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Substitution of Poly(chlorotrifluoroethylene) with Sulfur Dioxide under Reductive Conditions

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ABSTRACT

Treatment of Poly(chlorotrifluoroethylene) (in the forms of Kel-F 6061 and Neoflon M400H) with Zn/SO_2 in DMF results in substitution of the chloride ligand with the sulfinic acid moiety. Subsequent oxidation affords the sulfonic acid. The materials are characterized by elemental analysis, titration, scanning electron microscopy, and FT-IR. ATR-IR studies indicate that functionalization is probably not a surface-selective phenomenon. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:265–269, 1998

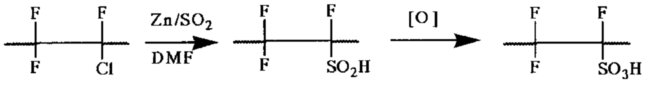
INTRODUCTION

For several years, our group has been engaged in efforts to carry out the selective functionalization of poly(chlorotrifluoroetylene) (PCTFE) [1–4]. Our main interest has been the substitution reaction of PCTFE by replacement of the chloride substituent. The use of such a strategy affords a derivatized polymer that could closely approximate the mechanical properties of PCTFE. Cais and Kometani [5] have reported the preparation of poly(trifluoroethylene) from PCTFE using tin hydride as a reducing agent. This work showed that the tin radical can selectively abstract a chlorine atom rather than a fluorine atom and that the resulting PCTFE radical is trapped by hydride prior to any further reaction (rearrangement or elimination). By following this route, our group began to develop new methods for generation of PCTFE radical with subsequent trapping by other types of radical scavengers. In our previous work, we have reported the reactions of PCTFE with sulfur, selenium, and phosphorus nucleophiles [6].

Wakselman and Tordeux [7,8] have reported a chemical method for the preparation of trifluoromethanesulfonic acid. This procedure involves the reaction of zinc metal with sulfur dioxide in DMF, followed by the addition of trifluoromethyl bromide. We report herein a method for the preparation of PCTFE-sulfinic acid from PCTFE, which is subsequently oxidized to the sulfonic acid (see Scheme 1). These ion-exchanging polymers are characterized by titrimetric analysis, scanning electron microscopy, ATR-FT-IR, and elemental analysis.

RESULTS

Using Zn and condensed SO_2 as a starting material, Kel-F and Neoflon were subjected to conditions that



SCHEME 1

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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generate free radicals [9]. Evidence for the proposed reaction can be gained from an analysis of the infrared results (see the ATR results below). Spectra of both sulfinated polymers show the presence of new absorptions located near 3173, 1504, 1093, 1020, 875, and 622 cm^{-1}. In addition, the band located near 963 cm^{-1} is reduced in intensity, and the band envelope centered near 1120 cm^{-1} is modified from that of Kel-F.

Examination of the infrared spectra of both Kel-F and Neoflon shows that the absorption located near 963 cm^{-1} is associated with the C–Cl stretch within the chlorinated fluorocarbon. The decrease in intensity of this absorption is supportive of the proposed reaction. Further evidence comes from the presence of absorptions located near 3172, 1093, and 875 cm^{-1} [10]. These absorptions are indicative of sulfinic acid and its characteristic infrared absorptions assigned to the O–H stretch, the S=O stretch, and the S–O stretch, respectively. The band located near 1020 cm^{-1} suggests the presence of the salt of sulfinic acid. These materials have absorptions located near 1020 and 980 cm^{-1} [11]. The absorption located at 980 cm^{-1} overlaps that of the C–Cl moiety remaining in the polymer. At present, there are three absorptions remaining in the spectra of the sulfinated polymer (1504, 665, and 622 cm^{-1}) whose origin is presently unknown. The sulfinated derivative was subsequently oxidized to the sulfonated derivative using hydrogen peroxide. The usual range of IR absorption of the SO_3 asymmetric stretch extends from 1230 to 1120 cm^{-1}. IR analysis of the sulfonated derivative did not show O–H stretch due to the formation of sulfonic acid salt but showed asymmetric SO_3 stretch at 1195 cm^{-1}.

