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## Chlorotrifluoroethylene Suspension Polymerization

MILTON H. ANDRUS, JR., ROBERT J. OLSEN,  
GILBERT L. EIAN, and RICHARD C. ALLEN

### 6.1. INTRODUCTION

Polychlorotrifluoroethylene (PCTFE) is ordinarily prepared by emulsion polymerization. A polymer suitable for thermal processing requires coagulation, extensive washing, and postpolymerization workup. Coagulation to provide a filterable and washable solid is a slow, difficult process and removal of surfactant is an important part of it. Complete removal may be extremely difficult depending on the extent of adsorption to the polymer particles. Consequently we set out to develop a suspension polymerization process, which would be surfactant-free and afford an easily isolated product requiring a minimum of postreaction workup.

Early work at Kellogg on Kel-F™ produced polymers with low zero strength time (ZST) values indicating low molecular weight.<sup>1</sup> These polymers had poor physical properties. Tseng and Young<sup>2</sup> in preliminary experiments in a water/alcohol medium made a suspension polymer that had ZST values approximately those of an emulsion polymer. These results led us to a study of the process variables and of different initiators in the suspension polymerization of chlorotrifluoroethylene. Polymer characterization, including inherent viscosity, GPC molecular weight, and melt flow behavior, was also studied. As a result of this study a suspension process was developed that gives high-molecular-weight product with outstanding physical properties.

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MILTON H. ANDRUS, JR., ROBERT J. OLSEN, GILBERT L. EIAN, and RICHARD C. ALLEN • Speciality Materials Division, 3M Company, St. Paul, Minnesota 55144-1000.

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## 6.2. EXPERIMENTAL

### 6.2.1. Materials

All monomers, surfactants, buffers, and chain transfer agents were used as provided. Water was deionized. Purchased organic peroxides were all reagent grade. Organic peroxides were prepared from the reaction products of acyl chlorides and sodium peroxide. Activity was determined by iodometric titration.

### 6.2.2. Preparation of Perfluorooctanoyl Peroxide

To a 1-liter three-necked flask fitted with an alcohol thermometer, an addition funnel, and a mechanical stirrer were charged 450g Freon 113, 6 g sodium hydroxide (0.15mol) in 45 g of water and 8.5g 30% hydrogen peroxide (0.075mol). The solution was stirred and cooled in an ice-salt bath until the temperature reached  $-10^{\circ}\text{C}$ . Perfluorooctanoyl chloride, obtained from 3 M, (64.9 g, 0.15 mol) was added quickly with rapid stirring, being careful to maintain a batch temperature below  $5^{\circ}\text{C}$ . When all the acyl chloride was added the reaction mixture was stirred for 3-5 min, then poured into a separatory funnel and the lower Freon layer drawn off and filtered through anhydrous sodium sulfate. The dried solution weighed 442 g and contained 0.22 meq peroxide/ml by idometric titration.

### 6.2.3. Polymerization

Polymerizations were carried out in a jacketed, 1-gal, stirred, pressure tank reactor. Typical reactions were run by adding water, alcohol, or chain transfer agent, phosphate buffer, and persulfate to the reactor. The reactor was pressurized with CTFE monomer. Sulfite solution was fed at a rate to maintain reaction. Copper and iron ions were used at times as catalysts by adding cupric sulfate or ferrous sulfate.<sup>3</sup> The product was filtered, washed with 90 : 10 water methanol followed with deionized water. The product was dried at  $110^{\circ}\text{C}$ .

### 6.2.4. Molecular Weight Measurements

Inherent viscosities were determined by dissolving PCTFE in refluxing pentafluorochlorobenzene, cooling, and subsequently measuring solution times at  $27^{\circ}\text{C}$  using a Canon-Fenske viscometer. The ability of pentafluorochlorobenzene to dissolve PCTFE while hot but maintain solubility at ambient temperature was discovered by J. Klein at 3M.<sup>4</sup>

Gel permeation chromatography was run by dissolving the polymer in hot 2,5-dichlorotrifluoromethylbenzene and eluting at  $130^{\circ}\text{C}$  with the same solvent as

eluent. The chromatograms were run on a Waters 150C HPCL using a Jordi Associates mixed bed Stryrogel column.

### 6.2.5. Polymer Testing

ZST tests were run according to the procedure described in ASTM D-1430-82. The results are reported as time to break (in minutes) at 250°C.

Melt viscosities were measured using an Instron capillary melt rheometer (Model 3210) using a 0.050-in. diameter capillary ( $L : D = 40 : 1$ ). Corrected viscosities were calculated in the conventional manner. In all cases, samples were preheated for 7 min prior to data acquisition.

