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NEW PENTAFLUOROTHIO(SF_5)FLUOROPOLYMERS

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SUMMARY

New fluorinated polymers containing the pentafluorothio group have been prepared from SF_5Br and the appropriate fluoroolefin under reaction temperatures of 90±5°C and autogeneous pressures of up to 90 atmospheres for periods of four days to two weeks. With ethylene, FCH_2CH_2Br and $SF_5CH_2CH_2Br$ were formed. A new monomer addition product, $SF_5CF_2CF_2Br$, is also reported for the first time.

INTRODUCTION

In our continuing studies of pentafluorothiocarbon systems, we have found that upon reacting SF_5Br with fluoroolefins not only monomeric liquids but polymeric solids are produced under proper conditions of heat and pressure.

Prior to our studies, other workers have prepared SF_5 containing polymers and telomers via the reaction of $CF_2=CF_2$ with SF_5Cl[1,2,3], $CF_3CF=CF_2$ with S_2F_{10}[4], $SF_5CF=CF_2$ with $CF_2=CF_2$[5] and with $CF_2=CH_2$[6]. Many of these polymers have not been well characterized.

RESULTS AND DISCUSSION

We have found that SF_5Br reacts with fluoroethylenes to form polymers incorporating the SF_5- group according to the following equations:

$$SF_5Br + XS\ CH_2{=}CHF \longrightarrow SF_5(CH_2CHF)_{10}Br \quad (1)$$

$$SF_5Br + XS\ CH_2{=}CF_2 \longrightarrow SF_5(CH_2CF_2)_8Br \quad (2)$$

$$SF_5Br + XS\ CFH{=}CF_2 \longrightarrow SF_5(CFHCF_2)_{30}Br_{0.7} \quad (3)$$

$$SF_5Br + XS\ CF_2{=}CF_2 \longrightarrow SF_5(CF_2CF_2)_{16}Br_{0.3} \quad (4)$$

With ethylene, essentially no polymer was formed. In addition to the above polymers (eqs. 1-4), the adducts SF_5RBr (R is $CH_2{=}CHF$, $CH_2{=}CF_2$, $CHF{=}CF_2$, $CF_2{=}CF_2$) are formed. The monomeric adducts with the exception of $SF_5CF_2CF_2Br$ have been previously reported [7].

The key factor in this preparative route seems to be high pressure along with a 90±5°C temperature; calculated pressures can possibly go as high as 90 atmospheres for reactions reported here.

All of the polymers are waxy and become whiter as the number of fluorines in the structure increases. Other trends also coincide with the increasing number of fluorines in the structure; and include: i) an increase in melting point, 2i) an increase in stability, and 3i) a decrease in solubility. These findings are summarized in Table I. Additional qualitative tests with the $SF_5(CFHCF_2)_{30}Br_{0.7}$ and $SF_5(CF_2CF_2)_{16}Br_{0.3}$ polymers found that they were not soluble or reactive with a variety of concentrated acids (HCl, HNO_3, H_2SO_4) or base (6N, NaOH) at temperatures of 100°C.

The empirical formulas of the polymers are given in Table I and are based upon elemental analyses. As with other polymer systems, we would expect a variety of chain lengths and end groupings depending upon the nature of the termination in each case; possibilities for termination include coupling of two chains with end groups (SF_5, SF_5) or termination with SF_5 or Br radicals resulting in end groups of (SF_5, SF_5) or (SF_5, Br). Chain termination, either

TABLE 1

Composition*	Melting Range (°C)	Decomp. (°C)	Solubility H_2O	Acetone
$SF_5(CH_2CHF)_{10}Br$	100-110	190	insol.	sol.
$SF_5(CH_2CF_2)_8Br$	118-150	330	insol.	sol.
$SF_5(CHFCF_2)_{30}Br_{0.7}$	130-160	460	insol.	slightly sol.
$SF_5(CF_2CF_2)_{16}Br_{0.3}$	310-318	>510	insol.	insol.

* Empirical compositions based on elemental analyses.

by coupling or reaction with SF_5 radicals would result in a lower bromine content in the polymer.