The bulk characteristics of this material were confirmed by elemental and titrimetric analysis. In a typical experiment, elemental analysis indicated 18.02% C, <0.5% H, 20.19% Cl, 32.78% F, and 6.67% S. Assuming an idealized conversion to a sulfinic acid modification, the sulfur analysis would indicate a 25.9% degree of functionalization and a loading of 2.08 meq/g. Back calculation of the other elements would indicate 21.18% Cl, 16.12% C, and 45.97% F. While there is rough agreement (except for the difficult fluorine analysis), the substitution is clearly more complex. Using an oxygen content equal to the sulfur content leaves a remaining elemental content of about 18%, which IR analysis would lead us to believe are counterions to the sulfinic acid salt. It would appear that there are some sulfinic acid sites that can be subject to ion exchange, while others remain in the salt form. The presence of such metal cations would serve to lower the predicted chlorine analysis and increase the carbon and fluorine analyses.

Calculations from titrimetric analysis [12] of the same lot was again consistent with incomplete exchange. An ion exchange capacity of 0.55 meq/gm was determined for the sulfinated derivative of Kel-F and 0.24 meq/gm in a similar reaction with Neoflon. Ion exchange capacity for the sulfonated derivatives (oxidation of the same materials) was found to be 0.317 and 0.173 meq/gm for Kel-F and Neoflon, respectively.

McCarthy [13] indicated some degree of surface selectivity in various reaction of PCTFE. To gain some insight into surface modification and depth profiling, we undertook SEM and ATR studies. The SEM of Kel-F and its sulfinated derivative as well as the analogous species using Neoflon showed no change in the nature of the polymer morphology following the reaction. While the surface edges were smoothed, no degradation or pitting was observed. The additional observation of no color change on reaction also was in accord with clean substitution. Elemental analysis (using SEM) of individual particles of sulfinated polymers (which was converted to acid before titration) showed the composition to be 9.88% sulfur, 18.21% zinc by weight for Kel-F and 4.76% sulfur, 8.31% zinc by weight for Neoflon, in accord with the isolation of the zinc salt. Thus elemental and titrimetric analyses show that the level of functionalization on Kel-F was more than double that of Neoflon, with a similar ratio of exchangeable sites.

The ATR–IR spectrometer consisted of a Nernst glower operated at 1050°C, a KBr beam splitter, and a deuterium tryglycine sulfate (DTGS) detector. The optical geometry of the ATR microscope consisted of a single bounce reflection at 45° within a hemispherical internal reflection element. The active area at the sample point is 200 μm in diameter. Both silicon and germanium internal reflection elements were employed yielding an average sampling depth, "d_p", of 2 and 1 μm over the mid-infrared spectrum, respectively. A 0.5 kg loading was employed to ensure constant pressure between the sample and the internal reflection element.

Each spectrum is the result of 32 co-additions at 4 cm^{-1} resolution. Fourier transforms were conducted using a fast Fourier transform and strong apodization function. The Neoflon pellets were analyzed as received, whereas the Kel-F powder was pressed into a pellet prior to analysis. ATR–Infrared spectra of the sulfinated derivatives of Kel-F and Neoflon are shown in Figures 1 and 2, respectively. Each figure compares the spectra of PCTFE (*bot-*

