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Cynthia A. Mertdogan[a]; Mark A. McHugh[a]; Howard G. Barth[b]; Dennis J. Walls[b]; William H. Tuminello[b]

[a] Department of Chemical Engineering, Johns Hopkins University, Baltimore, Maryland [b] The DuPont Company, Wilmington, DE, U.S.A.

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CYNTHIA A. MERTDOGAN[a], MARK A. McHUGH[a,*], HOWARD G. BARTH[b], DENNIS J. WALLS[b] and WILLIAM H. TUMINELLO[b]

[a]*Department of Chemical Engineering, Johns Hopkins University, Baltimore, Maryland 21218 and* [b]*The DuPont Company, Experimental Station, Wilmington, DE 19880-0356, U.S.A.*

A perfluorinated copolymer, poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene), is fractionated using supercritical SF_6. The fractionations are performed isothermally at 163°C using an increasing pressure profile to obtain gram-sized fractions that have molecular weight distributions that are narrower than that of the parent copolymer. The fractionation pressure is increased in increments of 34 bar from 276 to 683 bar. The parent material and the fractions are characterized using SEC and FTIR spectroscopy. The first seven samples, eluting between 276 and 552 bar, show a trend of increased molecular weight of the fraction with increasing fractionation pressure. Above 552 bar, the molecular weight of the remaining fractions decreases with increasing fractionation pressure. Although these last fractions do not differ in hexafluoropropylene content, they do differ in the type and concentration of their end groups. In particular, the fractions that eluted at pressures greater than 552 bar contain increasing amounts of carboxylic acid end groups. The strong hydrogen-bonding interactions of these end groups prevent oligomers with acid ends from eluting from the column at lower pressures, which was expected due to their lower molecular weight.

Keywords: Supercritical fluid, fractionation, perfluoropolymer, poly(tetrafluoroethylene-co-hexafluoropropylene), copolymer, SF_6

INTRODUCTION

The advantage of supercritical fluids (SCF) relative to liquid solvents is that the solvent power of an SCF can be adjusted with small changes in pressure. Furthermore, when the pressure is reduced to ambient conditions,

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*Corresponding author.

the solubility of a polymer in an SCF drops essentially to zero, which facilitates recovery of a solvent-free polymer fraction. The utility of SCF fractionation has repeatedly been demonstrated for fractionating ethylene-based copolymers.[1–5] However, fewer studies report the fractionation of fluorinated polymers. Krukonis performs one such fractionation of low molecular weight chlorotrifluoroethylene oils in supercritical CO_2.[6] However, to the best of our knowledge, no fractionation studies of fluoropolymers of high molecular weight (greater than 100,000) are found in the literature.

The purpose of this article is to describe the SCF fractionation of a single high-melting, high molecular weight, semicrystalline perfluorinated copolymer, poly(tetrafluoroethylene-*co*-19.3 mol % hexafluoropropylene) (FEP_{19}). The hexafluoropropylene (HFP) comonomer in FEP_{19} reduces the crystallinity of the polymer, thereby lowering the peak melting point from 327°C for highly crystalline PTFE to 147°C for FEP_{19}. Dispersion forces are expected to be the dominant type of intermolecular force of attraction between segments of FEP_{19} given that the HFP incorporated in the copolymer backbone exhibits characteristics of nonpolar perfluoropropane. The parent FEP_{19} has a weight-average molecular weight of ~210,000[7] and is end-capped with carboxylic acid groups which amount to approximately 1,000 ppm acid groups.

