

Supplemental Information for

Elucidation of Targeted and Non-Targeted Fluorinated Impurities in the manufacturing of PTFE utilizing a Non-Fluorinated Polymerization Aid

John C. Sworen^{#,*}, Peter A. Morken[#], Michael C. Davis[#], Adam P. Smith⁺, Jill E.
Boyle[#], Maria D. Cervantes Garcia[#], and Jordyn Kramer[#]

[#]The Chemours Company, 201 Discovery Blvd. Newark, DE.,

⁺The Chemours Company, 8480 DuPont Road, Washington, WV., ^{*} Corresponding Author.

Text S1. PTFE Polymerization Conditions and Methods

METHODS

Standard Specific Gravity (SSG) provides an indirect measure of polymer molecular weight and is obtained according to ASTM (American Society of Testing and Materials) D 792 and D 4894. Traditionally, SSG is related to PTFE molecular weight using the equation of Sperati:¹

$$M_n = 0.597[\log_{10}(0.157)/(2.306-SSG)]^{-1} \times 10^6$$

Polymerization – PTFE Fluoropolymer prepared with DOSS

The following example illustrates a semi-batch process for making aqueous fluoropolymer PTFE dispersion to produce an approximately 25 weight % solids batch. PTFE fine powder is produced from the dispersion.

To a nominally 10-gallon reactor was charged 600 g of paraffin wax, 5 mL of *tert*-butanol, and 15 mL of a 20% (w/w) aqueous solution of perfluoroionomer particulate as disclosed in US (United States) Patent 6,916,853.² After adding 24.0 liters of water, the reactor was heated to 65 °C then pressured to 400 PSIG with nitrogen and checked for leaks. After venting, the reactor was purged with TFE and evacuated. After heating to 70 °C, 600 mL of a 0.2% (m/v) solution of ascorbic acid was added. The reactor was charged with TFE to a pressure of 390 PSIG then to start the polymerization, 200 mL of a 0.5% (m/v) aqueous solution of *tert*-butyl hydroperoxide (TBHP) was added. After this injection was complete, kickoff was declared and TBHP injection continued until the end of the batch (by which time 505 mL additional TBHP solution was added). Also,

¹ Sperati, C. A.; Starkweather Jr., H. W. *Fortschr. Hochpolym.-Forsch.* **1961**, 2, 465.

² Curtin, D. E; Howard, Jr. E.G. Compositions containing particles or highly fluorinated ion exchange polymer. US 6916853 B2, 2005.

after kickoff, additional TFE was fed to the reactor to maintain a constant pressure of 400 PSIG. Also, after kickoff 1000 mL of a 3.0% (m/v) solution of dioctyl sulfosuccinate (DOSS) was added at a rate of 40.0 mL/min. After a total of 8.2 kg of TFE were added since kickoff, the reactor was vented. The resulting dispersion, containing 25.36% polymer, was discharged from the reactor.

Polymer was coagulated by diluting the dispersion to about 14 wt. % solids and by adding about 3.7% by mass (dry weight) of a 20 wt. % aqueous ammonium carbonate solution followed by vigorous agitation until the polymer fully separated from the water. The polymer was dried at 150 °C. The SSG of this polymer is 2.1917.

51 **Table S1: Additional LCMS parameters - LC Gradient Profile:**

Time (min)	Aqueous Mobile Phase (%)	Organic Mobile Phase (%)
0.00	100	0
1.00	100	0
14.50	0	100
16.50	0	100
16.60	100	0

52

53

54 **Table S2: Additional LCMS parameters - MS Source conditions:**

Gas Temp (°C)	325
Drying Gas (L/min)	12
Nebulizer (psig)	45
Capillary voltage (V)	3500
Fragmentor (V)	175
Skimmer (V)	65
Oct 1 RF Vpp	750
Mode	Negative

55

56

Table S3: Concentrations of diacids measured through targeted LC/QqQ. Since quantitative analytical standards are not available for all analytes in the homolog series these diacids are quantified from a C8 or C10 diacid standard, i.e., two carboxylic acids ends with a perfluorinated C6 (CF₂ = 6) or C8 (CF₂ = 8), standard.