Thermal stabilities were assessed by thermogravimetric analysis (TGA). Samples were held at constant temperature (290°C) for 1 h in air in a Perkin-Elmer TGA. Much of the weight loss, particularly for Kel-F 6060, is suspected to be emulsifier used during polymerization.

## 6.3. RESULTS AND CONCLUSIONS

### 6.3.1 Polymerizations

A suspension process using redox initiation in a water medium was developed. The redox system is a combination of persulfatesulfite. Often ferrous or cupric salts were added as a catalyst for the redox reaction. Polymerizations were run in water at low temperature (20–25°C) and low pressure (65–85 psi). Monomer to monomer-plus-water weight ratios of 0.20 to 0.25 were used. Good agitation was required to keep an adequate monomer concentration in the aqueous phase. Yields of up to 100% were obtained with polymer inherent viscosities of 0.4 to 1.5 dl/g in  $C_6F_5Cl$ . Reactions were run on both a 1-gal and a 100-gal scale.

A number of different materials were used as chain transfer agents to control molecular weight. These results are shown in Table 6.1. The effect of varying concentration of t-butyl alcohol and reaction temperature is shown in Figure 6.1. The results are consistent with normal free radical polymerizations. Polymer output was characterized by inherent viscosity and ZST tests.

The results for suspension polymerizations as well as polymer made by emulsion polymerizations by both 3M and Daikin are shown in Table 6.2. Examination of the results confirms that PCTFE can be prepared by suspension polymerization with molecular weights and physical properties comparable to or better than PCTFE from emulsion polymerization.

Many of the heat-pressured samples prepared for the ZST test showed bubbles and discoloration. This is thought to be due to oligomers formed at the end of the polymerization when the reaction is pushed to high conversion. In

Table 6.1. Chain Transfer Agents

Example	Agent	wt% Chain transfer agent	Inherent viscosity (dl/g)
1	None	—	1.36
2	None	—	1.57
3	Acetone	1.00	1.26
4	<i>t</i> -Dodecyl Mercaptan	0.14	1.11
5	Chloroform	0.54	0.99
6	Methanol	1.00	1.10
7	Isopropanol	1.70	0.38

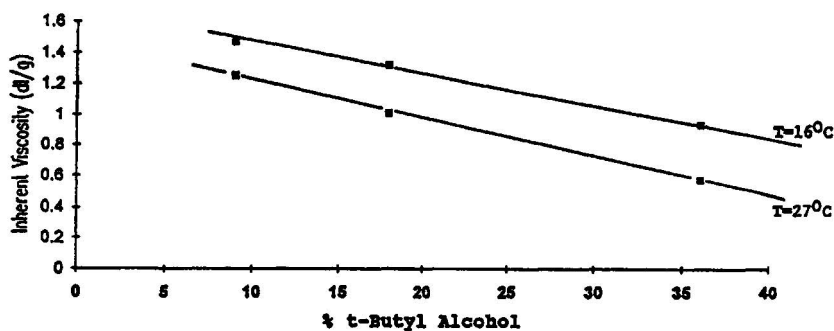


Figure 6.1. Effect of reaction variables.

Table 6.2. Comparison of Zero Strength Time and Inherent Viscosity

Example	Sample	Zero strength time (min)	Inherent viscosity (dl/g in C <sub>6</sub> F <sub>2</sub> Cl)
8	KEL F <sup>TM</sup> 6061	337	2.43
9	KEL F <sup>TM</sup> 6050 (A)	297	1.74
10	KEL F <sup>TM</sup> 6050 (B)	228	1.58
11	Revised emulsion	100	1.16
12	DAKIN <sup>TM</sup> M400H	368	1.77
13	DAMN <sup>TM</sup> M300P	276	1.62
14	ACLO <sup>TM</sup> 3000	—	—
15	Suspension with 4% <i>t</i> -BuOH	5000	1.75
16	Suspension with 9% <i>t</i> -BuOH	1473	1.25
17	Suspension with 18% <i>t</i> -BuOH	2700	1.01
18	Suspension with 1.7% IPA	—	0.91
19	Suspension with 1.0% MeOH	—	0.38
20	Suspension with MeOH/H <sub>2</sub> O wash	1696	1.23
21	Control with HNO <sub>3</sub> wash	159	1.23
22	Control with ethylenediamine wash	183	1.05

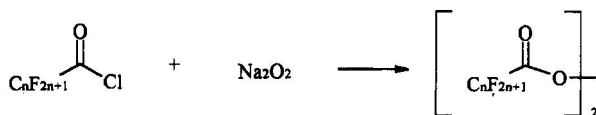
addition these polymers showed steep viscosity–shear rate responses (Figure 6.3). We attribute this behavior to ionic end groups.<sup>5</sup> The ionic end groups can form associations resulting in a virtual high-molecular-weight polymer. In addition the sulfate end groups can be hydrolyzed followed by loss of HF resulting in the formation of olefin and carboxyl end groups (Scheme 1). These end groups may then be responsible for degradation of the thermal properties.



