Synthesis of a Copolymer of Tetrafluoroethylene and 1-Fluorosulfonyl–Difluoroacetylfluoride

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SYNOPSIS

Tetrafluoroethylene (TFE) was copolymerized with 1-fluorosulfonyl–difluoroacetylfluoride (FSDFAF) in both the bulk and solution by using a free radical initiator at temperature 50°C. The presence of sulfonyl fluoride ($-SO_2F$) functional groups in the copolymers was proved by infrared (IR) spectroscopy. The copolymers were subjected to alkaline hydrolysis followed by an acid treatment and the $-SO_2F$ groups content was found not to exceed 0.40–0.50 meq/g with polymer yield ranging between 1 and 36%. Copolymerization in solution of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) under TFE pressure about 1.0 MPa and TFE/FSDFAF mole ratio 1.5–2.0 was proposed for further investigations. A random distribution of single FSDFAF units along the polymeric chain consisting mainly of TFE fragments was considered to exist. The copolymers had melting temperatures within 10–15°C lower than polytetrafluoroethylene and their thermal stability was 360–380°C.

INTRODUCTION

Copolymers of tetrafluoroethylene (TFE) and perfluorinated functional monomers, containing sulfonylfluoride ($-SO_2F$) or carboxylic ester (e.g., $-COOCH_3$) groups are considered to be valuable materials. This is particularly due to their high thermal and chemical stability, combined with the fact that after alkaline hydrolysis such copolymers acquire hydrophilic and ion-exchange properties. Application of these copolymers as cation-exchange membranes in chlor-alkali electrolytic cells[1,2] as well as heterogeneous polymeric catalysts in the organic synthesis[3] is known to be a very promising research and development area.

Synthesis of perfluorovinyl functional monomers with general formula

$$CF_2=CF(OCF_2CF)_nOCF_2$$
$$|$$
$$CF_3$$

CF_2SO_2F ($n = 0, 1$) or $CF_2=CFO(CF_2)_nCOOCH_3$ ($n = 1-5$) is a multistage and time-consuming procedure.[1,4] According to some authors, one of the intermediate fluoroorganic compounds, 1-fluorosulfonyl–difluoroacetylfluoride $FOC-CF_2-SO_2F$ (FSDFAF) can be subjected to free-radical copolymerization with TFE in nonaqueous medium.[5]

A few publications on the copolymerization of TFE with perfluorinated carbonyl compounds have been available so far. Typical examples of such comonomers include hexafluoroacetone $F_3C-CO-CF_3$ and 3-ketoglutarylfluoride $FOCCF_2-CO-CF_2-COF$.[6-9] These compounds are considered to contain weakly polarized carbonyl groups, due to the electron-attracting nature of the adjacent perfluoroalkyl radicals.[7] This is why perfluorinated carbonyl compounds of a similar structure are prone to a free-radical copolymerization with fluoroolefins, thus introducing perfluoroether bonds into the polymeric backbone.[8,9] No data concerning the content of perfluorinated carbonyl-containing comonomers in the polymers have been reported, presumably due to their low reactivity.

The aim of the present work was to study the possibilities of chemically-induced free-radical copolymerization of TFE with FSDFAF and to determine some basic properties of the products obtained.

EXPERIMENTAL

Reagents

Tetrafluoroethylene (TFE) was prepared by a debromination of 1,2-dibromotetrafluoroethane (Montedison) in a slurry of zinc powder and glacial

acetic acid (Merck).[10] According to gas-chromatographic analysis, the purity of monomer obtained was 99.7–99.9%. 1-Fluorosulfonyl–difluoroacetylfluoride (FSDFAF), bp 28–30°C, was synthesized by a reaction of TFE with freshly distilled sulfur trioxide (from 30% oleum, Merck), followed by isomerization of tetrafluoroethane–β-sultone thus obtained in the presence of catalytic amounts of triethylamine.[11] Bis(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox 16, 95%, Akzo Chemie) was used as a free-radical initiator. 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113, Merck) dried preliminarily on molecular sieves was employed as a solvent in some of the copolymerization experiments.

