3d) was found to result in the reduction of the T_d by some 10-20 °C. A lowering of the T_d value was also observed to take place on the introduction of sulfone and methylene linkages (polymers **3f-k**).

On the basis of DSC measurements it was shown (Table I and Figure 3) that some of these new polymers had glass transition temperatures T_g below their decomposition temperatures, a distinct relationship being found to exist between the molecular structure of the polymers studied and their T_g values. An increase in the amount of linkages making the polymer chain more flexible was accompanied by a decrease of T_g. Consequently, except for the polymers **3a** and **3b**, containing from one to two flexible linkages per repeating chain unit, for the remaining polymers it was shown that $T_g < T_d$.

Thermomechanical analyses carried out for the polymers **3i** and **3j**, forming strong polymeric films with tensile strengths of the order of 1000 kG/cm^2 at 20 °C (elongation 7-12%), showed that the thus obtained T_g values were higher by some 10-20 °C than those determined by DSC measurements.

X-ray analysis results showed the polymers herein described to be amorphous.

Conclusions

The above presented poly[bis(benzimidazobenzisoquinolinones)] constitute a group of macromolecular compounds exhibiting novel properties, hitherto unreported for polymers of that class. And thus, in sharp contrast to the poly[bis(benzimidazobenzophenanthrolines)] based on the 1,4:5,8-naphthalenetetracarboxylic dianhydride,[2,3] these new polymers are soluble not only in strong acids but also in organic solvents and exhibit glass transition temperatures that are below their corresponding decomposition temperature values while preserving a relatively high thermal and oxidative stability.

References and Notes

(1) Van Deusen, R. L.; Goins, O. K.; Sicree, A. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1966**, *7*, 528.
(2) Van Deusen, R. L.; Goins, O. K.; Sicree, A. J. *J. Polym. Sci., Part A1* **1968**, *6*, 1777.
(3) Arnold, F. E.; Van Deusen, R. L. *Macromolecules* **1969**, *2*, 497.
(4) Arnold, F. E. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1975**, *16* (2), 251.
(5) Korshak, V. V.; Rusanov, A. L.; Berlin, A. M.; Fidler, S. Kh.; Livshits, B. R.; Dymshits, T. Kh.; Silutina, L. N.; Blinov, V. F. *Vysokomol. Soedin., Ser A* **1979**, *21* (3), 657.
(6) Vogel, H.; Marvel, C. S. *J. Polym. Sci., Part A* **1963**, *1*, 1531.
(7) Stille, J. K.; Williamson, J. R.; Arnold, F. E. *J. Polym. Sci., Part A* **1965**, *3*, 1013.
(8) Bell, V. L.; Jewell, R. A. *J. Polym. Sci., Part A-1* **1967**, *5*, 3043.
(9) Jedliński, Z.; Gaik, U.; Mzyk, Z.; Fudal, M.; Kowalski, B. *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20* (2), 559.
(10) Sachs, F.; Mosebach, G. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2852.
(11) Fleischer, K.; Schranz, K. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 3253.
(12) Rapoport, H.; King, T. P.; Lavingne, J. B. *J. Am. Chem. Soc.* **1951**, *73*, 2718.
(13) Loughram, G. A.; Arnold, F. E. *Org. Prep. Proced. Int.* **1976**, *8*, 98.
(14) Berry, G. C.; Fox, T. G. *J. Macromol. Sci.* **1969**, *A3*, 1125.
(15) Young, P. R. *J. Heterocycl. Chem.* **1972**, *9*, 371; **1973**, *10*, 325.

Telechelic Perfluorocarbons. α,ω-Perfluorodicarboxylic Acids

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ABSTRACT: A homologous series of α,ω-perfluorodicarboxylic acids is generated in a controlled free radical polymerization of tetrafluoroethylene using aqueous peroxydisulfate with either an iron or a copper promoter. Even-numbered C_4 to C_{16} perfluorodicarboxylic acids are the major species formed, although small, but discrete quantities of the odd-numbered C_3 to C_{15} analogues are detected. Some higher molecular weight carboxylated poly(tetrafluoroethylene) is also isolated. The mass spectral cracking pattern of the methyl esters shows an unusual "unzipping" of tetrafluoroethylene units, especially with the higher molecular weight oligomers. A mechanism for chain initiation and termination of perfluoroalkyl radicals leading to carboxylic acid end groups is discussed.