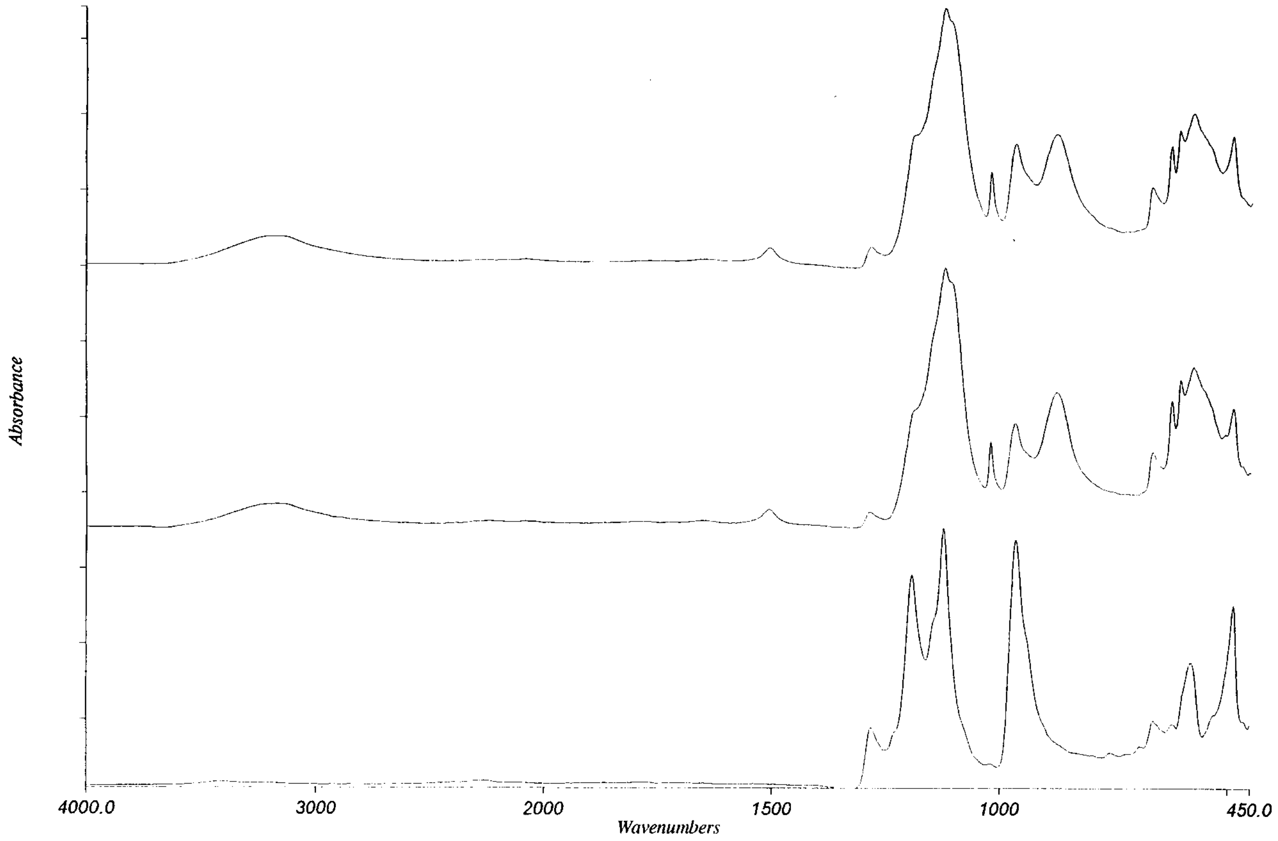


FIGURE 1 ATR analysis of KelF sulfinylation (see text).

tom), the sulfinated polymer at 0.6 μm penetration depth (*middle*), and the sulfinated polymer at 0.7 μm penetration depth (*top*). A comparison of the spectra as a function of depth shows little difference in the case of Kel-F; however, for those of Neoflon, some differences are observed in the C–Cl and sulfinic acid (875 cm^{-1}) absorptions. In probing the sulfinated polymer to a greater depth, the C–Cl absorption decreases, and the sulfinic acid absorption shows a moderate increase probing deeper into the polymer surface. At present, the cause for this observation is not clear and will be the subject of a future investigation.

EXPERIMENTAL

General

Kel-F 6061 was provided by 3M Corporation. Neoflon was provided by Daikin corporation. All other reagents were purchased from Aldrich Chemical Company and used as received.

IR spectra were obtained using a Perkin Elmer 1600 Series FT-IR spectrometer. ATR–IR spectra were collected with a Perkin Elmer Spectrum 2000 FTIR spectrometer interfaced to a Harrick split-pea attenuated total internal reflection (ATR) microscope. SEM spectra and polymer pictures were obtained on a Philips 505 SEM spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation of PCTFE–SO_2H

PCTFE (5.0 g, 43 meq), 5.59 g (86 mmol) zinc metal, and 35 mL (785 mmol, condensed using acetone/dry ice) sulfur dioxide were suspended in 300 mL of DMF under nitrogen. The resulting slurry was stirred at −23°C for about 4 hours, and an additional 35 mL sulfur dioxide was added. The slurry was then stirred for 4 hours and allowed to come to room temperature over 2 days. The cloudy yellow mixture was quenched with aqueous sodium hypochlorite, filtered, and washed sequentially with hexane, acetone, methanol, water, and methanol. The product was dried in an Abderhalden apparatus with refluxing toluene and reduced pressure overnight. The product (sulfinated derivative) was further characterized by titrimetric analysis. IR(KBr) 3445(br),