McHugh *et al.*[4] present guidelines for choosing an appropriate SCF for a given fractionation based on the solubility characteristics of the polymer as a function of temperature and pressure. In the work presented here, the choice of an appropriate SCF and the operating conditions is based on a detailed study of the solubility of FEP_{19} in a wide variety of SCF solvents.[8] Although CO_2 is generally the preferred SCF solvent,[9] in this case, CO_2 is a weak solvent for FEP_{19} since it requires pressures above 1,000 bar at temperatures greater than 185°C to obtain a single phase, as shown in Figure 1. For this fractionation study, sulfur hexafluoride (SF_6) is used since it is an excellent SCF for FEP_{19} with cloud-point pressures of ~500 bar at temperatures as low as 115°C. The properties of SF_6 are given in Table I. The operating temperature of 163°C is chosen for the fractionation since it is greater than the peak melting point of FEP_{19} yet less than the degradation temperature of the polymer. Furthermore, a wide range of operating pressures are available to work with since the operating temperature is much greater than the critical temperature of SF_6, which yields a broad range of possible SCF densities.
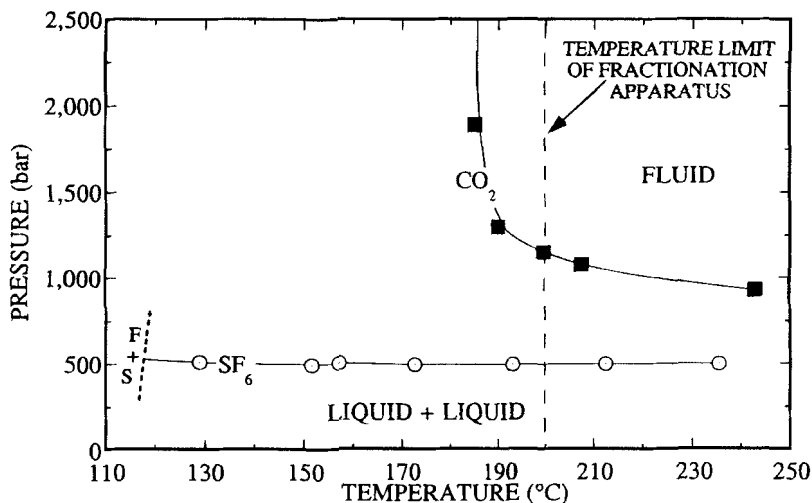
FIGURE 1   Comparison of the phase boundaries of 5 wt % poly(tetrafluoroethylene-*co*-19 mol% hexafluoropropylene) (FEP$_{19}$) in solution with SF$_6$ and CO$_2$[8] to demonstrate the preference of using SF$_6$ as a solvent for the fractionation of FEP$_{19}$, given that the operation of the fractionation apparatus is limited to a maximum of 200°C and 690 bar.

EXPERIMENTAL

The experimental apparatus and the techniques used in SCF fractionation are described in detail elsewhere[1,3,5] and are only mentioned briefly here. The fractionation schematic appears in Figure 2. Two fractionations were performed to confirm the reproducibility of the experimental yield. The fractionations employed a dynamic flow apparatus capable of operating to 200°C and 690 bar. The SCF flow rate varied from 2.5 to 7.0 L/min (STP) (~6.0 g/min) with the system pressure controlled to within ±5.0 bar and the system temperature to within ±1.0°C. The fractionation columns, filled with approximately 10 g of copolymer packed in steel mesh, are first purged with

TABLE I   Physical properties of sulfur hexafluoride (SF$_6$).[10,11] The polarizability was calculated using the method of Miller and Savchik.[12]

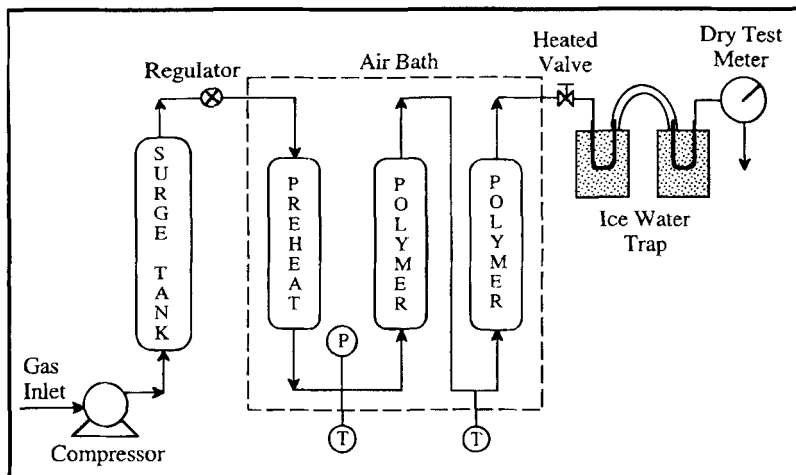| Solvent	Molecular Weight (g/mol)	Critical Temperature (°C)	Critical Pressure (bar)	Critical Density (g/cm³)	Polarizability (cm³ x 10⁻²⁵)	Dipole Moment (Debye)
SF$_6$	146.1	45.5	37.6	0.735	54.6	0.0

FIGURE 2   Schematic of the fractionation apparatus used in this experimental study.

nitrogen at room temperature to remove any air before introducing the SF_6 into the columns. The system is then heated to the desired temperature and allowed to equilibrate for 30 min under a blanket of gaseous SF_6. With the column pressure fixed, the flow is initiated by adjusting the metering valve at the end of the apparatus and the first sample is obtained. The loaded SCF exiting the column is expanded through a heated valve where copolymer precipitates into two preweighed U-tubes, which are connected in series and submerged in an ice-water bath. Glass-wool filters, at the exit of each U-tube, trap any fine mist entrained in the gas. The gas is routed to a dry-test meter to monitor the volumetric flow rate of the carrier gas through the extractors. After ~55 min or when polymer is no longer exiting the column, whichever requires the most time, the operating pressure is increased by 34 bar to obtain the next copolymer fraction. The copolymer in the U-tubes is weighed and analyzed for relative molecular weight and molecular weight distribution using size exclusion chromatography (SEC)[13] and for end-group content using Fourier-transform infrared spectroscopy (FTIR). The chromatography was performed at an elevated temperature with perfluo-rotetradecahydrophenanthrene (Flutec PP11) as the solvent.

