

Study on the Synthesis of Perfluorovinyl-Sulfonic Functional Monomer and Its Copolymerization with Tetrafluoroethylene

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SYNOPSIS

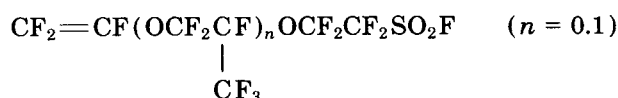
Tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) were subjected to reactions with freshly distilled sulfur trioxide to obtain 1-fluorosulfonyldifluoro-acetylfluoride (FSDFAF, yield 65–70%) and pentafluoro-2-propenylfluorosulfate (PPFS, yield up to 50%). A subsequent reaction of FSDFAF with PPFS under anhydrous conditions led to a preparation of 2-(1-pentafluoro-2-propenyloxy)tetrafluoroethanesulfonyl fluoride (PPOTESF, yield 40–41%) whose structure was proved by both infrared (IR) spectroscopy and nuclear magnetic resonance (^{19}F NMR). TFE was copolymerized with PPOTESF in bulk by using a free radical initiator of the hydrocarbon type at a temperature of 50°C. Various TFE/PPOTESF mole ratios were employed and the presence of sulfonyl fluoride ($-\text{SO}_2\text{F}$) functional groups in the copolymers was proven by IR spectroscopy. The copolymers were subjected to alkaline hydrolysis and the $-\text{SO}_2\text{F}$ content was found not to exceed 0.70–0.80 mEq/g with polymer yields in the range of 11–31%. The reactivity ratios r_1 and r_2 related to TFE and PPOTESF, respectively, were determined by using the Fineman-Ross method. A random distribution of PPOTESF units along the polymeric chain, consisting mainly of TFE fragments, was found to exist. The copolymers had melting temperatures 40–45°C lower than polytetrafluoroethylene and were thermally stable to 305–315°C.

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INTRODUCTION

Copolymers of tetrafluoroethylene (TFE) and perfluorinated functional monomers containing sulfonyl fluoride ($-\text{SO}_2\text{F}$) groups are valuable materials. The application of these copolymers as cation-exchange membranes in chlor-alkali electrolytic cells,^{1,2} as well as utility as heterogeneous polymeric catalysts in the organic synthesis,³ is due to their high thermal and chemical stability combined with facile alkaline hydrolysis. Thus, the perfluorinated functional copolymers are known to acquire hydrophilic and ion-exchange properties, extending the area of their utilization.

Synthesis of perfluorovinyl functional monomers with general formula



is a multistage and time-consuming procedure. A comparatively easy method of synthesizing such monomers has been suggested in the literature.⁹ According to some publications, TFE and hexafluoropropylene (HFP) can be subjected to reactions with sulfur trioxide^{5–8} followed by condensation of the products obtained to 2-(1-pentafluoro-2-propenyloxy)-tetrafluoroethanesulfonyl fluoride (PPOTESF) $\text{CF}_2=\text{CF}(\text{OCF}_2\text{CF})_n\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$. Some of the synthetic steps for PPOTESF preparation need, however, a further rationalization.

Copolymers of TFE and PPOTESF have also been prepared in both solution and emulsion by using pentafluoropropionyl peroxide as a free radical initiator.⁹ However, no data concerning the influence

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of the initial monomer composition on the content of perfluorovinyl functional monomer in the copolymers have been reported so far. The corresponding reactivity ratios remain unknown under the conditions studied.

The aim of the present work was to synthesize both the perfluorovinylsulfonic functional monomer (PPOTESF) and its copolymers with tetrafluoroethylene under various conditions by using a free-radical initiator of hydrocarbon type and to evaluate the corresponding reactivity ratios of the comonomers.

EXPERIMENTAL

Fluoroolefins

Tetrafluoroethylene (TFE) was prepared by 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%. Hexafluoropropylene (HFP) was a commercial product (Aldrich Chemical Co., Inc., USA).