Introduction

Since poly(tetrafluoroethylene)[1] exhibits a number of useful chemical and physical properties, it would be desirable to construct oligomeric perfluoroalkyl units with functionality at both termini, i.e., telechelic perfluorocarbons,[2] as building blocks for other polymers. Indeed, examples are to be found in the extant literature in which perfluoroacyl fluorides have been selectively photocoupled to higher molecular weight diacyl fluorides,[4] and α,ω-diiodoperfluoroalkanes have been generated from the controlled reaction of tetrafluoroethylene with iodine.[5,6]

In this paper we present the free radical oligomerization of tetrafluoroethylene as a route to a homologous series of α,ω-perfluorodicarboxylic acids. Previous reports[7,8] on the reaction of tetrafluoroethylene with free radical initiators describe the formation of high molecular weight, insoluble polymers, showing some evidence of carboxylic acid functionality when aqueous peroxydisulfate was used as the initiator.[9] However, the more common synthetic routes to perfluorodicarboxylic acids involve the oxidative cleavage of carbon-carbon double bonds present in either perfluorocycloalkenes[10,11] or perfluoro-α,ω-diolefins.[12] We thought a method for the preparation of perfluorodicarboxylic acids directly from tetrafluoroethylene could be developed if the reaction were carried out in a controlled aqueous environment of free radicals derived from peroxydisulfate and metal ions, i.e.

$$(n/2 + 1)\mathrm{CF_2{=}CF_2} + \mathrm{S_2O_8}^{2-} \xrightarrow[\mathrm{H_2O}]{[\mathrm{M}^{n+}]} \mathrm{HO_2C(CF_2)}_n\mathrm{CO_2H} \text{ etc.} \quad (1)$$

Since such an oligomerization occurs perforce in competition with the ready polymerization of tetrafluoroethylene, we carried out all of our reactions at relatively low pressures of monomer and high concentrations of initiator. The dichotomy between oligomerization and polymeriza-

Table I
Typical Reactions of Tetrafluoroethylene with Aqueous Peroxydisulfate[a]

no.	(CF_2=CF_2), psig	additive	temp, °C	time, min	oligomers, g		peroxydisulfate consumed,[b] %
					WS	P	
1	20	none	60-65	90	none	none	4
2	30	none	75-82	150	none	none	65[c]
3	40-50	$FeSO_4$[d]	20-25	100		7.0	
4	28-30	$FeSO_4$[e]	60-70	180	0.4	0.9	27
5	38-40	$FeSO_4$[e]	65-75	120	1.2	1.1	71
6	44-51	$CuSO_4$[f]	80-90	80	1.9	1.6	72

[a] With 10 psig Ar diluent over 100 mL of H_2O containing 5.4 g of $K_2S_2O_8$, unless noted otherwise. [b] Based on iodometry. [c] 10-psig pressure increase noted. [d] No Ar diluent, 2.7 g of $K_2S_2O_8$, and 57 mg of $FeSO_4 \cdot 7H_2O$. [e] 0.20 g of $FeSO_4 \cdot 7H_2O$. [f] 40 mg of $CuSO_4$ and 0.47 g of copper powder (not all used) with 8.1 g of $K_2S_2O_8$.

tion is best illustrated by initially describing a few, representative reaction conditions under which tetrafluoroethylene can be treated with aqueous peroxydisulfate. However, our principal goal in this study was to separate and identify the products as a series of α,ω-perfluorodicarboxylic acids derived from tetrafluoroethylene. As a result, optimum experimental conditions for the production of these diacids were not explored extensively.

Results

When an atmosphere of tetrafluoroethylene (20 psig) was exposed to an aqueous solution of potassium peroxydisulfate at 60–65 °C, essentially no change was detected after 90 min, as summarized by entry 1 in Table I. At the slightly higher temperature and pressure indicated in entry 2, 65% of the peroxydisulfate was consumed (by iodometric titration) after 150 min, but there was little apparent change in tetrafluoroethylene. However, in the presence of catalytic amounts of iron salt, tetrafluoroethylene was converted to high yields of insoluble poly(tetrafluoroethylene) at temperatures as low as 20–25 °C (see entry 3, Table I).[13]

Oligomerization of Tetrafluoroethylene in Aqueous Peroxydisulfate with Metal Ions. The foregoing experiments showed that both peroxydisulfate and iron salt were required for the reaction of tetrafluoroethylene under our prescribed conditions. In order to control the extensive polymerization in entry 3 of Table I, argon (10 psig) was introduced as a diluent for tetrafluoroethylene, and the temperature of the reaction was raised to 60–70 °C. Under these conditions, 27% of the peroxydisulfate was consumed within 180 min, and considerably less insoluble polymer was formed. After filtration, the workup of the clear, aqueous solution (as described in the Experimental Section) afforded a low-melting colorless solid, which we have characterized as a mixture of low molecular weight α,ω-perfluorodicarboxylic acids.[13] The fifth entry in Table I indicates that the yields of these water-soluble acids were enhanced when the reactions were carried out at slightly higher temperatures (65–75 °C). Relatively good yields of α,ω-perfluorodicarboxylic acids were also obtained when peroxydisulfate was used in conjunction with copper salt, as described in entry 6, Table I.

For convenience, let us henceforth consider the oligomeric products in two separate parts, viz., the low molecular weight fraction WS (which is water soluble) and the highly polymeric fraction P (which is water insoluble).[14] We first proceed to establish the identity of the low molecular weight components.