Calibration Standard	Analyte	MRM Transition	Concentration On Total Sample (ppbw)	Concentration on Polymer Basis (ppbw)
CF ₂ =6	CF ₂ =4	288.9 -> 181.0	6.24	24.6
CF ₂ =6	CF ₂ =5	338.9 -> 231.0	< 4.76	< 18.8
CF ₂ =6	CF ₂ =6	388.9 -> 281.0	28.1	111
CF ₂ =6	CF ₂ =7	438.9 -> 331.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =8	488.9 -> 381.0	27.6	109
CF ₂ =8	CF ₂ =9	538.9 -> 431.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =10	588.9 -> 481.0	12.2	48.2
CF ₂ =8	CF ₂ =11	638.9 -> 531.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =12	688.9 -> 581.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =13	738.9 -> 631.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =14	788.9 -> 681.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =15	838.9 -> 731.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =16	888.9 -> 781.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =17	938.9 -> 831.0	< 4.76	< 18.8
CF ₂ =8	CF ₂ =18	988.9 -> 881.0	< 4.76	< 18.8
Totals			74.2	293

Table S4: Concentrations of H-cap carboxylic acids measured through targeted LC/QqQ. Since quantitative analytical standards are not available for all analytes in the homolog series these acids are quantified from C5 (5H-acid), C7 (7H-acid), C9 (9H-acid), or C11 (11H-acid) standards.

Calibration Standard	Analyte	MRM Transition	Concentration On Total Sample (ppbw)	Concentration on Polymer Basis (ppbw)
5H-acid	5H-acid	245.0 -> 180.9	< 2.38	< 9.38
7H-acid	6H-acid	295.0 -> 230.9	1527	6020
7H-acid	7H-acid	345.0 -> 280.9	< 2.38	< 9.38
8H-acid	8H-acid	395.0 -> 330.9	2079	8199
9H-acid	9H-acid	445.0 -> 380.9	< 2.38	< 9.38
9H-acid	10H-acid	495.0 -> 430.9	1274	5025
11H-acid	11H-acid	545.0 -> 480.9	< 2.38	< 9.38
11H-acid	12H-acid	595.0 -> 530.9	1764	6955
11H-acid	13H-acid	645.0 -> 580.9	< 2.38	< 9.38
11H-acid	14H-acid	695.0 -> 630.9	1847	7283
11H-acid	15H-acid	745.0 -> 680.9	< 2.38	< 9.38
11H-acid	16H-acid	795.0 -> 730.9	2359	9303
11H-acid	17H-acid	845.0 -> 780.9	< 2.38	< 9.38
11H-acid	18H-acid	895.0 -> 830.9	1272	5017
11H-acid	19H-acid	945.0 -> 880.9	< 2.38	< 9.38
11H-acid	20H-acid	995.0 -> 930.9	96	378
Totals			12218	48179

Table S5: Concentrations of H-cap sulfonic acids measured through targeted LC/QqQ. Since quantitative analytical standards are not available for these analytes an analytical standard of PFOS is used for calibration.

Calibration Standard	Analyte	MRM Transition	Concentration On Total Sample (ppbw)	Concentration on Polymer Basis (ppbw)
PFOS 499	Adduct 281	281.0 -> 80.0	37.3	147
PFOS 499	Adduct 381	381.0 -> 80.0	252.2	994
PFOS 499	Adduct 481	481.0 -> 80.0	422.9	1668
PFOS 499	Adduct 581	581.0 -> 80.0	381.6	1505
PFOS 499	Adduct 681	681.0 -> 80.0	294.9	1163
PFOS 499	Adduct 781	781.0 -> 80.0	104.6	412
PFOS 499	Adduct 881	881.0 -> 80.0	102.1	403
PFOS 499	Adduct 981	981.0 -> 80.0	43.5	172
PFOS 499	Adduct 1081	1081.0 -> 80.0	10.6	42
PFOS 499	Adduct 1181	1181.0 -> 80.0	< 4.76	< 18.8
Totals			1650	6505