Synthesis of FSDFAF

Thirty cm³ 65% oleum (Merck) were charged into a round-bottomed flask connected to a condenser (cooling temperature 20°C) and a receiver. SO₃ (30 ÷ 35 g) was distilled slowly into the receiver and then was transferred into a 100 cm³ stainless-steel ampoule which had been thoroughly dried. The ampoule was evacuated for several seconds at room temperature. Then, from another stainless-steel ampoule, TFE was gradually introduced into the reactor with SO₃ to a maximum pressure of 0.35–0.45 MPa under external cooling and agitation. After 2 h TFE was stoichiometrically absorbed. A one-stage procedure for FSDFAF preparation was adopted in order to avoid an isolation of the unstable tetrafluoroethane- β -sultone.⁵ To this purpose, catalytic amounts of triethylamine (ca. 0.1%) were injected into the reactor, followed by further agitation for another 2 h at room temperature. FSDFAF (b.p. 28–30°C) was fractionally distilled under an atmospheric pressure in 65–70% yield.

Synthesis of Pentafluoro-2-Propenylfluorosulfate (PPFS)

A method described in the literature was employed without further modification.⁶ HFP and SO₃ (mole

ratio 1.4–1.6) reacted in the presence of B(OCH₃)₃ (Merck, 0.6–2.1 mass % related to SO₃) at 20–60°C for 9–70 h. After cooling the unreacted HFP was removed from the 100 cm³ ampoule, and the liquid mixture was subjected to three consecutive fractional distillations in order to separate PPFS CF₂=CF—CF₂OSO₂F, b.p. 60–64°C. Infrared spectra (Specord MBO, CCl₄) showed characteristic absorption bands at 1780 (CF₂=CF—), 1480 (S—O in —OSO₂F, 1400–1000 (C—F) and 900–910 cm⁻¹ (S—F in —OSO₂F) in accordance with literature data.^{7,11} PPFS yield varied within 30–50%, referred to SO₃, depending on the reaction conditions. The best results (PPFS yield 49.8%, HFP conversion 58.2%) were obtained as HFP and SO₃ were left at room temperature for 60 h in the presence of B(OCH₃)₃, followed by agitation at 40°C for 9 h.

Condensation of FSDFAF with PPFS

A slightly modified method as compared with the only literature source reported⁹ was employed in order to prepare 2-(1-pentafluoro-2-propenyloxy)-tetrafluoroethanesulfonyl fluoride (functional monomer PPOTESF). KF (0.052 mol) dried at 250–300°C under a reduced pressure of 1–2 mmHg for 10 h, was introduced into a 250 cm³ round-bottomed flask containing 50–60 cm³ dry acetonitrile (Merck) and connected with a reflux condenser. The mixture was stirred vigorously at room temperature. FSDFAF (0.057 mol) was then introduced into the suspension under an external cooling (5–10°C), while excluding moisture. After 30 min agitation accompanied by a dissolution of KF, an equimolar amount of PPFS was charged and the temperature was kept at 20–25°C for another 2 h. The reaction mixture was then poured into 250 cm³ cold distilled water, and the lower fluoroorganic layer was separated. It was extracted three more times with distilled water to remove acetonitrile and the inorganic salts presumably present. Then a vacuum distillation was conducted and the fraction with b.p. 50–55°C/145 mmHg was separated. PPOTESF yield related to PPFS initially introduced was 38–42%.

Copolymerization of TFE with PPOTESF in Bulk

A 10 cm³ stainless-steel ampoule was charged with *bis* (4-*tert*-butylcyclohexyl) peroxydicarbonate (Perkadox 16, 95%, Akzo Chemie) which was used as a free-radical initiator. PPOTESF was then introduced, followed by cooling with liquid nitrogen and evacuation. TFE (0.9–1 g) was subsequently

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 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113, Merck). The polymer was then filtered and dried overnight under vacuum at 120–130°C to constant mass.

Determination of Sulfonyl Fluoride Groups Content in the Copolymer

A sample of the copolymer (0.3–0.5 g) was subjected to alkaline hydrolysis treatment with 20 cm³ 2N NaOH under reflux and vigorous stirring at 80°C for 20 h. The sample was then filtered and washed with distilled water in order to remove any traces of alkaline solution, followed by a vacuum-drying at 90–100°C to constant mass. An aliquot of 0.2–0.4 g dry sample was immersed into exactly 40 cm³ 0.1N HCl, with subsequent stirring at room temperature for 24 h. After filtration, excess hydrochloric acid was determined by back titration with standard 0.1N NaOH. The sulfonyl fluoride groups content in the copolymer sample was calculated, as follows:

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

where B is the concentration of hydrophilic functional groups in the sample determined by back titration with 0.1N NaOH (mEq/g), $M = 330$ is PPOTESF molecular mass, m_2 represents PPOTESF content in the polymer sample (mol %), $m_1 = 100 - m_2$ is TFE content in the polymer (mol %), and 3.2, 320, and 3200 are coefficients derived from S atom mass and obtained by the interrelationships between mass % of sulfur in the polymer, PPOTESF content (mol %), and the concentration of $-\text{SO}_2\text{F}$ groups (mEq/g).