Samples for FTIR measurements are prepared by dissolving 1.1 mg of the copolymer in approximately 2 mL of Flutec PP11 at ~130°C. The solu-

tions are then transferred to cylindrical wells drilled into NaCl infrared windows. The solvent is removed from the sample by drying the sample overnight on a hot plate at ~100°C, leaving a film of polymer on the bottom of the well. The dimensions of the wells (5-mm i.d. by 1-mm deep) are chosen to confine the solution to a sufficiently small area in order to produce a thick film, which is critical to allow observation of weak absorptions, such as those involving end groups.

The films are analyzed with a NicPlan Infrared microscope interfaced to a Nicolet 800 FTIR spectrometer. A 15X Cassegrainian objective is used in conjunction with aperturing to analyze a 100-mm diameter spot at the bottom of the well. There is considerable variability in film thickness at the bottom of the well and, in general, the sample is positioned to analyze the thickest portion of the film. The variability of the thickness makes it impossible to measure with any accuracy the thickness directly in the region analyzed. A spectroscopic method is therefore adopted to correct for sample-to-sample differences in film thickness. The samples analyzed are listed in Table II with their designations as to the pressure at which they were fractionated. Two sets of IR measurements and calculations are made for 2K to check reproducibility.

TABLE II   Amount extracted during the fractionations of poly(tetrafluoroethylene-co-19 mol% hexafluoropropylene) (FEP_{19}) with sulfur hexafluoride at 163°C. Note that the initial screening was performed up to 655 bar while the second fractionation was performed up to 683 bar.

Pressure (±2 bar)	First Fractionation (Initial Screening)				Second Fractionation			
	Fraction #	Fraction Wt (g)	FEP_{19} Wt %	Sum Wt %	Fraction #	Fraction Wt (g)	FEP_{19} Wt %	Sum Wt %
276		0.00			2A	0.04	0.4	0.4
379	1B	0.12	1.2	1.2	2B	0.11	1.1	1.4
414	1C	0.09	0.9	2.1	2C	0.10	1.0	2.4
448	1D	0.18	1.8	3.9	2D	0.16	1.6	4.0
483	1E	0.43	4.3	8.2	2E	0.69	6.7	10.7
517	1F	3.56	35.2	43.4	2F	3.00	29.1	39.8
552	1G	2.52	24.9	68.3	2G	2.26	21.9	61.7
586	1H	0.77	7.5	75.8	2H	0.92	8.9	70.6
621	1I	0.28	2.7	78.5	2I	0.78	7.5	78.1
655	1J	0.27	2.7	81.2	2J	0.81	7.9	86.0
683					2K	0.86	8.4	94.4
Remaining in column	1L	1.8	17.8	99.0	2L	0.2	2.0	96.4

* L = Copolymer remaining unfractionated at 163°C and highest operating pressure.

Peak heights of the individual end-group components were obtained through the use of curve fitting analyses of baseline-corrected data in the region from 1650 to 1850 cm^{-1} (GRAMS/386, Galactic Industries). Tangent baselines were drawn based on extrapolation of the baseline in the vicinity of the peaks of interest to remove the broad background response observed in this region. Curve fitting analysis was needed due to the large amount of spectral overlap between the various spectral features present in this region. Peak locations for the curve fitting analyses were chosen based on the expected location of end group absorptions, along with second derivative and deconvolution analyses of the experimental data to directly assess their location. Peak heights were related to end-group densities using relations developed internally for calculating end-group content in fluoropolymers.[14]

MATERIALS

The FEP_{19} was kindly donated by the DuPont Company. More detailed information on the characteristics of FEP_{19} are given by Tuminello,[7] where FEP_{19} is designated LMFEP-2. The HFP content (19.3 mol %) was determined spectroscopically and the weight-average molecular weight (210,000) was calculated from low-strain-rate melt viscosity. SF_6 (CP grade, 99.0 % minimum purity) was obtained from MG Industries. The solvent was used as-received.