Scheme 1

### 6.3.2 Organic Peroxides

Both hydrocarbon and fluorocarbon organic peroxides were used to initiate polymerization. The half-lives of several that were used are shown in Table 6.3. The perfluoro-organic peroxides were prepared at temperatures below 0°C by the reaction of the corresponding acyl chloride and sodium peroxide (Scheme 2). Sodium peroxide was formed from an aqueous mixture of sodium hydroxide and hydrogen peroxide.



Scheme 2

The results of polymerizations using these various initiators are shown in Table 6.4. The best results were obtained with FC-8; thus a number of aqueous suspension polymerizations were run under a variety of conditions using FC-8 dissolved and fed to the reaction in several different solvents. The results are shown in Table 6.5. The low yields are probably due to precipitation, premature decomposition in the feed line, or hydrolysis of the FC-8 peroxide prior to

Table 6.3. Low-Temperature Initiators

Initiator	Trade name	$T_{1/2}$ (min) at 27°C	Reference
$[\text{Cl}_3\text{CCO}_2]_2$		< 10	6
$[\text{C}_3\text{F}_7\text{CO}_2]_2$	FC-4	209	7
$[\text{C}_7\text{F}_{15}\text{CO}_2]_2$	FC-8	159	7
$[(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{N}]_2$	VAZO 33	1300	8
$[(\text{CH}_3)_3\text{CC}_6\text{H}_{12}\text{-O-CO}_2]_2$	Percadox 16N	120	9
$[\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{OCF}_2\text{CO}_2]_2$	FC-4-2-2		

Table 6.4. New Initiators

Example	Initiator	Yield (%)	Inherent viscosity (dl/g in C <sub>6</sub> F <sub>5</sub> Cl)
23	Bu <sub>3</sub> B/H <sub>2</sub> O	Tr.	<0.1
24	vazo 33	0	
25	[Cl <sub>3</sub> CCO <sub>2</sub> ] <sub>2</sub>	5	
26	Percadox 16N	10	0.4
27	Percadox 16N	15	0.94
28	FC-8	5	0.5
29	FC-8	55	1.3
30	FC-4-2-2	8	1.0
31	[C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> ] <sub>2</sub>	<5	

initiation. A high-molecular-weight polymer was obtained as indicated by the high viscosities shown in Table 6.4.

### 6.3.3 Gel Permeation Chromatography

Gel permeation chromatography was run in 2,5-dichlorotrifluoromethylbenzene at 130°C. The results of samples from different sources are shown in Table 6.6. The results indicate, based on the styrene equivalent molecular weights, that a moderately high-molecular-weight polymer is formed and that the molecular weight of the suspension polymer (Examples 2 and 27) is comparable to that formed by the emulsion polymerization (Example 9). The chromatograms (Figure 6.2), although of low quality, indicate that both the emulsion polymer and the redox suspension polymer and the redox suspension polymer contain some high-molecular-weight material although in slightly different ratios. Daikin polymer, with very good thermal properties, has very little of the high-molecular-weight fraction (Example 12). We attribute the high-molecular-weight fractions to association of ionic end group.<sup>5</sup>

Table 6.5. FC-8 Initiator [C<sub>7</sub>F<sub>15</sub>CO<sub>2</sub>]<sub>2</sub>

Example	Initiator (%)	Solvent <sup>a</sup>	Temperature (°C)	Yield (%)	Inherent viscosity (dl/g C <sub>6</sub> F <sub>5</sub> Cl)
32	0.22	F-113	13	7	0.80
33	0.20	FC-80	27	55	0.62
34	0.05	FC-75	27	31	0.74
35	0.20	FC-75	17	43	0.72
36	0.10	FC-75	19	46	1.26

<sup>a</sup>FC-75 and FC-80 are inert fluorochemical fluids from 3M.