Identification of Perfluorosuccinic, -glutaric, and -adipic Acids. The water-soluble fraction WS is a solid, partially crystalline material which melts over a range from ~35 to 70 °C. The infrared spectrum of a thin pressed film showed intense absorption bands for the carboxylic acid functionality [3500–2500 cm^{-1} (OH) and 1750 cm^{-1} (C═O)], as well as characteristic bands for perfluoroalkyl groups previously described for other perfluorocarboxylic acids.[15] In water, the oligomeric fraction WS is a relatively strong acid (pH ~1). Quantitative acidimetry with standard alkali revealed an overall neutralization equivalent of 170, which varied slightly from run to run. Since all monofunctional perfluorocarboxylic acids with molecular weights less than 364 are known to be liquids at 20 °C,[16] we inferred that the oligomeric fraction WS most likely consisted of a mixture of dicarboxylic acids.

Accordingly, a partial separation of the oligomeric fraction WS was effected by treatment with phosphorus pentoxide, followed by the removal of the volatile anhydrides with the aid of a heating mantle up to ~200 °C. This procedure allowed a mixture of perfluorosuccinic anhydride (bp_{760} 54–55 °C),[17] perfluoroglutaric anhydride (bp_{760} 72 °C),[18,19] and perfluoroadipic anhydride[20] to be isolated.

$$\underset{\text{WS}}{HO_2C(CF_2)_nCO_2H} + P_2O_5 \xrightarrow[\text{distill}]{-H_2O} (CF_2)_n(CO)_2O \qquad n = 2\text{–}4 \qquad (2)$$

Thus the gas chromatographic analysis of this mixture of volatile anhydrides on a silicone (SE-30) column at 40 °C revealed the presence of only three components with relative retention times of 2.7, 3.5, and 5.7, which are all less than that of tetrahydrofuran (>6). The mixture of cyclic anhydrides was treated with a small amount of water and directly converted to the corresponding methyl diesters with an ethereal solution of diazomethane.

$$(CF_2)_n(CO)_2O + H_2O \xrightarrow{CH_2N_2} CH_3O_2C(CF_2)_nCO_2CH_3 \qquad n = 2\text{–}4 \quad (3)$$

Gas chromatographic analysis of the mixture of methyl esters also revealed the presence of only three components—the first two of which coincided with the retention times of the methyl esters of authentic succinic and glutaric acids.[21] Indeed the GC–MS analysis of the mixture of esters confirmed that the first two components were dimethyl perfluorosuccinate and dimethyl perfluoroglutarate.

The identification of the third component in the distillate as perfluoroadipic anhydride was based on the unmistakable similarity of the mass spectral cracking pattern with those of the lower homologues (n = 2, 3) in Table II.

Separation and Structural Characterization of Oligomeric α,ω-Perfluorodicarboxylic Acids. In order to characterize all of the principal reaction products from tetrafluoroethylene and aqueous peroxydisulfate, we simply dissolved the oligomeric acid fraction WS completely in ether and treated the solution with diazomethane. The

Table II
Mass Spectra of Cyclic Perfluoroanhydrides $(CF_2)_n(CO)_2O$[a]

m/z (%)		
succinic ($n = 2$)	glutaric ($n = 3$)	adipic ($n = 4$)[b]
44 (11)	44 (4)	44 (1)
50 (33)	50 (16)	50 (1)
69 (23)	69 (22)	69 (22)
100 (100)	100 (100)	100 (100)
	131 (16)	131 (44)
	150 (30)	
[119]	[151]	[200]

[a] Only those peaks with relative abundances >1% are included. The ions (traces) with the highest m/z are indicated in brackets. [b] Inferred; see text.

Table III
Relative Abundance of $[CO_2CH_3]^+$ in the Mass Spectra of Dimethyl Perfluorodicarboxylates $MeO_2C(CF_2)_nCO_2Me$[a]

	n									
	1	2	3	4	5	6	7	8	9	10
rel abundance, %	24	98	68	85	51	77	52	75	38	59

[a] Average values at an ionizing voltage of 70 eV.

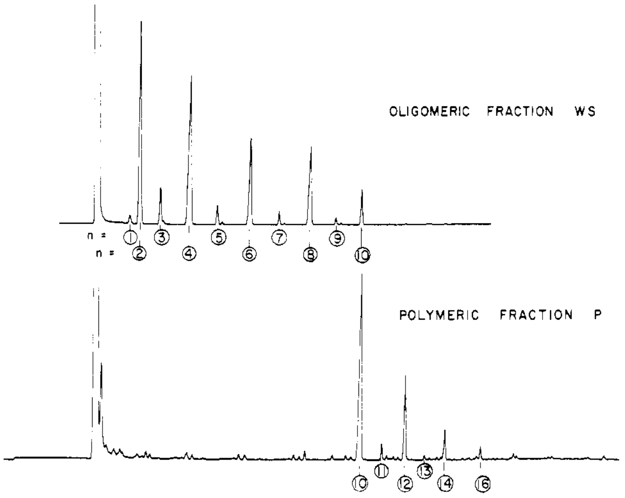

Figure 1. Upper: Typical gas chromatogram of the methyl esters derived from the oligomeric acid fraction WS. Lower: Gas chromatogram of the methyl esters derived from the polymeric acid fraction P, as described in the text.

capillary gas chromatogram of the resultant mixture of methyl esters is reproduced in Figure 1. Since the polymeric fraction P was more or less insoluble in ether, it was treated as a suspension with diazomethane and macerated for a prolonged period. The gas chromatogram of the soluble methyl esters derived from P is illustrated in Figure 1 (lower).