Polymer Characterization

Infrared spectra were recorded on a Specord MBO spectrometer (Germany) between 4000 and 600 cm⁻¹ samples having been prepared as KBr pellets (2 mg/300 mg KBr). Quantitative IR spectroscopy was also employed in order to evaluate $-\text{SO}_2\text{F}$ functional

group content by using an instrumental method. For this purpose the characteristic absorption band at 1468.8 cm⁻¹, whose intensity corresponded to the Lambert–Berr relationship within the concentration range studied, was used. IR spectra of five copolymer samples were recorded within 1550–1380 cm⁻¹ under the following conditions: slit 12, integration time (IT) 5, zero adjustment (0.00), expansion Y = 1.00, expansion X = 10. The corresponding equation expressing the dependence between the absorbance A and the functional monomer content in the copolymer m_2 (mol %) may be expressed, as follows (Fig. 1):

$$A = (0.0481 \pm 0.0100)m_2 + (0.1420 \pm 0.0648)$$

Differential scanning calorimetry (DSC) measurements were conducted with a DSC-111 instrument (Setaram, France) in an argon atmosphere at a heating rate of 10°C/min and with sample mass 40 mg.

RESULTS AND DISCUSSION

Preparation of PPOTESF

The three-stage procedure of the functional monomer preparation may be outlined as follows:

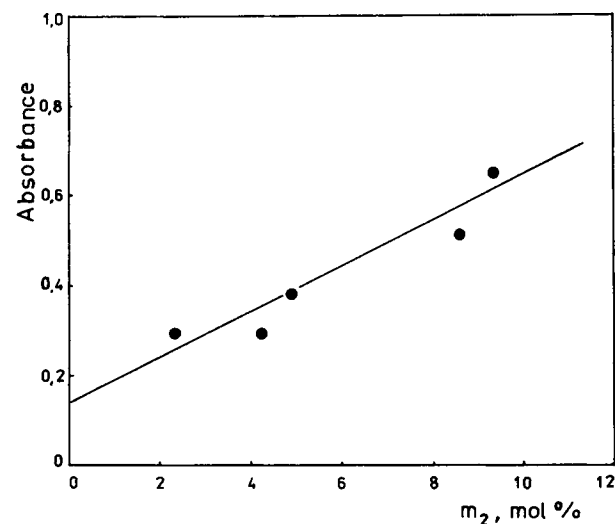
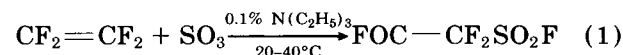
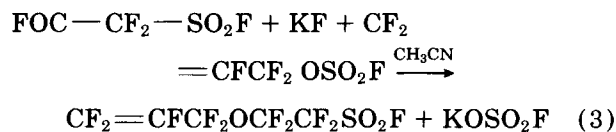
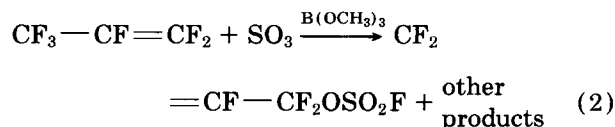


Figure 1 Dependence of absorbance A at 1468.8 cm⁻¹ (IR, $-\text{SO}_2\text{F}$) on the functional monomer content (m_2) in the copolymer.