RESULTS AND DISCUSSION

An initial screening for the fractionation was performed to determine at which pressures the fluorinated oligomers would elute from the column. Attention was focused on determining the general trends of the fractionation rather than on obtaining precise measurements or closing the mass balance. The copolymer was isothermally fractionated with SF_6 at 163°C starting at 138 bar with pressure increments of 34 bar. The first fraction, representing 1 wt % of the parent copolymer, began eluting from the column at 379 bar, followed by another 1 wt % of polymer at 414 bar, 2 wt % at 448 bar, and 4 wt % at 483 bar. At this point, the amount of copolymer eluting from the column increased dramatically to 35 wt % exiting the

column at 517 bar and 25 wt % exiting at 552 bar. This elution rate decreased to 7.5 wt % exiting at 586 bar and to 2.7 wt % at both 621 bar and 655 bar. The fractionation was terminated at 655 bar since the key pressures, where copolymer fractions exited the fractionation column, had been located. The initial screening provided a check for future fractionations on the reproducibility of the pressures at which much of the copolymer eluted as well as the relative amounts of copolymer eluting from the column.

With knowledge of the characteristic pressures for the fractionation of FEP_{19} in SF_6, more care is given to obtaining precise measurements and to closing the mass balance in the following fractionation experiment. Therefore, the isothermal fractionation of FEP_{19} in SF_6 is repeated at 163°C. The amount of copolymer extracted with respect to fractionation pressure appears in Table II. The yields of the second fractionation are in fair agreement with those of the initial screening. At 379 bar, 1 wt % of copolymer was extracted, followed by another 1 wt % at 414 bar. The elution amount steadily increased to 2 wt % at 448 bar and 7 wt % at 483 bar. The largest fractions of 29 wt % and 22 wt % eluted at 517 bar and 552 bar, respectively, which is consistent with the elution amounts from the initial screening. The remaining fractions exited between 586 bar and 683 bar and each contained ~8 wt % of copolymer. Approximately 2 wt % copolymer remained in the column at the end of the fractionation.

The yield from the initial screening, 81.2 wt %, as shown in Table II, suggests that 17.8 wt % more copolymer is expected to elute at pressures above 655 bar. The second fractionation experiment was carried out to 683 bar, and the higher pressure did, in fact, help improve the yield from 81.2 wt % to 94.4 wt %.

In Figures 3 and 4, polymer mass is plotted against elution time to show the relative molecular weight of the fractions. Note that the molecular weight of the fractions decrease with increasing elution time. SEC analysis ranked the fractions according to increasing molecular weight in the initial screening as

$$1D < 1E < 1K < 1K < 1J < 1I < 1F \sim 1G < 1H$$

and in the second fractionation as

$$2C < 2D < 2E < 2L < 2K < 2J < 2I < 2H < 2F < 2G$$

which shows that the fractions C, D, E, F, and G, which eluted between 414 and 552 bar, exhibit increasing molecular weight with respect to increasing
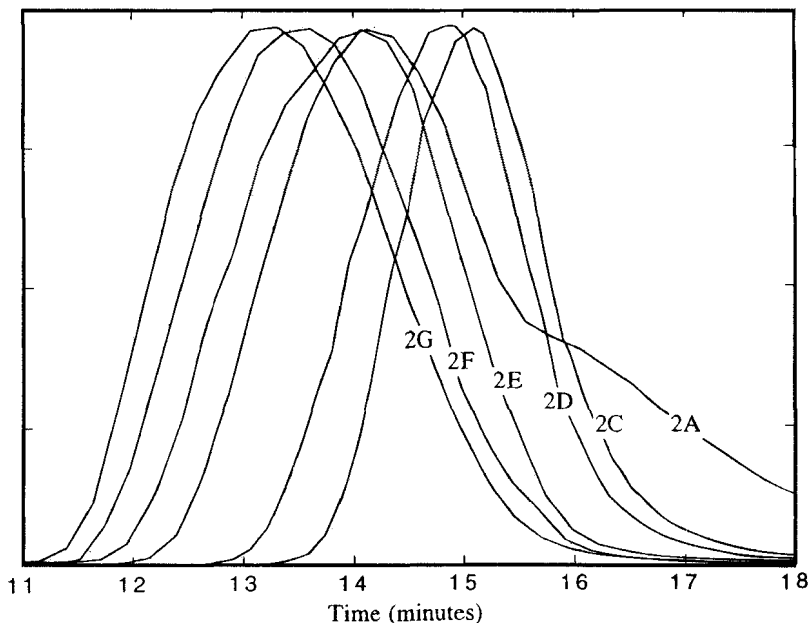
FIGURE 3   SEC plot shows increasing relative molecular weights of the fractions 2A through 2G. Note that molecular weight decreases with increasing elution time.