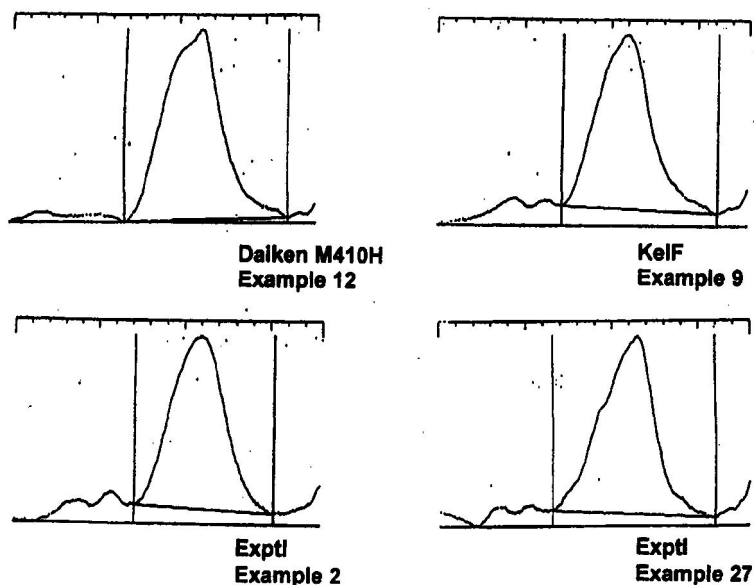


Figure 6.2. Chromatograms.

Table 6.6. Gel Permeation Chromatography<sup>a</sup>

Example	Sample	Zero strength time	Inherent viscosity (dl/g C <sub>6</sub> F <sub>5</sub> Cl)	$M_n$	$M_w$	$P$
12	Daikin M400H	368	1.78	3.56E4	7.80E4	2.19
9	Kel-F 6050	297	1.74	2.85E4	7.39E4	1.92
2	Suspension-redox	711	1.57	3.23E4	7.19E4	2.22
27	Suspension-C <sub>8</sub> Peroxide	116	0.94	3.45E4	6.74E4	1.96

<sup>a</sup>Conditions: eluent: 2,5-dichlorotrifluoromethyl benzene, temperature 130°C (Run by Mike Stephens, CRL Analytical).

### 6.3.4 Capillary Rheometry

A similar variety of samples was tested for thermal stability by capillary rheometry and TGA. Figure 6.3 shows the viscosity-shear rate dependence for PCTFE homopolymers and one copolymer (Alcon 3000). All materials, save one, showed virtually identical viscosity relationships despite large changes in inherent viscosity. Only the polymers from runs initiated by fluorochemical peroxides (FCP) showed a dependence of molecular weight (as measured by inherent viscosity) upon melt viscosity.

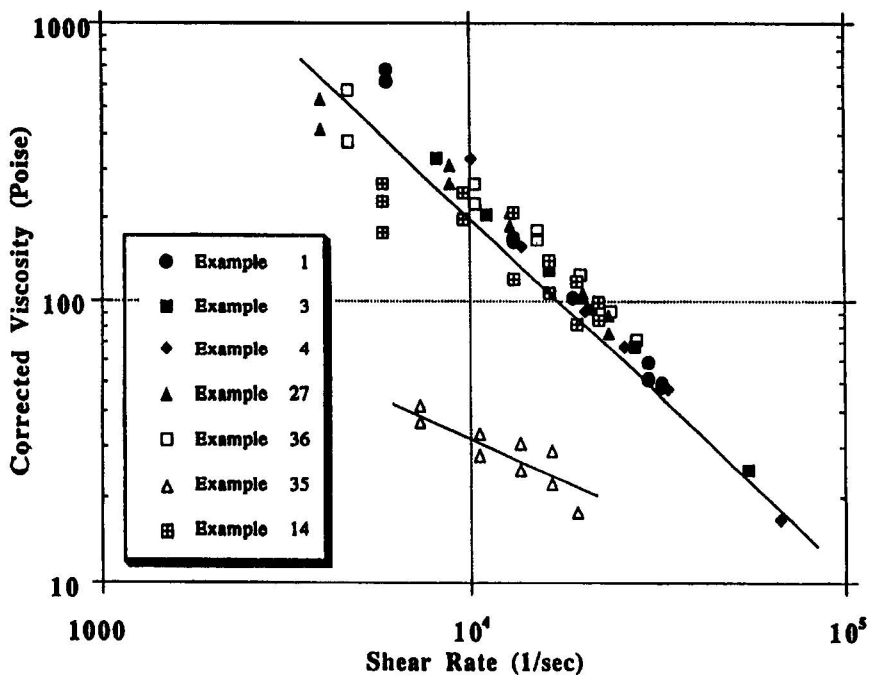


Figure 6.3. Corrected viscosity vs. shear rate.