Cross and coworkers [8] reported that for compounds in which the SF_5 group is bound to an aliphatic hydrocarbon, a very intense infrared band centered on or about 870 cm^{-1} and a less intense but sharp band at or near 600 cm^{-1} are always found. For the polymers reported in this paper, we find the S-F stretching mode and one of the S-F deformation modes are located in the region 845-899 cm^{-1} and 606-600 cm^{-1}, respectively; for $SF_5CF_2CF_2Br$ the corresponding modes were located at 903 and 609 cm^{-1}, respectively. It is known that for monomeric compounds with C-F and $-CF_2-$ groupings, strong C-F stretching vibrations are usually located in the 1000-1250 cm^{-1} region of the infrared; appropriate carbon fluorine absorption bands are found for these new compounds. The absorption bands in the 2941-3010 cm^{-1} region are attributed to C-H stretching modes. The C-Br stretching bands for fluoroalkyl bromides [9] are reported to be in the 740-770 cm^{-1} region, while for alkylbromides [10] the range is 515-680 cm^{-1}. For the new compounds described in this paper, the bands in the 766-705 cm^{-1} region may well be due to the C-Br stretching mode.

The mass spectrum for $SF_5CF_2CF_2Br$ did not contain a molecular ion but other appropriate fragment peaks were found: $(C_2F_4Br)^+$, $(C_2F_3Br)^+$, $(CF_2Br)^+$, $(SF_5)^+$, $(SF_4C)^+$, $(CFBr)^+$, $(SF_4)^+$, $(C_2F_4)^+$, $(SF_3)^+$, and Br^+.

The nmr spectra for all the polymers except $SF_5(CF_2CF_2)_{16}Br_{0.3}$ consist of complex multiplets from which representative chemical shift values were found. The ^{19}F nmr pattern for the SF_5 group consisted of the expected AB_4 pattern with the B_4 equatorial fluorines split into a complex doublet and the axial fluorine, A, into a nine-line pattern. The chemical shift values for the equatorial fluorine are found in a range of Ø54 to 66 ppm while for monomeric adducts the corresponding values range from Ø44 to 67 ppm [7]. The axial fluorine values range from Ø71 to 83 ppm for polymers and Ø61 to 80 ppm for the respective monomeric adduct [7]. In the trifluoroethylene polymer, two types of SF_5 groups were present. For the $SF_5(CH_2CHF)_{10}Br$ and $SF(CHFCF_2)_{30}Br_{0.7}$ polymers, the ^{19}F resonances for C-F are found at Ø-183 ppm and Ø-211 ppm, respectively. By comparison, the ^{19}F chemical shift values for C-F in polyvinylfluoride are located at Ø-178 to -185 ppm (broad peaks); chemical shifts at Ø-190 to -200 ppm represent inversion defects in the chain [11]. The ^{19}F chemical shift values for the CF_2 group vary from Ø-93 to -130 ppm. Wilson and Santee report regions of CF_2 shifts in polyvinylidene fluoride of Ø-91.6, -94.8, -113.6 and -115.6 ppm depending on the relationship of the CF_2 to other CH_2 and CF_2 groups in the chain [12].

The new monomeric adduct, $SF^{a}SF_{4}{}^{b}CF_{2}{}^{c}CF_{2}{}^{d}Br$, has ^{19}F chemical shift values for CF_2 groups in the characteristic region and contains the AB_4 pattern for the SF_5 group. The equatorial fluorines are split into the typical doublet and the axial fluorine into a nine-line pattern with Ø44.3 ppm and Ø61.5 ppm, respectively. The coupling constant J_{a-b}=146.6 Hz. For the CF_2 groups, the fluorines (c) and (d) are assigned at Ø-93.5 ppm and Ø-66.5 ppm, respectively with J_{b-c}=14.4 Hz, J_{a-c}=4.23 Hz, J_{b-d}=11.3 Hz and J_{c-d} estimated at 4.5 Hz. The chemical shifts are consistent with other monomeric adducts [7,14].