Copolymerization of TFE with FSDFAF in Bulk

A 50 cm³ stainless-steel ampoule was charged with an initiator followed by thorough evacuation (10^{-2} mm Hg) at room temperature. After cooling to −30°C, FSDFAF was introduced slowly into the ampoule through a vacuum manifold system. TFE (7–10 g) was then condensed at liquid nitrogen temperature by using a metal vacuum line for transferring gases. The reaction mixture was subjected to several freeze–thaw cycles in order to remove traces of oxygen presumably present. The ampoule was then dipped into a thermostatic bath and the copolymerization was carried out under vigorous shaking. Finally, the reaction mixture was cooled to room temperature; the residual monomers were removed by outgassing and thorough washing with distilled water. The polymer was then washed with methanol, filtered, and dried overnight under vacuum at 130–140°C to constant mass.

Copolymerization of TFE with FSDFAF in a Solution

Copolymerization experiments were carried out in 500 cm³ stainless-steel reactor provided with an electromagnetic stirrer, heating mantel, and electronic devices for reaction parameters control (Büchi, Germany). The reactor was initially dried and deoxygenated by flushing nitrogen, followed by evacuation and cooling to 0–5°C. A solution of Perkadox 16 in Freon 113 (170 cm³) and FSDFAF previously cooled down to −80°C and evacuated were consecutively introduced. The reactor was charged with TFE to a certain pressure and then was heated to the reaction temperature under vigorous agitation ($13.5 \ s^{-1}$). After finishing copolymerization the product was treated as described above.

Determination of Sulfonyl Fluoride Groups Content in the Copolymer

A sample of the copolymer (∼ 2 g) was subjected to hydrolysis treatment with 50 cm³ of 1 : 1 volumetric mixture of methanol and 5N NaOH at 70°C for 16 h under reflux and vigorous stirring. The sample was then filtered and washed with distilled water in order to remove any traces of alkaline solution. The polymer was transferred to another flask and was stirred with 50 cm³ 2N HCl at 60°C for 10 h. After washing and vacuum drying to constant mass, 0.5–1 g accurately weighed dry sample was immersed into a solution prepared by adding 25 cm³ 0.1N NaOH to 25 cm³ methanol. The mixture was stirred for 24 h at room temperature and excess sodium hydroxide was determined by back titration with standard 0.1N HCl. The FSDFAF content in the polymer sample was calculated, as follows:

$$m_2 = \frac{320}{320 - 3.2M + 3200/A} \times 100$$

where A is the concentration of hydrophilic functional groups in the hydrolized and acidified sample determined by backtitration with 0.1N HCl (meq/g). $M = 180$ is FSDFAF molecular mass. m_2 represents FSDFAF content in the polymer sample (mol %). $m_1 = 100 - m_2$ is TFE content in the polymer (mol %). 3.2, 320, and 3200 are coefficients derived from S atom mass and obtained by the interrelationships between mass % of sulfur in the polymer, FSDFAF content (mol %), and the concentration of $-SO_2F$ groups (meq/g).