fractionation pressure. However, a simple relationship does not exist between molecular weight and fractionation pressure. Fractions H, I, J, K, and L, obtained at pressures above 552 bar, decrease in molecular weight as the fractionation pressure increased, which indicates that something other than molecular weight governs the fractionation of samples H through L. Thus, the next analysis, using FTIR, investigated compositional differences between the fractions as a potential second variable controlling the copolymer fractionation. Fractions from each representative elution group analyzed using FTIR included 2A, 2C, 2G, and 2K, the first, third, sixth, and ninth fractions, respectively.

Figure 5 shows the FTIR spectra for the parent FEP_{19} copolymer in the range of 4000–700 cm^{-1}, which is the useful portion of the spectra. This spectra and its labeled peaks are typical for the fractions. All of the spectra show strong absorption between 1050 and 1400 cm^{-1} due to $-CF_2$ stretching. Note that the absorptions near 1100–1200 cm^{-1} are offscale with severe over-absorption due to the thickness of the films. However, the film
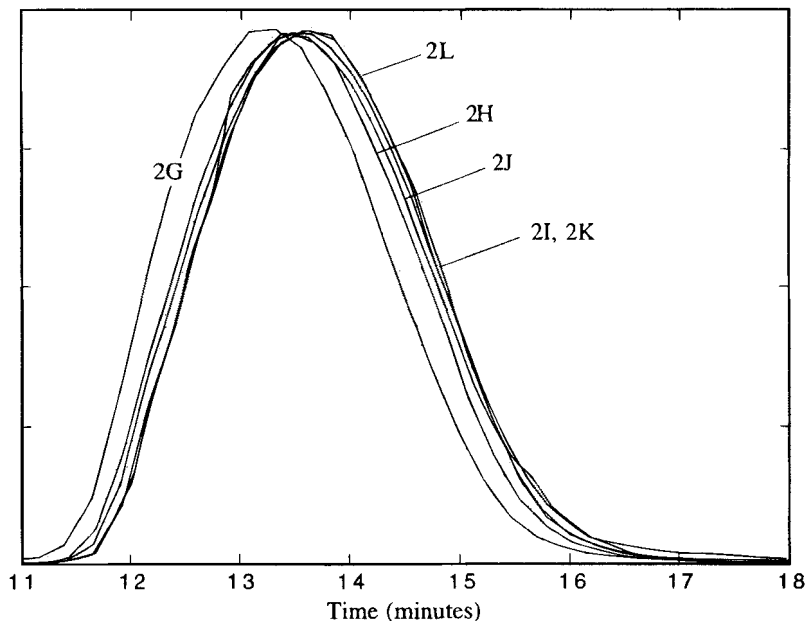
FIGURE 4   SEC plot shows decreasing relative molecular weights of the fractions 2G through 2L. Note that molecular weight decreases with increasing elution time.

thickness is appropriate for the measurement of the end groups and the comonomer bands. The spectra also include a band at 982 cm^{-1} due to the presence of pendant perfluoromethyl groups associated with the HFP comonomer and a broad band centered near 2370 cm^{-1} associated with $-CF_2$ overtones.

The comonomer content is calculated from the infrared spectra using the intensity of the comonomer band at 982 cm^{-1} relative to the intensity of the overtone absorption at 2370 cm^{-1}. The intensity of the overtone band is used as an internal reference since this intensity is not expected to change with small variations in comonomer content. NMR measurements of the comonomer content in the unfractionated material is used to determine a scaling factor to relate the infrared intensity ratio directly to relative comonomer content. The mole fraction of HFP as determined by NMR is 0.193 while the infrared ratio of the comonomer band to the overtone band is 9.93, which gives a normalization factor of 0.0194. The data in Table III, which shows the "corrected" mole fraction using the normalization factor,
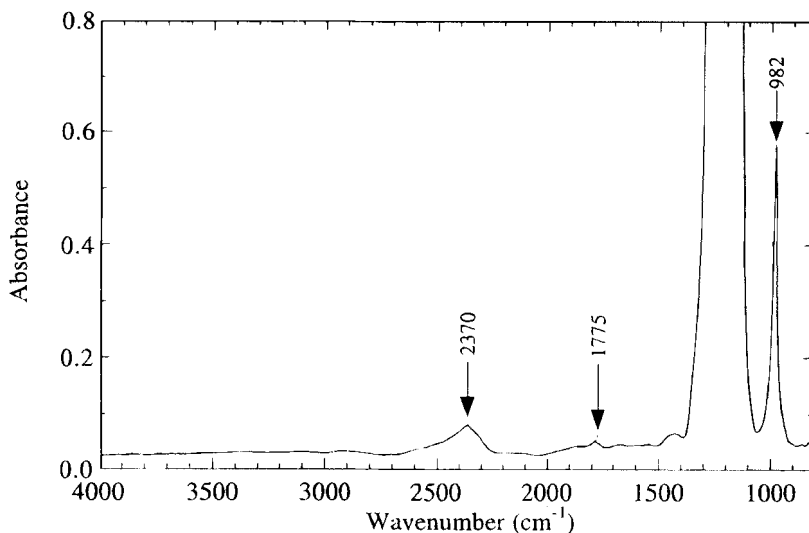
FIGURE 5   The FTIR spectrum of the parent FEP_{19} copolymer highlights peaks due to the comonomer band at 982 cm^{-1}, the $-CF_2$ overtone band at 2370 cm^{-1}, and an end-group band at 1775 cm^{-1}.