Tetrafluoroethane- β -sultone as an intermediate in reaction (1) was prepared *in situ* in the reaction mixture and subsequent isomerization to FSDFAF occurred in the presence of $\text{N}(\text{C}_2\text{H}_5)_3$ without the cumbersome procedures of sultone isolation and purification. The prolonged contact of SO_3 with $\text{B}(\text{OCH}_3)_3$ (60 h at room temperature) led to a formation of an efficient catalytic complex acting as a very strong Lewis acid.^{7,8} This, in turn, promoted a selective preparation of $\text{CF}_2=\text{CFCF}_2\text{OSO}_2\text{F}$ as the main reaction product (yield $\sim 50\%$).²

Infrared spectra of PPOTESF synthesized according to reaction (3) showed characteristic absorption bands at 1785–1790 ($\text{CF}_2=\text{CF}_2-$), 1465–1470 (S—O in $-\text{SO}_2\text{F}$), 1000–1400 (C—F), and 810–820 cm^{-1} (S—F in $-\text{SO}_2\text{F}$) (Fig. 2). These data corresponded to the results obtained in the literature for perfluorinated compounds of a similar type.^{9,12} The products structure was also confirmed by ^{19}F NMR (CCl_3F), +44.9 (1F, FSO_2), -71.8 (2F, $\text{OCF}_2\text{C}=\text{C}$), -83.0 (2F, $\text{CF}_2\text{CF}_2\text{O}$), -90.1 (1F, *cis*-

$\text{CF}_2\text{CF}=\text{CF}_2$), -104.3 (1F, *trans*- $\text{CF}_2\text{CF}=\text{CF}_2$), -113.0 (2F, FSO_2CF_2), and 190.9 ppm (1F, $\text{CF}_2\text{CF}=\text{C}$) which corresponded to the literature data.⁹

Copolymerization of TFE with PPOTESF

Figure 3 shows the infrared spectra of the TFE-PPOTESF copolymer containing ca. 9 mol % sulfonyl fluoride groups. The function of sulfonyl fluoride ($-\text{SO}_2\text{F}$) was established by the S=O stretching vibrations at 1460–1470 cm^{-1} and 810–820 cm^{-1} (S—F).^{9,12,13} 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^{1,4} (Fig. 3). The absorption bands at 2800–3000 cm^{-1} (C—H stretching vibrations) are likely to derive from a possible incorporation of the initiator hydrocarbon fragments into the perfluorinated polymeric chain ends. This is why a perfluorinated type low temperature initiator (perfluoropropionyl peroxide) has been employed previously, although it is hardly accessible and should be kept under special conditions.

Some of the results obtained which are associated with copolymerization of TFE and PPOTESF in bulk are shown in Table I. The initiator content was selected according to some literature data.⁹ The amount of TFE introduced into the 10 cm^3 reactor was suggested in accordance with the pressure nec-

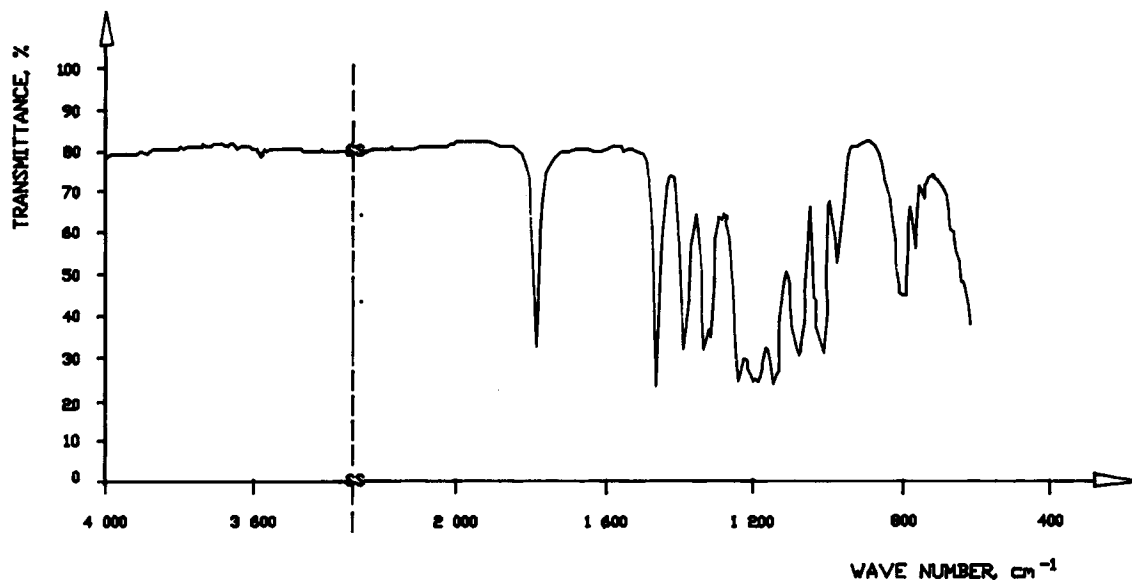


Figure 2 Infrared spectrum of 2-(1-pentafluoro-2-propenyloxy)-tetrafluoroethanesulfonyl fluoride (PPOTESF).