The ^{1}H nmr spectra for the polymers are complex multiplets in which characteristic chemical shift values are found. For $SF_5(CHFCF_2)_{30}Br_{0.7}$, the ^{1}H chemical shifts occur at δ1.3 to 3 ppm and δ5.5 ppm corresponding to the CH in the chain and the CH next to the SF_5, respectively. The monomer adduct has a value of δ5.58 ppm next to the SF_5 [7]. In $SF_5(CH_2CHF)_{10}Br$ the CH chemical shift is assigned to the band at δ4.74 ppm and overlaps with the CH_2 resonances when the CH_2 is attached to the SF_5 group; in the corresponding monomeric adduct the CH_2 value is found at δ4.27 ppm [7]. The chemical shift of the CH_2 group located in the chain is found at δ1.8 ppm. By comparison, it is reported that for polyvinyl chloride, the chemical shift values, in the δ1.9-2.3 ppm region, are attributed to the α protons (CH) and the values at δ4.2-4.5 to the β (CH_2) protons [13]. In the polymer $SF_5(CH_2CF_2)_8Br$, ^1H chemical shift values are found at δ2.8 and δ4.5 ppm corresponding to the chain CH_2 groups and the CH_2 next to the SF_5, respectively. The monomeric adduct has a CH_2 chemical shift of δ4.46 ppm [7].

In general, we find that for SF_5 containing fluoropolymers, when the SF_5 group is attached to a CH_2 group in the chain, the proton chemical shift is found near δ4.5 ppm; for the rest of the CH_2 in the chain, the chemical shift values are located in the δ1.8-2.8 ppm region. We find the chemical shift at δ5.15 ppm for the C-H group when attached to SF_5, while for the rest of the CH groups in the chain, chemical shift values are located in the range of δ 1.3-3.0 ppm.

EXPERIMENTAL

SF_5Br was prepared as previously reported [7] and used without further purification. $CF_2{=}CF_2$, $CFH{=}CF_2$, $CH_2{=}CF_2$, $CHF{=}CH_2$ and $CH_2{=}CH_2$ were obtained from SCM Specialty Chemicals and used as received.

General Procedure. Gases were manipulated in a conventional Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Infrared spectra were obtained by using a Pyrex-glass cell with KBr windows or as solids between KBr disks on a Nicolet 20DX spectrometer. The nmr spectra were recorded with a Varian Model EM-390 spectrometer operating at 90.0 MHz for proton and 84.67 MHz for fluorine resonances. TMS, F-11, and trifluoroacetic acid were used as external standards. The melting points were determined using a Mel-Temp capillary melting point apparatus.

The mass spectrum was taken on a CEC 21-110 B double-focus mass spectrometer equipped with a 6-kV ion accelerator and operated at 70V. Perfluorokerosene was used as an internal standard.

Elemental analyses were determined by Beller Microanalytical Laboratory in Gottingen, West Germany.

$CF_2=CF_2$ with SF_5Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 64 mmol of SF_5Br and 75 mmol of $CF_2=CF_2$. The mixture was heated for 5.8 days at 90±5°C. The volatile materials were transferred out leaving behind 6.44g of a white solid.

The melting range for the white solid is 310-318°C with no decomposition observed up to 510°C.

The infrared spectrum of the solid has bands (cm^{-1}): 1216 (s, with sh at 1244), 1152 (s), 899 (ms, with sh at 866), 847 (w), 825 (w), 781 (w), 741 (w), 719 (w), 688 (w), 640 (m), 625 (m), 606 (wm), 556 (m), 503 (s,b).

Anal. for $SF_5(CF_2CF_2)_{16}Br_{0.3}$, calcd: C, 21.95; S, 1.83; F, 74.87; Br, 1.35. Found: C, 21.42; S, 1.89; F, 72.8; Br, 1.38.

In a second run, 61.0 mmol of $CF_2=CF_2$ and 62.2 mmol of SF_5Br were heated at 90±5°C (2d). Distillation of the volatile material gave 3.71 mmol of $SF_5CF_2CF_2Br$, bp. 60-62°C, leaving behind 8.91 grams of solid polymer. The molecular weight of $SF_5CF_2CF_2Br$ (calc. 307.0, found 303.6).