Polymer Characterization

Infrared spectra were recorded by spectrometer Specord M-80 (Germany) between 4000 and 600 cm^{-1}, samples having been prepared as films of ∼200 μm thickness. Differential thermal analysis (DTA) of selected samples was conducted by using OD-102 instrument (Hungary) in nitrogen atmosphere at a heating rate of 7.5°C/min within 20–600°C. Differential scanning calorimetry (DSC) measurements were conducted with DSC-111 instrument (Setaram, France) in an argon atmosphere at heating rate of 10°C/min. X-ray diffraction data were recorded by using a TURM 61 instrument provided with diffractometer HZG-3 at CuK$_\alpha$ radiation ($\lambda = 1.54$ Å).
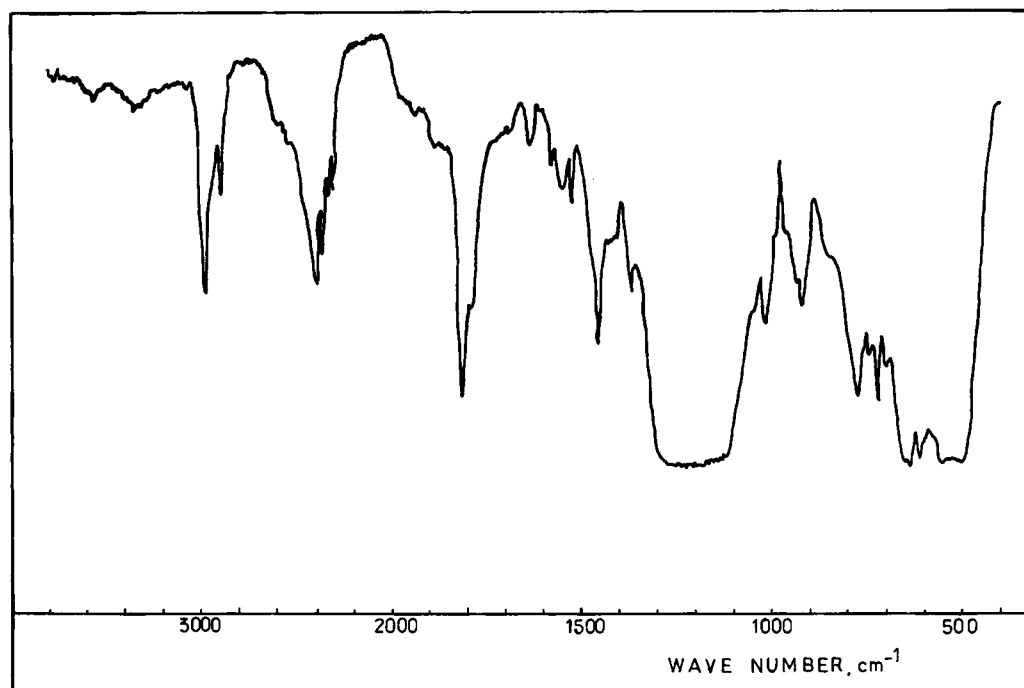
Figure 1   Infrared spectra of TFE–FSDFAF copolymer, film thickness 100–200 μm.

RESULTS AND DISCUSSION

Infrared Spectra

Figure 1 shows the infrared spectra of the TFE–FSDFAF copolymer, containing $\sim$ 3 mol % sulfonyl fluoride groups. The function of sulfonyl fluoride was established by the S=O stretching vibrations at 1460 cm^{-1}.[5,12] The very strong 1000–1400 cm^{-1} bands were assigned to the CF, CF$_2$, and (presumably) perfluoroalkyl ether C—O—C stretching vibrations, which are indistinguishable within this region.[13] Besides, the polymer had a band at 1020 cm^{-1}, where polytetrafluoroethylene does not absorb.[8]

Copolymerization of TFE with FSDFAF in Bulk

A summary of results obtained which are associated with copolymerization of TFE with FSDFAF in bulk is shown in Table I.

It was established that FSDFAF alone did not undergo any chemical changes when subjected to the reaction conditions employed in Table I. The copolymer yield decreased as a certain excess of FSDFAF with respect to TFE was used. A tendency towards slight decrease of FSDFAF content in the polymer, when using higher initial FSDFAF concentrations was also observed, regardless of the longer copolymerization time employed. These re-

Table I   A Bulk Copolymerization of TFE with FSDFAF[a]

Initial Monomers Composition (mol %)		Time (h)	Polymer Yield (%)	Copolymer Composition— SO$_2$F Content A (meq/g)	TFE (mol %)	FSDFAF (mol %)
TFE	FSDFAF					
74.3	25.7	6	4.7	0.41	95.8	4.2
45.2	54.8	6	12.4	0.56	94.1	5.9
40.4	59.6	6	1.1	0.43	95.6	4.4
33.8	66.2	6	0.8	0.34	96.5	3.5
48.8	51.2	12	9.0	0.50	94.8	5.2
40.0	60.0	12	11.5	0.34	96.5	3.5

[a] Temperature 50°C, initiator content 0.6–0.7 mass % referred to the monomers charged.

sults suggest that FSDFAF becomes included into the polymeric backbone quite randomly, and, probably, during the first several hours of copolymerization. The fact that FSDFAF alone remained unchanged under the copolymerization conditions suggests a minor probability of existence of two (or more) adjacent FSDFAF units within the polymeric chain.