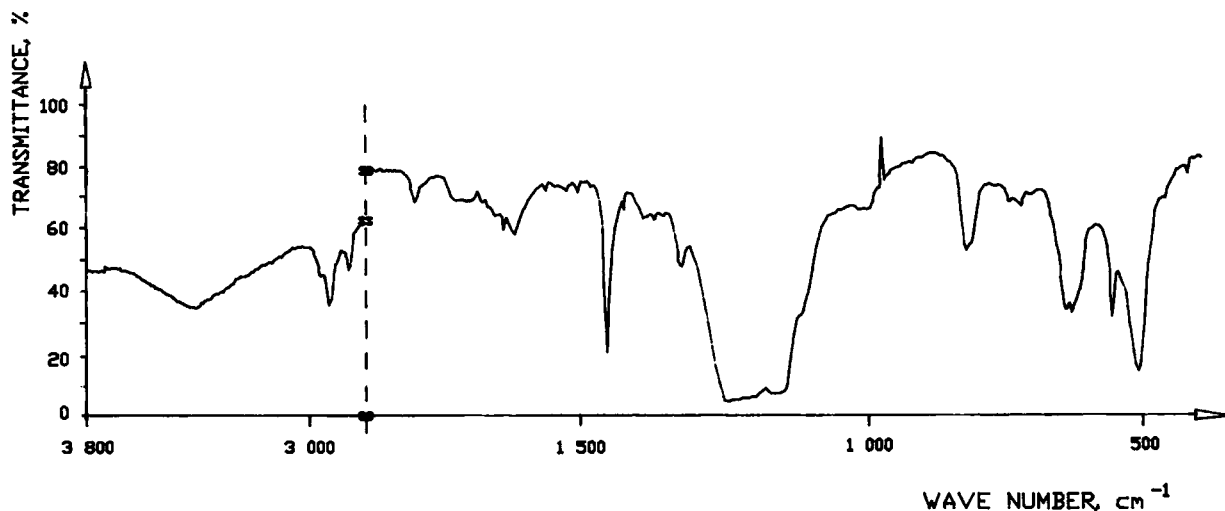


Figure 3 Infrared spectrum of TFE-PPOTESF copolymer, KBr pellets (2 mg/300 mg KBr).

essary for conducting such polymerizations (0.5–2.0 MPa).^{9,16} Both the temperature and polymerization time were selected taking into account the corresponding characteristics of the low temperature initiator Perkadox 16.¹⁵

The melting temperature depression as compared with polytetrafluoroethylene (PTFE, 327°C) was within 40–45°C. As might be expected, thermal stability of the copolymers was lower than PTFE (above 400°C) but a favorable difference between melting and decomposition temperatures still existed. DSC data confirmed a decrease in the degree

of crystallinity compared with PTFE. Thus, the enthalpy of melting for sample 2 ΔH_m was 25.5 J/g, which, relative to PTFE (58.7 J/g), gave 43% degree of crystallinity, approximately. In addition, the single DSC melting/crystallization peak indicated formation of a “true” copolymer rather than mixture of PTFE and TFE-PPOTESF copolymer.

Figure 4 provides data related to the copolymer yield (Y) as a function of PPOTESF content in the initial monomers mixture (M_2). As might be ex-

Table I Copolymerization of TFE with PPOTESF in Bulk^a

Parameters	Samples		
	1	2	3
TFE/PPOTESF mole ratio in the initial polymer mixture	2.95	0.77	0.50
Sulfonyl fluoride groups (—SO ₂ F) content in the copolymer:			
B, mEq/g	0.39	0.72	0.77
m ₂ , mol %	4.28	8.63	9.36
Copolymer yield, %	30.8	14.3	11.3
Melting temperature, °C	—	282.3	287.3
Thermal stability, °C	—	314.0	308.0

^a Reactor volume 10 cm³; TFE amount 0.9–1.0 g; temperature 50°C; initiator content 0.5 mass % referred to the monomers charged; copolymerization time 10 h.