indicates that each of the fractions and the parent material have essentially the same HFP content. The slight increase in HFP content of Fraction 2A is not unexpected since this fraction elutes from the column at very low pressures and Fraction 2A represents less than 0.5 wt % of the parent material. Since compositional differences in copolymer content of the fractions are not significant, the compositional differences in end-group content was examined next to determine whether this variable controlled the later stages of the fractionation.

TABLE III   Comonomer content for four fractionated samples and the parent copolymer as determined from FTIR and NMR measurements

Fraction #	mol fraction HFP
2A	0.24
2C	0.20
2G	0.21
2K	0.20
Parent	0.19

The FTIR spectra in Figures 6 and 7 focus on the region in which significant end-group bands are present. A comparison of these spectra show the variation of end-group distribution between the various fractions analyzed. Monomeric and dimeric carboxylic acid (–COOH), carboxylate salt (–COO⁻M⁺), and perfluorovinyl (–CF = CF₂) end groups for selected fractions are identified and quantified using a curve fitting analysis described in the experimental section. Results are listed in Table IV for each end group as well as the total number of end groups. It should be noted that the acid monomer-dimer content is a function of sample preparation and solution composition. Therefore, the monomer and dimer amounts are combined to form a total acid end-group content. Fraction 2A, collected at the
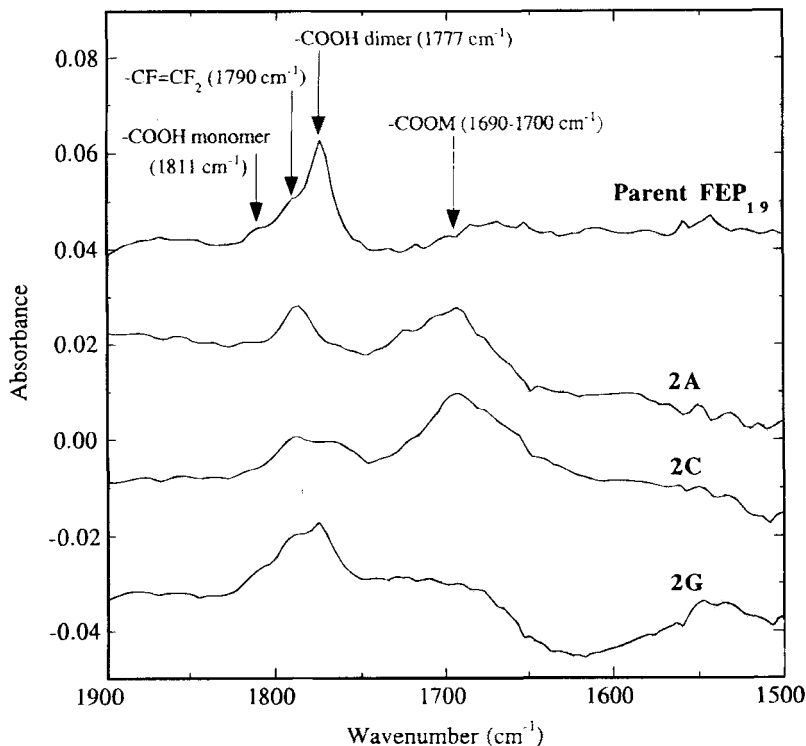

