solution generally had an x-ray diffractometer-determined crystallinity of about 75%, while suspension-polymerized samples with an identical thermal history had a crystallinity of about 68%.

The nature of the solvent had a definite effect on the polymer yield at a given radiation dose and dose rate. Lead shields which were capable of reducing the dose rate by 50, 70, and 90% were used in an attempt to reduce the number of chains which were undergoing propagation at any time. However, for an identical total absorbed dose, there did not appear to be any noticeable difference in the physical properties of the polymer. Infrared spectra of the acetone solution-polymerized PVF<sub>2</sub> indicated that no acetone molecules were incorporated into the chain. However, when VF<sub>2</sub> was bubbled through acetone under atmospheric pressure in the  $\gamma$ -radiation source, a low-melting (110°C) white powder resulted. Infrared spectra then indicated that acetone had been copolymerized with VF<sub>2</sub>.<sup>12</sup>

By comparing the melting points in Table I, it can be seen that for every solvent system used, except the  $\gamma$ -butyrolactone, the melting point was higher than that of the PVF<sub>2</sub> resulting from suspension polymerization. The x-ray photographs of the PVF<sub>2</sub> polymerized in a solution of  $\gamma$ -butyrolactone indicated a much greater degree of disorder (diffuse rather than sharp rings) than was observed in photographs of PVF<sub>2</sub> polymerized in other solvents.

When VF<sub>2</sub> was polymerized using DMSO, DMF, or DMAC as the solvent system, x-ray photographs of the as-polymerized material indicated that the polymer had crystallized in the planar zigzag chain conformation (phase I). The polymers that resulted from the use of these three solvents were very unstable to thermal treatments. They appeared to partially decompose upon melting. Upon recrystallization after melting, these samples crystallized in phase II.

Two strongly hydrogen-bonding, fluorinated solvents (hexafluoroacetone sesquihydrate, HFAS, and trifluoroacetic acid, TFAA) were tried, and they gave the results shown in Table II. By using either solvent, the polymerization went essentially to completion at a total radiation dose as low as 0.66 Mrad. With a total radiation dose of 0.33 Mrad, the polymerization reaction still went nearly to complete conversion with the use of either solvent, HFAS or TFAA. However, by reducing the radiation dosage to 0.165 Mrad, almost no polymer resulted. This would indicate that there may be an induction period before the polymerization reaction starts and that the rate of polymerization must be rapid after the induction period is finished. For most of the other solvent systems considered, very little polymerization occurred until the system received a dose in excess of 1 Mrad. Samples which were polymerized from these fluorinated solvents had very good molding characteristics. They could be oriented to a draw ratio of 5:1 and gave extremely sharp x-ray fiber photographs.

TABLE II  
Fluorinated Solvent Polymerization Experiments for Vinylidene Fluoride

Solvent	Special polymerization conditions	Radiation dose, Mrad	Temperature of polymerization, °C	Head to Head, %	$T_m$ , °C	$[\eta]$	Moldability	Yield	Crystallinity, %
Hexafluoroacetone sesquihydrate (HFAS)	—	0.165	35	—	—	—	—	VVP	—
HFAS	—	0.33	35	—	172	—	G	F	—
HFAS	—	0.66	35	8.3	168	1.76	G	VG	75
HFAS	50% transmission lead shields	0.66	35	—	169	—	G	G	—
HFAS	—	0.66	0	6.4	173	—	G	VG	—
HFAS	—	1.33	35	—	172	—	G	VG	—
HFAS	30% transmission lead shields	0.165	35	—	—	—	—	None	—
Trifluoroacetic acid (TFAA)	—	0.33	35	—	172	—	G	G	—
TFAA	—	0.66	35	7.3	172	2.1	G	G	—
TFAA	—	1.00	35	—	—	—	G	G	—
TFAA	30% transmission lead shields	0.165	35	—	—	—	—	N	—

The intrinsic viscosity of the sample polymerized in TFAA (Table II) was considerably higher than values obtained for the intrinsic viscosities of the PVF<sub>2</sub> sample polymerized in HFAS or the commercial suspension-polymerized PVF<sub>2</sub> (Table I). The intrinsic viscosity data indicated that, with the same total radiation dose, the molecular weight of the sample polymerized in TFAA is higher than that of the polymer resulting from the HFA solution. Since the value of the intrinsic viscosity of the sample polymerized in HFA is similar to that of the suspension-polymerized sample, the molecular weights of these two samples would be of the same general magnitude.