Copolymerization of TFE with FSDFAF in a Solution

Figure 2 provides data related to the pressure in the autoclave as a function of copolymerization time. Since the autogenic pressure depended mainly on the amount of TFE, it was obvious that the rate of pressure drop increased as more TFE was introduced into the reactor initially. Such a dependence was consistent with TFE main contribution to the overall copolymerization rate, due to its much higher reactivity than FSDFAF. These considerations were confirmed by the results presented in Table II, where the polymer yield increased sharply as more TFE was charged into the reactor. The products with higher yields (32–37%) were insoluble in the solvent employed. The slight decrease in the polymer yield from the last experiment was presumably due to the lower TFE/FSDFAF mole ratio in the initial monomer mixture, as compared with the previous run.

FSDFAF was subjected to the polymerization conditions described above in the absence of TFE. No chemical changes were observed. Besides, a neg-

Table II Copolymer Yield in the Solution Copolymerization of TFE with FSDFAF[a]

TFE Charged (mol)	TFE/FSDFAF Mole Ratio	Polymer Yield (%)
0.36	0.97	5.5
0.50	1.76	36.9
0.62	1.10	32.2

[a] Temperature 50°C, copolymerization time 12 h, initiator content 0.7–0.8% referring to the monomers charged.

ligible amount of oligomeric product was formed under the same conditions, without using a free-radical initiator.

Table III provides some experimental data, concerning the sulfonyl fluoride groups content in the polymeric products obtained under various conditions of solution copolymerization of TFE with FSDFAF.

Any certain conclusions about the influence of copolymerization conditions on the functional groups content in the products are doubtful. Samples prepared under conditions of an excess of TFE in the initial monomer mixture contained more FSDFAF units within the polymer chain (3–5 mol %), which is contrary to the basic copolymerization processes, employing the "traditional" vinyl monomers. More TFE charged into the reactor combined with more FSDFAF led to a negligible $-SO_2F$ content in the copolymer. These phenomena could be
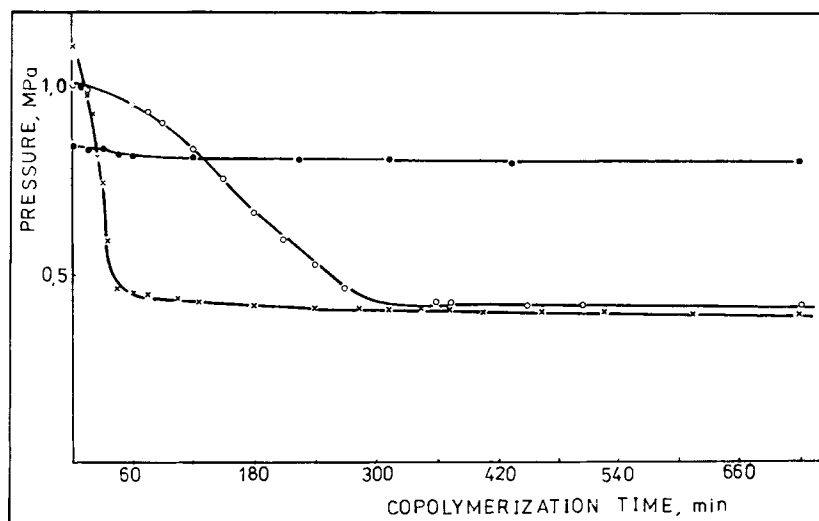

Figure 2 Variation in the autogenic pressure with copolymerization time in a solution of Freon 113. Temperature 50°C, initiator content 0.7–0.8% referring to the monomers charged: (●) TFE introduced 0.36 mol; (○) 0.50 mol; (×) 0.62 mol.