FIGURE 6   The FTIR spectra focused on the region of end-group bands for the parent FEP₁₉ copolymer and fractions 2A, 2C, and 2G. Note that the plot identifies the major peaks due to end groups, which include monomeric and dimeric carboxylic acid (–COOH), carboxylate salt (–COO⁻M⁺), and perfluorovinyl (–CF = CF₂) groups.
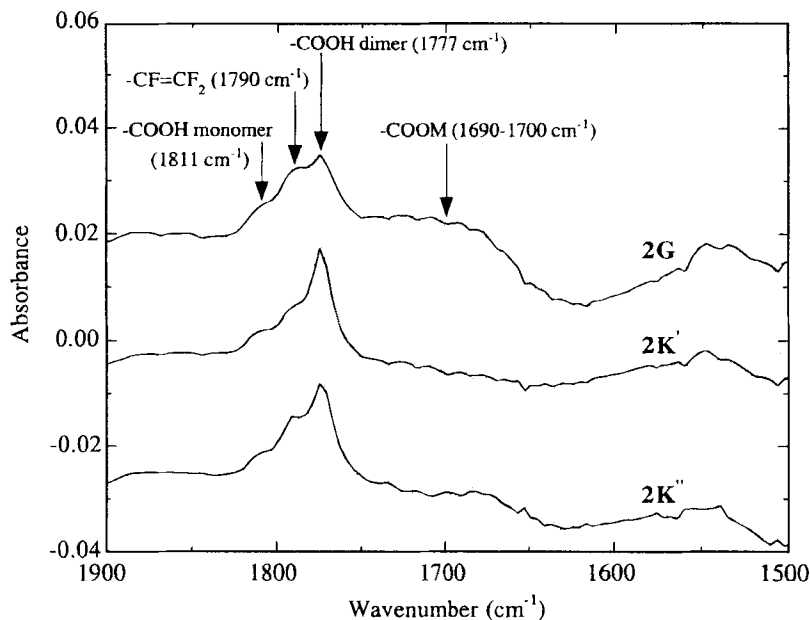
FIGURE 7 The FTIR spectra focused on the region of end group bands for fractions 2G, 2K′, and 2K″. Note that the plot identifies the major peaks due to end groups, which include monomeric and dimeric carboxylic acid (–COOH), carboxylate salt (–COO⁻M⁺), and perfluorovinyl (–CF = CF₂) groups.

TABLE IV End group (per 10^6 CF_2) content and number-average molecular weight results obtained from FTIR analysis for four fractions and the parent copolymer. The type of end groups include monomeric and dimeric carboxylic acid (–COOH), carboxylate salt (–COO⁻M⁺), and perfluorovinyl (–CF = CF₂) groups. The total carboxylic acid (–COOH) content is the sum of the number of monomers and two times the number of dimers, given that each dimer is made up of two associated monomer ends. Note that two different analyses of fraction 2K are presented as 2K′ and 2K″.

Fraction #	–COOH Monomer	–COOH Dimer	Total –COOH	–CF=CF₂	–COO⁻M⁺	Total End Groups	M_N
frequency (cm⁻¹)	1811	1777		1790	1690–1700		
2A	190	0	190	2,530	1,380	4,100	29,800
2C	130	0	130	1,170	930	2,230	54,700
2G	140	200	540	480	120	1,140	107,000
2K′	160	370	900	570	0	1,470	83,000
2K″	150	400	950	650	90	1,690	72,200
Parent	80	320	720	480	90	1,290	94,600

lowest pressure, has significant absorptions near 2855 and 2926 cm^{-1}, indicating the presence of aliphatic methylene and methyl groups. This is the only fraction to show significant levels of aliphatic hydrocarbons, which may be present due to residual solvent or impurities. Given that end-group content differs between the fractions, it is important to determine if a correlation can be drawn between fractionation pressure and end-group content.

The data in Table IV show a decrease in the number of carboxylate end groups with increasing fractionation pressure. However, it is difficult to analyze the absolute numbers of carboxylic acid and perfluorovinyl end groups since they do not vary consistently with fractionation pressure. For example, the number of acid and perfluorovinyl ends decreases from 2A to 2C and then increases from 2G to 2K' and 2K". When the end groups are presented as percentages of total end groups for each fraction, trends in end group content between the fractions become apparent, as seen in Table V. The percent of carboxylic acid ends increases with increasing fractionation pressure while the percent of perfluorovinyl and carboxylate ends decreases with increasing fractionation pressure. Figure 8, which shows the end-group distribution of the various fractions, can be used to estimate the end group content of the fractions not analyzed with FTIR. The number-average molecular weight M_n for four fractions and the parent copolymer is calculated from the total number of end groups, with the results shown in Table IV. The M_n is consistent with the SEC analysis. While SEC detected that the later fractions possessed a lower molecular weight than earlier fractions, the FTIR similarly showed that these fractions had more end groups, implying shorter chains, than fraction 2G.