It has been suggested that hexafluoroacetone will copolymerize with vinylidene fluoride.<sup>8,9</sup> Rather extensive studies of the reaction between HFA and either VF or TFE have been performed,<sup>10</sup> but little has been reported of the reaction between HFA and VF<sub>2</sub>. Our infrared spectra of solution-polymerized PVF<sub>2</sub> using HFAS as a solvent do not indicate any differences when they are compared with spectra of suspension-polymerized material. Peaks for unassociated hydroxyl (2.78  $\mu$ ) or carbonyl bands (5.8  $\mu$ ) were not observed in the infrared spectra of the solution-polymerized PVF<sub>2</sub>. Absorption peaks for ether linkages (8.1  $\mu$ , 8.6  $\mu$ ) would be obscured by the very strong peaks associated with the carbon-fluorine modes. However, for this material the melting point was 10–12° higher than for a typical suspension polymerized material while the melting point of a copolymer would be expected to be lower than that of the homopolymer.

By using the x-ray diffractometer scans, the crystallinity was found to be about 75% for the HFAS solution-polymerized PVF<sub>2</sub>. Debye-Scherrer photographs indicated that the *a* and *b* unit cell dimensions were slightly reduced while the *c*-axis dimension was slightly increased when they were compared with the unit cell dimensions determined for normal PVF<sub>2</sub> phase II.<sup>13</sup> (HFAS solution-polymerized PVF<sub>2</sub>: *a* = 4.99 Å, *b* = 9.61 Å, *c* = 4.64 Å [chain axis] versus normal lattice constants for phase II, *a* = 5.02 Å, *b* = 9.63, Å, *c* = 4.62 Å.) Since the lattice constants lateral to the chain axis appear to decrease slightly and the crystallinity increases, any branching or copolymerization should be minor. If hexafluoroacetone does copolymerize with VF<sub>2</sub> by this solution-polymerization technique, the infrared melting point, and x-ray techniques would suggest a copolymer having less than 1% HFA. Infrared spectra of the PVF<sub>2</sub> polymerized in TFAA also indicated that very little if any TFAA was incorporated into the chain. The resulting polymer had a higher degree of crystallinity and a higher melting point than the suspension-polymerized PVF<sub>2</sub>.

The NMR results indicate that the head-to-head content was not reduced to any extent by solution polymerization. NMR spectra of samples of VF<sub>2</sub> polymerized in the gas phase at 0°C indicate that the head-to-head content increases for this type of polymerization.

### SUMMARY

From the above results of this preliminary survey of the solution polymerization of VF<sub>2</sub> in various solvents, the following can be concluded: (1)

Solution polymerization using the above solvents and conditions does not appreciably alter the head-to-head content. (2) Infrared spectra indicate that the solvents are not incorporated as comonomers. (3) All the solvents used, with the exceptions of HFAS and TFAA, appeared to act as good chain-transfer agents. (4) The melting points and crystallinities of all the solution-polymerized samples, with the exception of the sample polymerized in  $\gamma$ -butyrl lactone, were higher than those of the suspension-polymerized PVF<sub>2</sub>. (5) The polymers resulting from the solution polymerization using HFAS and TFAA will be studied further, since they exhibited good physical properties. Since VF<sub>2</sub> in HFAS will polymerize almost to completion with a total absorbed dose of 0.33 Mrad,  $\gamma$ -radiation might lead to a commercially feasible process.

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