The striking regular pattern of a homologous series of methyl esters derived from both fractions WS and P is readily apparent in Figure 1. Moreover, the synchronous overlap of the retention times in the upper and lower gas chromatograms in Figure 1 indicates that the succession of peaks derives from one continuous series of related compounds proceeding from the oligomeric fraction WS through to the polymeric fraction P.

The GC–MS analysis of the peaks designated as 2, 3, and 4 in Figure 1 establishes them to be associated with the dimethyl esters of perfluorosuccinic, -glutaric, and -adipic acids, respectively, as described in the foregoing section. Although authentic samples of the higher homologues of α,ω-perfluorodicarboxylic acids were unavailable to us (some are also unreported), we believe that the analysis of the mass spectral cracking patterns obtained by the GC–MS of each of the methyl esters in fractions WS and P allows a reasonable assignment to be made of the other principal components in Figure 1. Thus, the dominant nature of the ion $[CO_2CH_3]^+$ with m/z 59 in the electron-impact mass spectra of each of the GC peaks labeled 1 through 10 establishes all of them as methyl esters. The relative abundance of this ion is listed in Table III. Interestingly, it is found to be higher in the even-numbered homologues.

The mass spectra of components 1–11 in Figure 1 are rather uncomplicated (as characteristic of perfluoroalkyl compounds generally), and they show a regular progression of cracking patterns with increasing molecular weight. Thus the mass ions resulting from the loss of F (−19), CF (−31), CO_2 (−44), and COF (−47) are common throughout the mass spectra of components 1–10. Furthermore, an unusual, repetitive phenomenon is observed in the regular "unzipping" by units of 100 (C_2F_4) and 50 (CF_2), as shown in column 3 of Table IV. The same regular trend is also apparent in the other ions, especially with the higher molecular weight analogues. The more complete mass spectral cracking patterns for components 1–10 are listed in the Experimental Section.

In order to substantiate the foregoing structural assignments based on electron-impact mass spectroscopy, we repeated the GC–MS analysis of the oligomeric ester fraction using chemical ionization with isobutane. The mass spectral analysis by chemical ionization indeed demonstrated that each diester fraction from components 1–10 afforded the parent molecular ion plus one $(M + 1)^+$ as the dominant species—i.e., $n = 1$, 169; $n = 2$, 219; $n = 3$, 269, etc. Furthermore, the unzipping by units of 100 (as revealed in the electron-impact mass spectra) was also observed for the diesters with $n \geq 5$. A typical example

Table IV
Mass Spectra of the Homologous Series of Methyl Esters of α,ω-Perfluorodicarboxylic Acids[a]

$MeO_2C(CF_2)_nCO_2Me$ n	mol wt	homologous ions,[b] %	highest mass ion detected[c]	other high mass ions[c]	
1	168	124 (16)	168	137 (−31)	124 (−49)
2	218	174 (32)	187 (−31)	174 (−44)	159 (−59)
3	268	224 (2)	237 (−31)	224 (−44)	221 (−47)
4	318	274 (6)	274 (−44)	271 (−47)	259 (−59)
5	368	324 (24)	324 (−44)	321 (−47)	309 (−59)
6	418	399 (2)	374 (−44)	359 (−59)	331 (−87)
7	468	449 (5)	449 (−19)	424 (−44)	421 (−47)
8	518	499 (2)	499 (−19)	374 (−144)	274 (−244)
9	568	549 (13)	549 (−19)	524 (−44)	521 (−47)
10	618	599 (16)	599 (−19)	574 (−44)	571 (−47)
11	668		649 (−19)	624 (−44)	524 (−144)

[a] At an ionizing voltage of 70 eV. [b] Base peak = 100, lower abundance cutoff at 1%. [c] Base peak = 59, lower abundance cutoff at 0.3%.

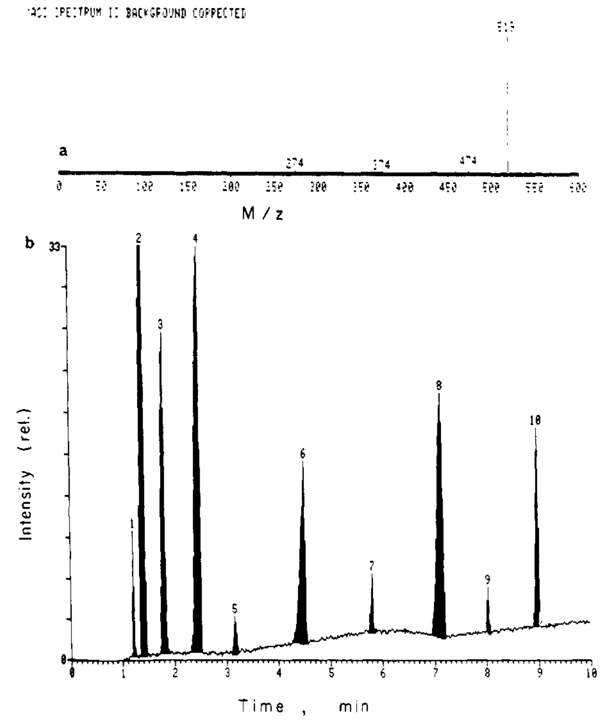

Figure 2. (a) Chemical ionization mass spectrum of the oligomeric diester fraction 8 with $n = 8$ using isobutane at 70 eV. (b) Total ion chromatogram from GC–MS (chemical ionization) analysis of oligomeric ester fraction using isobutane at 70 eV.