The infrared spectrum had the following bands (cm^{-1}): 1216 (ms), 1194 (m), 1173 (w), 1152 (s), 1061 (m), 1047 (w), 934 (m), 903 (vs,b), 859 (vw), 831 (m), 766 (vs), 684 (w), 609 (ms), 591 (w), 578 (w).

The ^{19}F nmr spectrum contained a multiplet at ϕ 61.5 (nine line pattern of triplets), a doublet of multiplets at ϕ 44.3 ppm, a pentet of multiplets at ϕ-93.5 and -66.5 ppm (relative band area for SF to SF_4 was 1.0:3.9, theor. 1.0:4.0 and for $\underline{CF_2}Br$ to $SF_5\underline{CF_2}$ was 1.0:1.0). Coupling constants for $F^aSF_4{}^bCF_2{}^cCF_2{}^dBr$ were J_{a-b}=146.6, J_{a-c}=4.23, J_{b-c}=14.4, J_{b-d}=11.3, $J_{c-d}\sim$4.5 Hz.

A molecular ion was not observed but other fragment ions were found: 179,181 $(C_2F_4Br)^+$, 160,162 $(C_2F_3Br)^+$, 129,131 $(CF_2Br)^+$, 127 $(SF_5)^+$, 120 $(SF_4C)^+$, 110,112 $(CFBr)^+$, 108 $(SF_4)^+$, 101 $(SF_3C)^+$, 100 $(C_2F_4)^+$, 89 $(SF_3)^+$, 79,81 $(Br)^+$, 70 $(SF_2)^+$, 69 $(CF_3)^+$, 63 $(SFC)^+$, 51 $(SF)^+$, 50 $(CF_2)^+$, 44 $(SC)^+$.

Anal. Calcd for C_2F_9SBr: C, 7.82; F, 55.70; S, 10.44; Br, 26.03. Found: C, 7.83; F, 55.40; S, 10.59; Br, 25.98%.

$CFH{=}CF_2$ with SF_5Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 93 mmol of SF_5Br and 100 mmol of $CF_2{=}CFH$; after heating this mixture at 90±5°C (4d) an additional 52 mmol of SF_5Br and 64 mmol of $CF_2{=}CFH$ were added. The reaction mixture was heated at 90±5°C (3d). The volatile materials at room temperature (58 mmol of SF_5CFHCF_2Br) were removed leaving behind 9.0 grams of a white waxy solid.

In an additional run, 58.8 mmol of SF_5Br and 75.8 mmol of $CFH{=}CF_2$ were heated at 90±5°C for four days. To this reaction mixture an additional 69.7 mmol of $CF_2{=}CFH$ was added and heated at 90±5°C (3d); in this run 10.8 grams of the same white waxy solid was formed. The melting range of this polymer was 130-160°C with decomposition at 460°C.

The infrared spectrum of this solid had the following bands (cm^{-1}): 2994 (w), 1394 (m), 1350 (m), 1281 (ms), 1244 (ms), 1197 (s), 1156 (s), 1112 (s), 991 (w), 978 (w), 875 (ms with sh. at 922), 834 (ms), 728 (w), 669 (w), 628 (w), 606 (wm), 547 (wm), 509 (wm), 466 (w), 438 (w).

The ^{19}F nmr spectrum contained a complex doublet of doublets at ϕ 56 and 54 (SF_4) and a multiplet at ϕ 71 (SF); multiplets at ϕ -120, -122, -125, -129 (CF_2) and at -211 (CF) ppm are present. The ^1H nmr spectrum has two broad multiplets centered at 5.5 and a series of peaks in the range of 1.3-3.0 ppm.

Anal. for $SF_5(CHFCF_2)_{30}Br_{0.7}$ calcd: C, 27.42; H, 1.14; F, 68.12; S, 1.21; Br, 2.11. Found: C. 27.34; H, 1.19; S, 1.44; F, 68.2; Br, 2.01%.