Table III Copolymers with Different Sulfonyl Fluoride Groups Content Prepared under Various Conditions of Copolymerization in Solution[a]

TFE Charged (mol)	Initial Monomers Composition (mol %)		Copolymer Composition— SO$_2$F Content (meq/g)	TFE (mol %)	FSDFAF (mol %)
	TFE	FSDFAF			
0.36	49.2	50.8	0.20	98.0	2.0
0.50	63.8	36.2	0.48	95.0	5.0
0.62	52.4	47.6	0.05	99.5	0.5
0.80	66.4	33.6	0.30	96.9	3.1

[a] Temperature 50°C, copolymerization time 12 h, initiator content 0.7–0.8 mass % referring to the monomers charged.

explained by a possible increase of TFE reactivity with its amount introduced into the reactor to a much greater extent than FSDFAF. This was illustrated by the sharp decrease of the pressure in the autoclave with the copolymerization time (Fig. 2). Another explanation seems to be a formation of more soluble oligomeric products with the increase of FSDFAF content in the initial mixture, which are likely to be "washed away" during the post-copolymerization treatment. Therefore, an optimal combination between TFE pressure and TFE/ FSDFAF mole ratio under the conditions employed is still to be searched in future examinations. Besides, a perfluorinated low temperature initiator, such as perfluoropropionyl peroxide,[9,14] could be used, which is likely to improve the results.
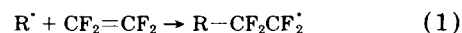
Thermal Properties

Table IV shows the basic thermal properties of different copolymer samples, compared with polytetrafluoroethylene. The small melting temperature depression (within 10–15°C) compared to polytetrafluoroethylene was in accordance with the low content of sulfonyl fluoride functional groups in the copolymers and might also be assigned to the short
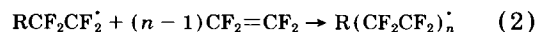
side molecular chains of FSDFAF units included along the fluorocarbon macromolecules. As might be expected, thermal stability of the copolymers was lower than polytetrafluoroethylene, but a favorable difference between melting and decomposition temperatures still existed.

Both DSC and X-ray diffraction data confirmed a small decrease in the degree of crystallinity compared to polytetrafluoroethylene. The single DSC melting/crystallization peaks indicated also a formation of "true" copolymers rather than mixture of polytetrafluoroethylene and TFE–FSDFAF copolymer (samples A and B, Table IV).

The results obtained suggest a possible free-radical polymerization with the normal initiation (1) and propagation (2) steps:
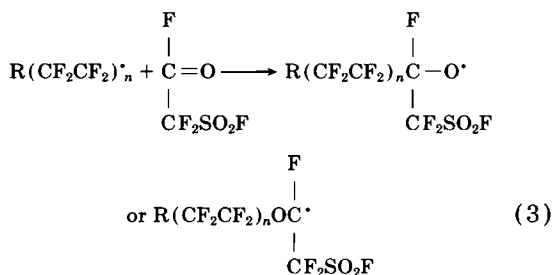
$$R^{\bullet} + CF_2{=}CF_2 \rightarrow R{-}CF_2CF_2^{\bullet} \tag{1}$$

$R^{\bullet}$ = radical derived from the initiator

$$RCF_2CF_2^{\bullet} + (n-1)CF_2{=}CF_2 \rightarrow R(CF_2CF_2)_n^{\bullet} \tag{2}$$
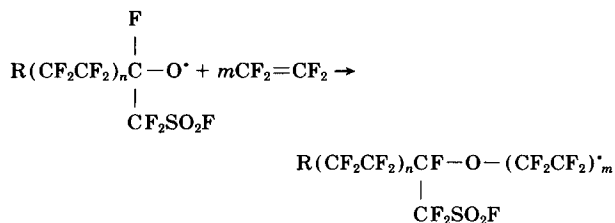
FSDFAF can react by radical attack at the oxygen or at the carbon of the carbonyl group in the following manner:

Table IV Thermal Properties of TFE-FSDFAF Copolymers

Property	TFE–FSDFAF Copolymer (Sample A)	TFE–FSDFAF Copolymer (Sample B)	Polytetrafluoroethylene Hostaflon (Hoechst, Germany)
—SO$_2$F content (meq/g)	0.48	0.30	—
Melting temperature (°C)	320	325	335
Thermal stability (TGA, °C)	365	380	485
TGA (5% weight loss) (°C)	455	460	510
TGA (10% weight loss) (°C)	500	485	530

$$R(CF_2CF_2)^{\cdot}_n + \overset{\overset{\displaystyle F}{\displaystyle |}}{\underset{\underset{\displaystyle CF_2SO_2F}{\displaystyle |}}{C}}{=}O \longrightarrow R(CF_2CF_2)_n \overset{\overset{\displaystyle F}{\displaystyle |}}{\underset{\underset{\displaystyle CF_2SO_2F}{\displaystyle |}}{C}}{-}O^{\cdot}$$

$$\text{or } R(CF_2CF_2)_n \overset{\overset{\displaystyle F}{\displaystyle |}}{\underset{\underset{\displaystyle CF_2SO_2F}{\displaystyle |}}{O}}C^{\cdot} \qquad (3)$$

The chain might continue to propagate, as follows:

$$R(CF_2CF_2)_n \overset{\overset{\displaystyle F}{\displaystyle |}}{\underset{\underset{\displaystyle CF_2SO_2F}{\displaystyle |}}{C}}{-}O^{\cdot} + mCF_2{=}CF_2 \rightarrow$$

$$R(CF_2CF_2)_n \underset{\underset{\displaystyle CF_2SO_2F}{\displaystyle |}}{CF}{-}O{-}(CF_2CF_2)^{\cdot}_m$$

where $m, n \geq 15-20$.

A random distribution of single FSDFAF units along the polymer chain, consisting mainly of TFE block fragments, is believed to exist. This assumption has been indirectly confirmed by the results in both the bulk and solution copolymerization obtained so far.

CONCLUSIONS

A free-radical chemically induced copolymerization of tetrafluoroethylene and 1-fluorosulfonyl–difluoracetylfluoride in both the bulk and solution in the presence of bis(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox 16) was conducted. From the experimental results obtained the following conclusions can be made:

1. The reactivity of 1-fluorosulfonyl–difluoroacetylfluoride under the conditions studied was found to be much lower than tetrafluoroethylene. The sulfonyl fluoride functional groups content in the copolymers did not exceed 0.40–0.50 meq/g which corresponded to 4.2–5.0 mol % functional comonomer.

2. The melting point depression of the copolymers, compared to polytetrafluoroethylene was small and a significant degree of crystallinity was observed. The copolymers had thermal decomposition starting points within 360–380°C.

REFERENCES

1. H. Ukihashi, *CHEMTECH*, **2**, 118 (1980).
2. U. S. Pat. 4626553 (1986).
3. G. A. Olah, P. S. Iyer, and G. K. S. Prakash, *Synthesis*, 513 (1986).
4. U. S. Pat. 4536352 (1985).
5. Jpn. Pat. 78-33296 (1978); *Chem. Abstr.*, **89**, 110795 (1978).
6. Br. Pat. 1020678 (1966).
7. E. G. Howard, P. B. Sargeant, and C. G. Krespan, *J. Am. Chem. Soc.*, **89**(6), 1422 (1967).
8. E. G. Howard and P. B. Sargeant, *J. Macromol. Sci. Chem.*, **A1**(6), 1015, 1023 (1967).
9. Ger. Pat. DE 3042726 (1981).
10. M. Hagiwara, T. Miura, and T. Kagiya, *Bull. Chem. Soc. Jpn.*, **42**(12), 3380 (1969).
11. D. C. England, M. A. Dietrich, and K. V. Lindsey, *J. Am. Chem. Soc.*, **82**, 6181 (1960).
12. J. M. Canich, M. M. Ludvig, G. L. Card, and M. Shreeve, *Inorg. Chem.*, **23**, 4403 (1984).
13. G. E. Gerhardt, R. J. Lagow, *J. Chem. Soc. Perkin Trans. 1*, **5**, 1321 (1981).
14. U. S. Pat 4292449 (1981).