of this phenomenon is shown in Figure 2 for the diester with $n = 8$.

Having assigned the GC peaks 1–10 in Figure 1, we proceeded to ascertain whether the measured neutralization equivalent of the oligomeric acid fraction WS (vide supra) was consistent with that calculated from the composition of this mixture of esters. The structural assignments indeed support the acidimetric results. For example, the WS fractions with titrimetric neutralization equivalents of 170 and 159 corresponded to calculated neutralization equivalents of 161 and 155, respectively, based on the GC analysis of the methyl ester derivatives.[22,23] (See Experimental Section for details.)

Carboxylated Polymer. Treatment of the polymeric acid fraction P with diazomethane only converted a small fraction of the material to ether-soluble methyl esters, and most of it remained insoluble in ether. It was cold pressed into thin translucent films, some of which were tinged with either red when iron was the promoter or blue when copper salts were used. The infrared spectrum indicated the presence of both free carboxylic acid groups [ν(CO) 1750 cm^{-1}] and carboxylate groups [ν(CO) 1675 cm^{-1}] expected from the incorporation of iron(III) and copper(II) ions as carboxylate salts. Owing to its intractability, no further attempts were made to characterize P.

Oxidative Decarboxylation of α,ω-Perfluorodicarboxylic Acids. A visual inspection of the gas chromatograms in Figure 1 readily reveals that the even-numbered oligomers are significantly more abundant than the odd-numbered ones. The observation of the latter was initially surprising since the stepwise oligomerization of tetrafluoroethylene was expected to generate only even-number carbon chains, which indeed is the major pathway. In order to test whether the odd-numbered homologues derive from a secondary reaction, we subjected perfluoroglutaric acid (as a representative component) to aqueous peroxydisulfate and ferrous salt under the conditions of the oligomerization experiment. Workup of the mother liquors by the standard procedure resulted in the

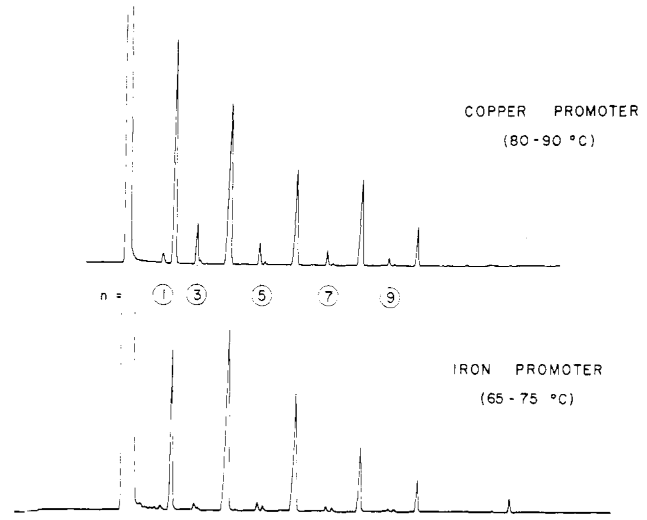

Figure 3. Upper: Gas chromatogram of the methyl esters derived from the oligomeric acid fraction WS prepared from tetrafluoroethylene and aqueous peroxydisulfate with a copper promoter, as in entry 6, Table I. Lower: Similar to upper chromatogram, except methyl esters derived from WS prepared with an iron promoter, as in entry 5, Table I.

production of substantial amounts of perfluorosuccinic acid and to a lesser extent difluoromalonic acid. The identity of the acidic products was confirmed by conversion to their methyl esters and GC–MS analysis, as described above.

$$\mathrm{HO_2C(CF_2)_3COOH} \xrightarrow[\mathrm{[Fe^{2+}]}]{\mathrm{S_2O_8^{2-}}} \mathrm{CO_2} + \mathrm{HO_2C(CF_2)_2COOH} \tag{4a}$$

$$\mathrm{HO_2C(CF_2)_2COOH} \xrightarrow[\mathrm{[Fe^{2+}]}]{\mathrm{S_2O_8^{2-}}} \mathrm{CO_2} + \mathrm{HO_2CCF_2CO_2H} \tag{4b}$$