$CF_2=CH_2$ with SF_5Br

To a 75 mL stainless steel vessel equipped with a Whitey (20-VF4) stainless steel valve were added 96.2 mmol of SF_5Br and 118.3 mmol of $CF_2=CH_2$. The reaction mixture was maintained at 90±5°C (12h), room temperature (5h), and 90±5°C (3d). The products, 69.4 mmol of $SF_5CH_2CF_2Br$ (bp 86-87°C) and 3.0 grams of a waxy solid were formed. The waxy solid (slightly discolored) melted in 118-150°C range and decomposed at 330°C.

The infrared spectrum of the solid had the following bands (cm^{-1}): 3010 (w), 2984 (w), 1422 (m), 1399 (m), 1384 (m), 1270 (m), 1209 (s), 1183 (s), 1158 (s), 1077 (m), 1012 (w), 975 (m), 941 (m), 871 (s), 838 (s), 796 (m), 762 (m), 727 (w), 657 (wm), 600 (wm), 576 (w), 566 (wm), 531 (wm), 509 (w), 493 (wm). The ^{19}F nmr spectrum contained a complex doublet at Ø 71 (SF_4) and a multiplet at Ø 81 (SF); multiplets at Ø -93 and Ø -98 (CF_2) were present. The ^1H nmr spectrum contained broad complex multiplets with the bands centered at δ2.8 and δ4.5 ppm.

Anal. for $SF_5(CH_2CF_2)_8Br$, calcd: C, 26.70; H, 2.22; F, 55.40; S, 4.46; Br, 11.10. Found: C, 26.83; H, 2.33; F, 54.2; S, 4.54; Br, 10.91%.

$CFH=CH_2$ with SF_5Br

The reactants, SF_5Br (84 mmol) and $CFH=CH_2$ (102.9 mmol) were condensed into the 75 mL reaction vessel. The reaction mixture was heated at 90±5°C (3d) and at 60°C (1d). The volatile materials, containing SF_5CH_2CHFBr were removed leaving behind 1.68 g of a waxy solid (slight discoloration). The waxy solid melted in the 100-110°C range and decomposed at 190°C.

The infrared spectrum of this solid had the following bands (cm^{-1}): 2970 (s), 2941 (s), 1446 (m), 1426 (s), 1411 (s), 1370 (ms), 1257 (m), 1067 (s with sh. at 1087), 845 (s), 830 (s), 824 (s), 720 (m), 705 (m), 642 (m), 601 (m), 565 (m), 457 (m).

The ^{19}F nmr spectrum contained a complex doublet at ϕ 66 (SF_4) and a multiplet at ϕ 83; J_{SF-SF_4}=155 Hz, the CF resonance was a complex multiplet centered at ϕ -183 ppm. The ^1H nmr spectrum contained two broad multiplets centered at δ1.8 (CH_2) and $\sim\delta$4.7 (CH) ppm; relative band areas 2.1:1.0 (theor. 2.0:1.0).

Anal. for $SF_5(CH_2CFH)_{10}Br$, calcd: C, 35.98; H, 4.54; S, 4.80; F, 42.69; Br, 11.97. Found: C, 35.79; H, 4.39; S, 4.86; F, 43.0; Br, 11.95%.

CH_2=CH_2 with SF_5Br

To the 75 mL reactor described earlier, 99 mmol of SF_5Br and 136 mmol of CH_2=CH_2 were added. The reaction mixture was warmed to room temperature (16 h), heated at 55±2°C (2d) and 90±5°C (3d). The volatile materials were removed leaving behind 1.1 g of charred material. Distillation of the volatile materials gave a fraction boiling at 74-77°C (3.77 g). The molecular weight of this fraction (137 g/mole), its characteristic infrared and nmr spectra confirmed the material to be a mixture of FCH_2CH_2Br (91%) and $SF_5CH_2CH_2Br$ (9%).

In a second run, under mild conditions, 84.3 mmol of SF_5Br and 109.2 mmol of CH_2=CH_2 were used. The reaction mixture was warmed to room temperature (16h). Again, a volatile fraction boiling at 74-77°C (3.06 g) and a small amount <1 g of charred material was formed.

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