Thermal stabilities were assessed by the time-dependent change of melt viscosity at a constant temperature and shear rate (290°C, 50 s<sup>-1</sup> respectively). Figure 6.4 shows that three of the six resins showed a significant drop in viscosity as a function of time at 290°C. The average decrease in viscosity for Kel-F 6050, Alcon 3000, and an experimental suspension is 37%.

TGA results (Figure 6.5) confirm the improved stability of suspension polymers, especially when organic peroxides are used.

## 6.4. SUMMARY

Suspension polymerization was shown to give high yields of controlled high-molecular-weight polymers. The presence of bubbles in the thermally pressed samples, especially the high-yield polymers, suggest that low-molecular-weight oligomers are formed at the end of the polymerization. The perfluoroorganic peroxides gave high-molecular-weight polymers albeit with low yields. These polymers exhibited “standard” viscosity–shear rate response compared to the



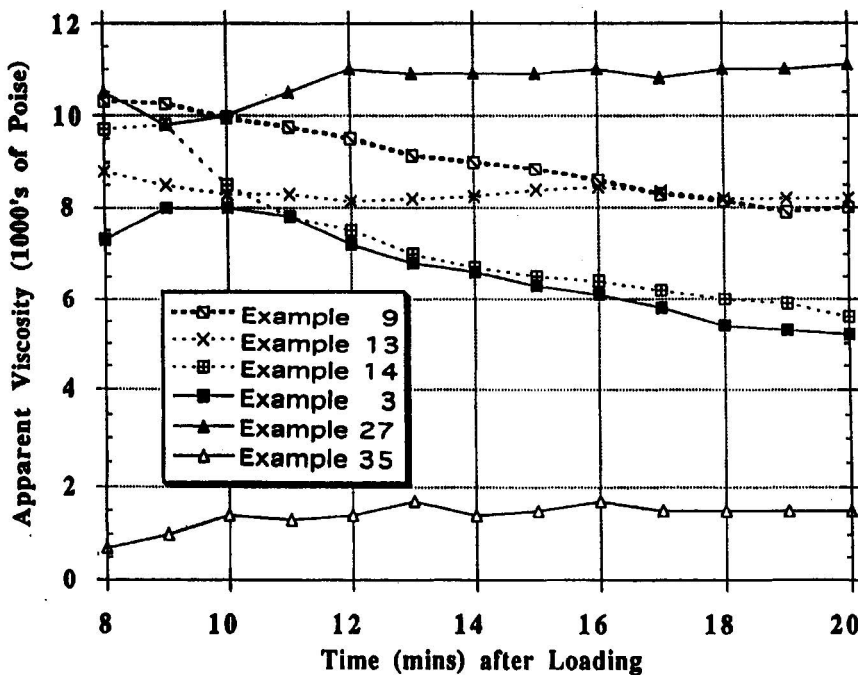


Figure 6.4. Apparent viscosity vs. time after loading.

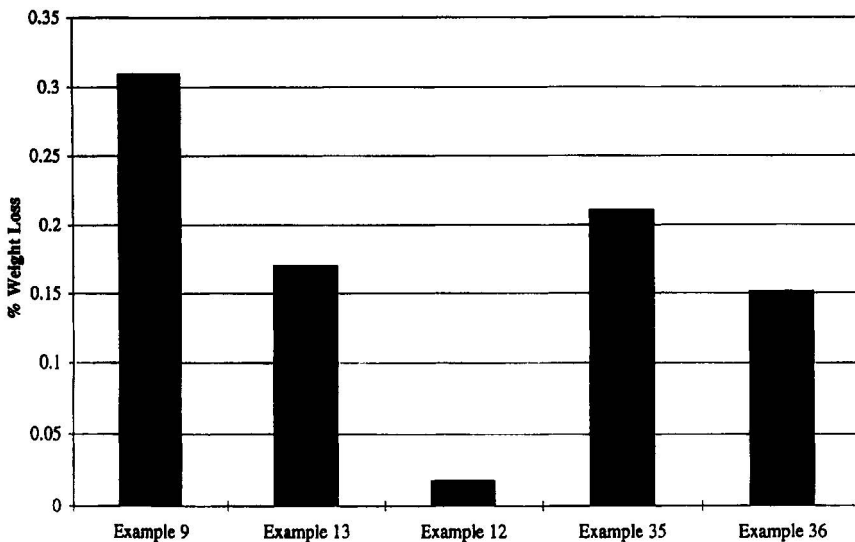


Figure 6.5. Thermogravimetric analysis.

redox initiated products. The thermal stability of the suspension polymer was shown to be better than the emulsion polymer.

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