These experiments clearly show that oxidative decarboxylation is a viable pathway for the production of the odd-numbered α,ω-perfluorodicarboxylic acids. The extent to which these homologues are produced during oligomerization depends on the metal promoter and the temperature. Thus Figure 3 shows that the yields of the odd-number acids are uniformly higher with a copper promoter (upper chromatogram) relative to an iron promoter employed at a lower temperature. When the latter was carried out at a slightly higher temperature of 80–90 °C, the relative yields of the even- and odd-numbered oligomeric acids was essentially the same as that obtained with the copper promoter (shown in Figure 3 upper).[23]

Discussion

The propagation steps in the free radical polymerization of tetrafluoroethylene by the efficient addition of perfluoroalkyl radicals is well established. However, the chain initiation and chain termination processes, which determine the nature of the end groups in the polymer, are less easily characterized, particularly in those systems leading to long kinetic chains.[24] Thus the isolation and characterization of the oligomeric α,ω-perfluorodicarboxylic acids in this study provide some insight into the nature of the chain initiation and termination processes operative with peroxydisulfate and metal ions. Indeed the latter has been extensively employed as an initiator in the vinyl polymerization of various olefinic substrates. Unlike a growing alkyl radical chain, however, the growing perfluoroalkyl radical chain is not subject to rearrangement and disproportionation. Consequently, the possibility of selective free radical reactions can be seriously entertained, if the propagation is carried out in the absence of chain transfer agents such as hydrogen and halogen donors, etc. Accordingly, our choice of an highly aqueous medium allows us to focus primarily on the role of peroxydisulfate and the metal ion promoter.

The problem is essentially contained in accounting for the formation of the lowest molecular weight components of the oligomeric mixture, viz., perfluorosuccinic, -glutaric, and -adipic acids. We proceed from the knowledge that metal ions such as iron(II) and copper (I) effect the efficient reduction of peroxydisulfate, i.e.[25-28]

$$\mathrm{Fe^{II}} + \mathrm{S_2O_8^{2-}} \rightarrow \mathrm{Fe^{III}(SO_4)^+} + \mathrm{SO_4^{-}\cdot} \qquad (5)$$

In an aqueous environment, the initiating free radical (X·) may be either $SO_4^{-}\cdot$ or HO· derived from water.[29] In either case, the free radical addition to tetrafluoroethylene

$$\mathrm{X\cdot} + \mathrm{CF_2{=}CF_2} \rightarrow \mathrm{XCF_2CF_2\cdot} \qquad (6)$$

$$\mathrm{XCF_2CF_2\cdot} + p\mathrm{CF_2{=}CF_2} \rightarrow \mathrm{X(CF_2CF_2)_{\mathit{p}+1}\cdot} \qquad (7)$$

where X = SO_4^- or HO, followed by free radical coupling, e.g.

$$\mathrm{XCF_2CF_2\cdot} + \mathrm{X(CF_2CF_2)_2\cdot} \rightarrow \mathrm{X(CF_2CF_2)_3X} \qquad (8)$$

would afford structures that are readily converted to α,ω-perfluorodicarboxylic acids upon hydrolysis.[30,31]

$$\mathrm{X(CF_2CF_2)_3X} \xrightarrow{\mathrm{H_2O}} \mathrm{HO_2C(CF_2CF_2)_2CO_2H} \qquad (9)$$

As attractive as this direct mechanism is, it does not readily account for the *catalytic* role of the metal promoter, which must be rereduced in order to repeat its function in eq 5.[32,33] Such a pathway for the rereduction of the oxidized form of the promoter is provided by the growing perfluoroalkyl radical, e.g.

$$\mathrm{X(CF_2CF_2)_{\mathit{p}}\cdot} + \mathrm{Fe^{III}X} \rightarrow \mathrm{X(CF_2CF_2)_{\mathit{p}}X} = \mathrm{Fe^{II}},\ \text{etc.} \qquad (10)$$

Indeed a variety of iron(III) and copper(II) species are known to be easily reduced by numerous types of alkyl radicals.[35]

The series of oxidation–reduction reactions to generate $SO_4^{-}\cdot$ and HO· from peroxydisulfate and to terminate the growing perfluoroalkyl radical chain thus provide a ready rationale to the formation of the even-numbered oligomeric α,ω-perfluorodicarboxylic acids from tetrafluoroethylene. Moreover, the same intermediates and redox reactions pertain directly to the formation of the odd-numbered analogues as byproducts derived by oxidative decarboxylation, as described in eq 4. For example, it has been established that $SO_4^{-}\cdot$ and HO· are capable of decarboxylating a variety of fatty acids in two successive free radical steps.[36,37] As applied to the perfluorodicarboxylic acids of this study, the sequence of reactions leading to oxidative decarboxylation is

$$\mathrm{HO_2C(CF_2)_{\mathit{n}}CO_2H} + \mathrm{X\cdot} \rightarrow \mathrm{HO_2C(CF_2)_{\mathit{n}}CO_2\cdot} + \mathrm{HX} \qquad (11)$$

$$\mathrm{HO_2C(CF_2)_{\mathit{n}}CO_2\cdot} \xrightarrow{\text{fast}} \mathrm{CO_2} + \mathrm{HO_2C(CF_2)_{\mathit{n}}\cdot} \qquad (12)$$

which is followed by the redox reaction and hydrolysis presented above in eq 10 and 9, respectively, i.e.