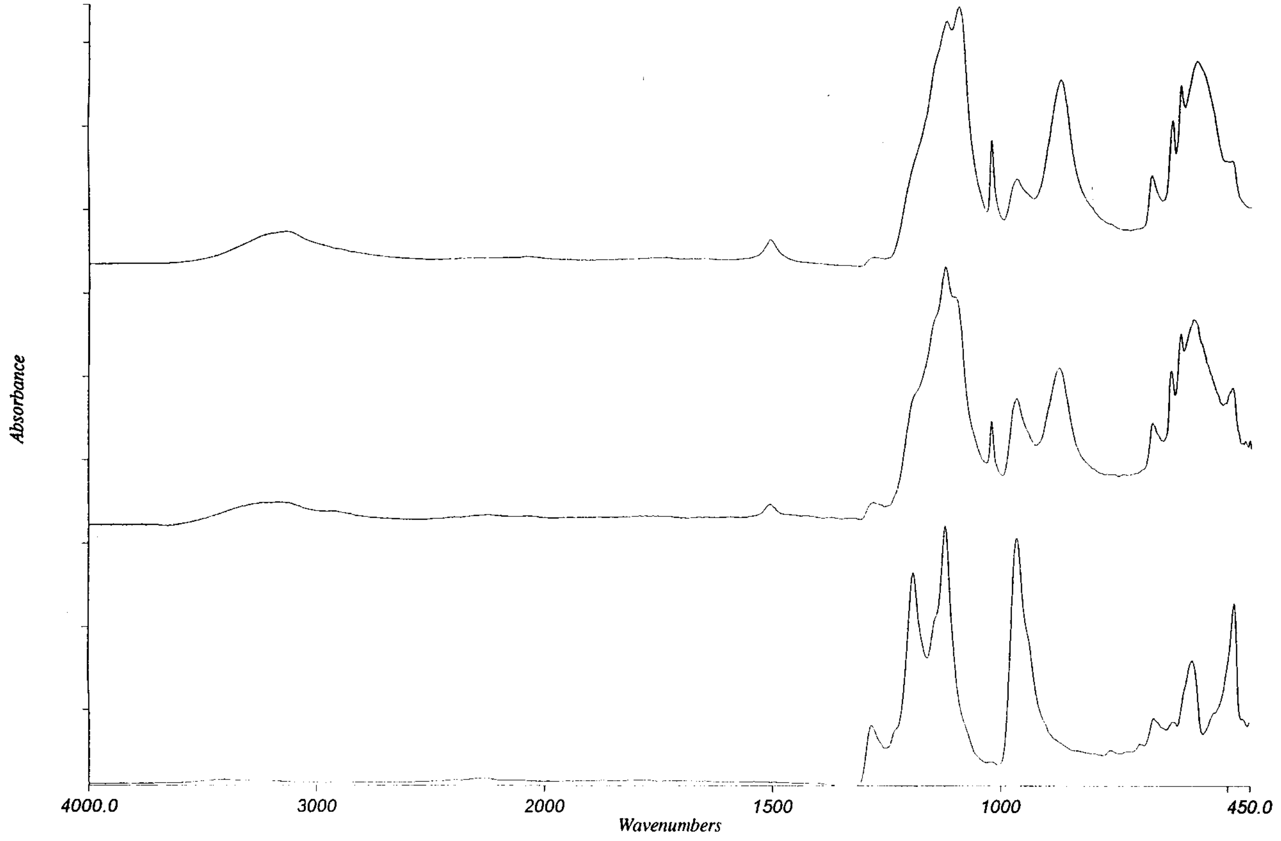


FIGURE 2 ATR analysis of Neoflon sulfinylation (see text).

1288, 1151, 1121, 978 cm^{-1}; titrimetric analysis—0.55 meq/gm ion exchange capacity for Kel-F and 0.24 meq/gm for neoflon; SEM—9.88% sulfur and 18.21% Zn by weight for Kel-F; 4.76% sulfur and 8.31% Zn by weight for Neoflon.