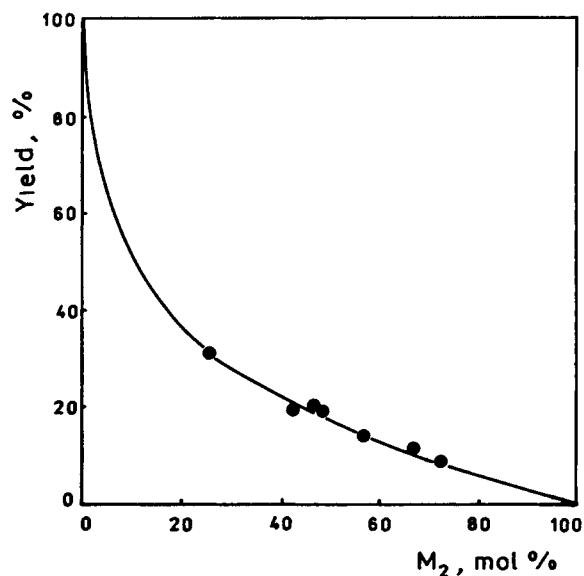


Figure 4 Variation in the copolymer yield (Y) with the functional monomer content (M_2) in the initial mixture. Temperature 50°C, initiator content 0.5% referred to the monomers charged, copolymerization time 10 h.

pected, the copolymer yield decreased² as more PPOTESF was introduced into the reactor initially. No polymeric product was observed in the absence of TFE ($M_2 = 100$ mol %), in other words, PPOOTESF did not undergo any homopolymerization under the conditions studied.

The dependence between PPOTESF content in the copolymer m_2 and its content in the initial monomers mixture M_2 is shown in Figure 5. The functional monomer content in the copolymer was found to increase to a lesser extent with the increase of its concentration in the monomer mixture, as compared with other TFE copolymers of a similar type. Thus, a functional monomer $\text{CF}_2 = \text{CFO} - (\text{CF}_2)_3\text{COOCH}_3$ content in the initial monomers mixture 65–70 mol % gave the corresponding content in the copolymer 15–20 mol %, whereas the same initial mixture quantitative composition studied in the present work led to a maximum PPOTESF content in the copolymer 0.7–0.8 mEq/g (8.5–10 mol %). The perfluorovinylethersulfonyl fluoride $\text{CF}_2 = \text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$ also has been found to be more reactive.¹⁶ Therefore, perfluorovinyl functional monomers containing $\text{CF}_2 = \text{CF} - \text{O} -$ (perfluorovinylloxy) structural fragment appear to have higher reactivity in a free radical chemically induced copolymerization with TFE than PPOTESF containing $\text{CF}_2 = \text{CFCF}_2 - \text{O} -$ (perfluoroallyloxy) group. The presence of an oxygen atom adjacent to the perfluorovinyl group seems to influence favourably the corresponding ef-

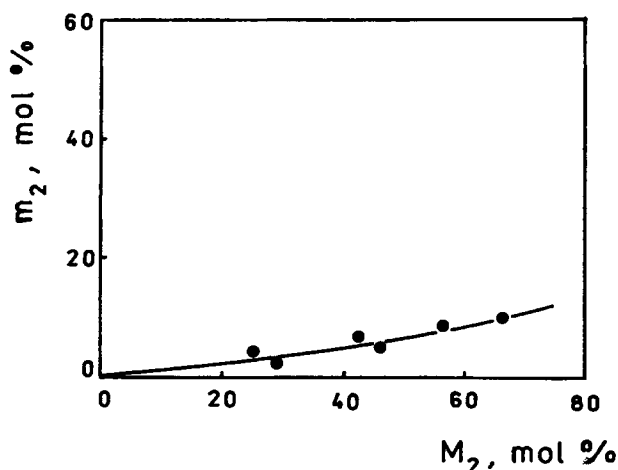


Figure 5 Dependence of the functional monomer content (m_2) in the copolymer on its concentration in the initial monomers mixture (M_2). Temperature 50°C, initiator content 0.5% referred to the monomers charged, copolymerization time 10 h.

fects of conjugation and polarity in both the functional monomers and radicals derived therefrom.