$$\mathrm{HO_2C(CF_2)_{\mathit{n}}\cdot} \xrightarrow{\mathrm{Fe^{III}X}} \xrightarrow{\mathrm{H_2O}} \mathrm{HO_2C(CF_2)_{\mathit{n}-1}CO_2H} \qquad (13)$$

Indeed the formation of the off-numbered byproducts provides the best support for the mechanism of oligomerization presented above.[38]

Summary

Tetrafluoroethylene has been oligomerized to a homologous series of α,ω-perfluorodicarboxylic acids, in which the even-numbered members are the dominant species. The generation of free radicals from peroxydisulfate and either an iron or a copper promoter in aqueous solution leads to an initiating reaction with tetrafluoroethylene and a limited propagation to give relatively high yields of low molecular weight diacids. The formation of small amounts of α,ω-perfluorodicarboxylic acids with odd-numbered carbon chains has been shown to occur by oxidative decarboxylation. The redox mechanism for the formation of the even-numbered diacids is in complete accord with that proposed for oxidative decarboxylation. Importantly, the principles delineated in this study are applicable to a wide variety of end-group functionalities on perfluorocarbons other than carboxy groups—limited only by the myriad of oxidation–reduction reactions of free radicals with metal complexes extant.[35]

Experimental Section

Materials. Tetrafluoroethylene (inhibited with α-limonene) was obtained from PCR Research Chemicals. The inhibitor was removed from the monomer by passing the gas over a series of three silica gel traps[39] at atmospheric pressure and room temperature and finally condensing it into a small stainless steel ampule, which could be closed and weighed separately. Potassium peroxydisulfate was Mallinckrodt analytic reagent grade. Ferrous sulfate $FeSO_4 \cdot 7H_2O$ and cupric sulfate were obtained from Fisher Scientific and used as such. Perfluorosuccinic acid and perfluoroglutaric acids were obtained from PCR Research Chemicals, Inc.

Oligomerization of Tetrafluoroethylene with Aqueous Peroxydisulfate. Typical Procedure. A solution of potassium peroxydisulfate (5.4 g) in 100 mL of distilled water was placed in an autoclave with approximately 300-mL total capacity (Magnedrive Packless Autoclave manufactured by Autoclave Engineers, Inc., Erie, Pa.). Ferrous sulfate (200 mg) was sealed in a fragile glass tube which was carefully placed in the autoclave so that it would rupture when the drive was activated. The autoclave was chilled in dry ice and alternately evacuated and repressured with argon to remove air from the system. After the autoclave was heated to 65 °C, the argon pressure was readjusted to 10 psig and the stirrer turned on to break the ampule. Tetrafluoroethylene was introduced to bring the total pressure of the system to 40 psig. Over a period of 120 min, the tetrafluoroethylene pressure was repeatedly adjusted to maintain it at a relatively constant value. Upon completion of the reaction, the pressure was released from the autoclave and the contents passed through a sintered glass funnel. The solid polymer (1.1 g of P) was treated with the washings of the autoclave, and the combined filtrates were treated with potassium iodide to destroy the unreacted peroxydisulfate. The aqueous solution was distilled to remove iodine. Ether extraction of the concentrate, followed by removal of the ether, afforded 1.2 g of oligomeric acids (WS), which crystallized upon standing (melting range between 35 and 48 °C).

Anhydrides of α,ω-Perfluorodicarboxylic Acids. The anhydrides were prepared by Henne's procedure for perfluorosuccinic anhydride.[17] A composite sample of 4.5 g of crude oligomeric acids (WS) from several experiments was treated with 11.2 g of P_2O_5 in a small glass distillation apparatus. The heterogeneous mixture was slowly heated with a mantle over a 6-h period at an internal pot temperature that increased gradually from 50 to 130 °C. (The bath temperature varied correspondingly between 100 and 205 °C.) The distillate (0.4 g) was collected in a chilled receiver.

Analysis of α,ω-Perfluorodicarboxylic Acids. The gas chromatographic analysis of the dimethyl esters of α,ω-perfluorodicarboxylic acid was carried out either on a fused-silica capillary column with a DB-1 phase[40] or on an $^1/_8$-in. column of silicone SE-30 or OV101 on Chromosorb. The Varian 3700 gas chromatograph with a digital integrator (CDS-111) provided the relative peak areas (percent).