TABLE V   The percent of end-group type (per 10^6 CF$_2$) for four fractions and the parent copolymer to show a correlation between end group concentration and fractionation pressure. The end-group types include carboxylic acid (–COOH), carboxylate salt (–COO⁻M⁺), and perfluorovinyl (–CF = CF$_2$) ends. Two different analyses of fraction 2K are presented as 2K' and 2K".

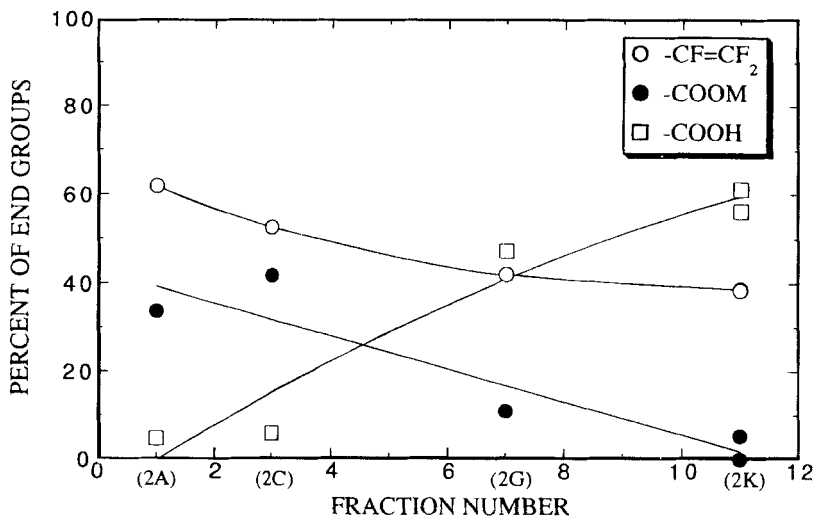| Fraction #	% –COOH	% –CF=CF$_2$	% –COO⁻M⁺
2A	4.6	62	34
2C	5.8	52	42
2G	47	42	11
2K'	61	39	0
2K"	56	38	5.3
Parent	56	37	7.0

FIGURE 8   Distribution of end groups with increasing fraction number of poly(tetrafluoroethylene-*co*-19 mol% hexafluoropropylene) (FEP_{19}) in SF_6 at 163°C, where fraction numbers one to eleven correspond to fractions 2A through 2K.

The increase in the percent of carboxylic acid end groups with increasing fractionation pressure suggests that the oligomers that elute after fraction 2G are hydrogen bonded with one another. The strong cohesive interactions between polymer chains with acid ends make these oligomers less soluble in nonpolar SF_6 relative to higher molecular weight chains that are not hydrogen bonded. Thus, the strong hydrogen-bonding interactions between the end groups on polymer chains dominate the effect of molecular weight as the controlling factor in the later stages of the fractionation. The fractionation results also suggest that a fluorocopolymer with carboxylate ends would be soluble at lower pressures and temperatures in a nonpolar SCF than a copolymer with acid end groups even though the copolymer molecular weight is on the order of 100,000.

CONCLUSIONS

SF_6 is used to fractionate FEP_{19} since SF_6 is perhaps the most effective low molecular weight SCF for FEP_{19} due to its large polarizability and high density relative to other low molecular weight SCF solvents.[8] The

fractionation of FEP_{19} is controlled by copolymer molecular weight at fractionation pressures below 552 bar. Fractions obtained at pressures greater than 552 bar had molecular weights that are lower than those obtained at lower pressures, which suggests that a second variable controls the fractionation at high pressures.

FTIR analyses of the FEP_{19} fractions revealed that the fractionation is also controlled by the distribution of end-group types. At pressures up to 552 bar, the number of weakly polar carboxylate and perfluorovinyl end groups decreases with increasing fractionation pressure while the number-average molecular weight of the fractions increases simultaneously. The percent of carboxylic acid end groups increases as the percent of weakly polar carboxylate and perfluorovinyl end groups decreases with increasing fractionation pressure throughout the fractionation. As a result, midway through the fractionation, the number-average molecular weight of the fractions decreases and the fractionation switches from molecular weight controlling to end group controlling. The strong hydrogen-bonding interactions between copolymer acid ends dominate copolymer-nonpolar SF_6 interactions and prevent removal of these lower molecular weight fractions from the fractionation column at lower pressures. The fractionation results reported here reveal the impact of end-group type on copolymer solubility in SCF solvents.

Acknowledgements

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