Preparation of PCTFE–SO_3H

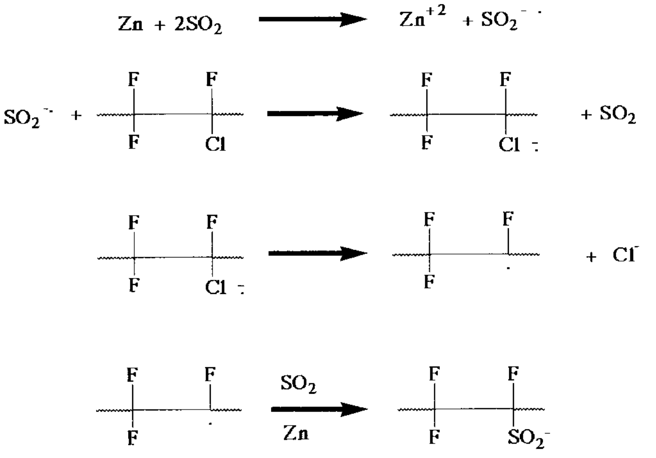
Into 200 mL THF was mixed the above-prepared PCTFE-SO_2H and 50 mL 30% hydrogen peroxide. The slurry was stirred for 24 hours at room temperature. The resulting off-white powder was filtered off, washed with water then acetone, and dried in an Abderhalden apparatus with refluxing toluene and reduced pressure overnight. The product was further characterized by titrimetric analysis. IR(KBr) 3448 (br), 1291, 1202, 1154, 1124, 977 cm^{-1}; titrimetric analysis—0.31 meq/gm ion exchange capacity for Kel-F and 0.17 meq/gm for Neoflon.

Procedure for Titrimetric Analysis

A slurry of each polymeric acid and 3M HCl was stirred at approximately 80°C for 3 hours. The resin was filtered off on a Buchner funnel and washed with distilled water. The sample was then dried in an Abderhalden apparatus with refluxing toluene and reduced pressure over night. The sample was then prepared for titration as follows: A mixture of the acid (1.0 g), NaCl (1.0 g; 17.1 mmol), 10 mL distilled water, and 3–5 mL methanol was stoppered and sonicated overnight. Phenolphthalein (3–5 drops of 1% in methanol solution) was added to this mixture and titrated against 0.05 M standardized NaOH solution. Ion exchange capacity was determined to be 0.55 meq/gm for (Kel-F) PCTFE–SO_2H, 0.31 meq/gm for (Kel-F) PCTFE–SO_3H, 0.24 meq/gm for (Neoflon) PCTFE–SO_2H, and 0.17 meq/gm for (Neoflon) PCTFE–SO_3H.

DISCUSSION

The reaction of PCTFE and zinc (two solids) does not proceed without the presence of condensed sulfur dioxide. In the presence of sulfur dioxide, this reaction is proposed to take place by a completely analogous single-electron transfer process (Scheme 2). Sulfur dioxide is reduced by zinc to form sulfur dioxide radical anion, which transfers an electron to PCTFE to give a new radical anion. This radical an-



SCHEME 2

ion can dissociate to give a perfluoroalkyl radical and chloride anion. The perfluoroalkyl radical can combine with the sulfur dioxide radical anion to give PCTFE–sulfinate. In the literature, it has been reported that such a reaction can be carried out using dithionate or rongalite (hydroxymethane sulfinate) [14,15]. However, we found the Zn/SO_2 system more effective. We have not been successful in trapping species other than sulfur dioxide, although our efforts to decompose the sulfinic acid intermediate in the presence of radical traps continues.

The relative inaccessibility of a majority of the modified sites is not unexpected. The reactivity and selectivity of a functional group anchored to a polymer may be significantly altered. The origins of such effects may be chemical or physical in nature. The various "polymer effects" are difficult to separate and assess individually but are likely due to individual effects on the microenvironment due to intrapolymer interactions.

CONCLUSION

We have shown that PCTFE sulfinate can be prepared by a one-electron transfer process. The Zn/SO_2 system is capable of functionalizing PCTFE without degradation of polymer backbone and no apparent side reaction. Ion exchange properties can be examined by titrimetric analysis. While not all sulfur-containing groups are actively exchanging, there is a rough correspondence between ion exchange capacity and total sulfur content. While the level of functionalization of KelF 6061 seems to be depth independent, that of Neoflon M400H may be at least somewhat surface selective. Future efforts in our research group will include the trapping of the perfluoroalkyl radical intermediate by a species other than sulfur dioxide.

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