The reactivity ratios r_1 and r_2 for TFE and PPOOTESF were determined by employing both the Fineman-Ross and Kelen-Tüdös methods.¹⁷ The corresponding functions

$$G = \frac{X(x-1)}{x} \quad \text{and} \quad F = \frac{X^2}{x}$$

were calculated, where $X = M_1/M_2$ and $x = m_1/m_2$ are related to the composition of the initial monomers mixture and the copolymer, respectively (mol %). By using the least-squares method the corresponding reactivity ratios

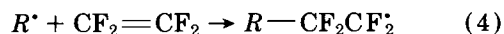
$$r_1 = 10.02 \pm 0.63 \quad r_2 = 0.31 \pm 0.09$$

for the Fineman-Ross method were determined, whereas the Kelen-Tüdös method gave:

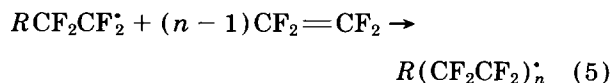
$$r_1 = 10.81 \pm 1.68 \quad r_2 = 0.23 \pm 0.08$$

Therefore, $r_1 r_2 > 1$ and similar results have been reported in the literature for acrolein-methylacrylate system ($r_1 = 10.0$, $r_2 = 0.2$), etc.¹⁸

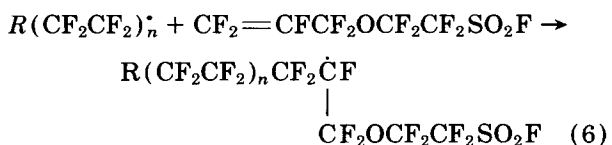
A random distribution of single PPOTESF units along the polymer chain, consisting mainly of TFE block fragments seems to be the predominant macromolecular structure. However, the existence of possible PPOTESF sequences within the polymeric chain cannot be excluded. The results obtained suggest a free-radical copolymerization with the normal initiation (4) and propagation (5) steps:



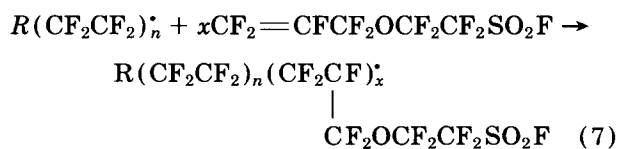
R^* is the radical derived from the initiator



PPOTESF can further react in the following manners:

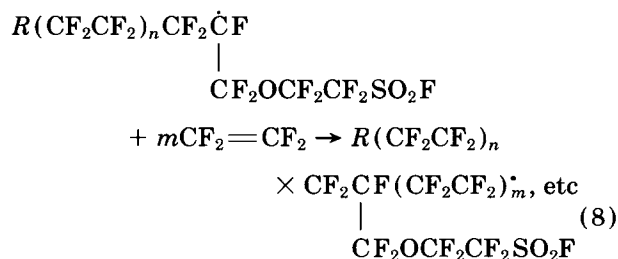


or



(much less probable sequence, $x \ll n$).

The chain might continue to propagate as follows:



where m , n values are determined by the copolymer composition corresponding to a maximum 9–10 mol % content of the perfluorinated functional monomer.

CONCLUSIONS

1. The perfluorovinyl functional monomer 2-(1-pentafluoro-2-propenyloxy)tetrafluoroethanesulfonyl fluoride was synthesized in 40–41% yield by using a modified three-stage procedure. The product obtained was characterized by both IR and ^{19}F NMR spectroscopy.
2. A free-radical chemically induced copolymerization of tetrafluoroethylene and 2-(1-pentafluoro-2-propenyloxy)-tetrafluoroethanesulfonyl fluoride in bulk in the presence of *bis*-(4-*tert*-butylcyclohexyl) peroxydicarbonate (Perkadox 16) was conducted. The reactivity of the functional monomer under the conditions studied was found to be significantly lower than tetrafluoroethylene.
3. Under certain conditions (temperature 50°C, mole ratio of tetrafluoroethylene to the functional monomer 0.7 : 0.8, an initiator content 0.5%, copolymerization time 10 h) the co-

polymer yield was 10–15% with sulfonyl-fluoride functional groups content 8–10 mol %. The copolymer had a partly crystalline structure with melting temperature 280–290°C and thermal decomposition starting points within 305–315°C.

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