The electron-impact mass spectral analysis was obtained at 70 eV using an SE-30 column fitted to a Hewlett-Packard Model HP 5992 GC–MS instrument. The mass spectral cracking pattern for each oligomeric methyl ester from $n = 1$ to $n = 11$ is tabulated below as m/z (%). The lower abundance cutoff of 1% was taken.

n = 1: 46 (1.2), 47 (1.5), 50 (6.3), 51 (5.3), 59 (100.0), 60 (2.5), 65 (8.9), 78 (4.9), 79 (3.1), 81 (9.1), 93 (1.2), 94 (7.7), 95 (1.1), 109 (7.9), 110 (1.2), 121 (1.1), 124 (14.1). *n* = 2: 46 (1.1), 47 (1.2), 50 (4.7), 51 (1.8), 59 (100.0), 60 (2.8), 62 (1.3), 65 (1.8), 69 (7.5), 74 (5.2), 78 (1.5), 81 (15.8), 93 (1.7), 97 (3.3), 100 (13.3), 101 (2.6), 106 (3.8), 109 (6.2), 124 (5.2), 129 (4.4), 131 (6.6), 140 (1.6), 143 (2.1), 144 (3.4), 159 (3.9), 174 (4.0). *n* = 3: 47 (1.1), 50 (2.0), 51 (1.6), 59 (100.0), 60 (2.4), 65 (2.4), 69 (6.5), 79 (1.9), 81 (13.2), 93 (2.2), 94 (3.2), 100 (13.9), 106 (1.0), 109 (5.1), 119 (17.5), 124 (50.5), 125 (2.3); 131 (2.2), 147 (2.1), 150 (1.2), 151 (1.7), 209 (4.9). *n* = 4: 50 (2.1), 59 (100.0), 65 (1.5), 69 (10.9), 74 (2.6), 81 (7.5), 93 (3.2), 100 (16.5), 106 (1.1), 109 (3.6), 112 (3.4), 119 (2.3), 124 (11.1), 129 (1.8), 130 (9.9), 143 (3.4), 144 (1.2), 169 (5.5), 174 (4.8), 231 (1.9), 259 (1.5). *n* = 5: 59 (100.0), 60 (2.3), 65 (1.3), 69 (8.4), 81 (4.6), 93 (2.0), 100 (7.0), 109 (3.2), 112 (1.0), 119 (2.1), 124 (18.3), 125 (1.0), 131 (16.1), 143 (1.0), 174 (2.5), 181 (1.0), 224 (3.3), 324 (2.2). *n* = 6: 50 (1.2), 59 (100.0), 65 (1.8), 69 (10.2), 81 (5.5), 93 (2.0), 100 (7.1), 109 (3.5), 112 (1.7), 119 (2.0), 124 (5.1), 131 (14.9), 143 (1.4), 169 (1.1), 174 (2.3), 181 (1.4), 274 (1.7), 374 (1.1). *n* = 7: 59 (100.0), 60 (2.4), 65 (1.7), 69 (8.6), 81 (3.4), 93 (1.2), 100 (6.9), 109 (3.1), 119 (3.0), 124 (6.0), 131 (12.0), 174 (1.1), 181 (1.7), 224 (2.0), 324 (2.4), 424 (2.5). *n* = 8: 59 (100.0), 65 (1.6), 69 (10.0), 81 (3.9), 93 (1.1), 100 (5.4), 109 (2.5), 119 (2.8), 124 (2.0) 131 (11.9), 169 (1.2), 181 (1.7), 274 (1.2). *n*= 9: 59 (100.0), 60 (2.2), 65 (1.5), 69 (8.8), 81 (2.9), 100 (4.7), 109 (2.3), 119 (3.2), 131 (12.8), 169 (1.5), 181 (1.9), 324 (1.5) 424 (1.1), 524 (1.7). *n* = 10: 59 (100.0), 60 (2.2), 65 (1.5), 69 (9.2), 81 (3.0), 100 (4.9), 109 (2.7), 119 (3.1), 131 (13.0), 169 (1.4), 181 (1.7), 574 (2.4). *n* = 11: 59 (100.0), 60 (3.2), 65 (2.1), 67 (1.1), 69 (9.1), 81 (2.7), 100 (2.7), 109 (3.2), 119 (4.3), 124 (1.1), 131 (12.8), 132 (1.1), 155 (1.1), 159 (1.1), 162 (1.1), 169 (1.1), 181 (1.6), 231 (1.1), 271 (1.1). 624 (1.1).

It is singularly noteworthy that the (GC) mass spectral cracking pattern of dimethyl perfluorosuccinate made by tetrafluoroethylene oligomerization was essentially identical with that obtained from the oxidative decarboxylation of perfluoroglutaric acid, or from perfluorosuccinic anhydride. The same applies to the homologues with *n* = 3 and *n* = 4.

The chemical ionization mass spectral analysis of the oligomeric diesters was obtained with isobutane at 70 eV using a DuPont DP-102 GC–MS instrument.

Acidimetric Analysis of the Oligomeric Acid Fraction WS. Typical Example. A weighed sample of the oligomeric acid fraction WS (which was dissolved in distilled water and titrated with a standard solution of 0.10 N NaOH to the phenolphthalein end point) gave a neutralization equivalent of 159. The sample of WS was converted to the methyl esters $MeO_2C(CF_2)_nCO_2Me$ with diazomethane. On a typical sample, the gas chromatographic analysis revealed the components 1–11 with the following relative areas (percent): *n* = 1 (1.6), 2 (30.3), 3 (5.1), 4 (28.4), 5 (2.2), 6 (13.3), 7 (1.3), 8, (12.2), 9 (0.6), 10 (3.8), 11 (0.3). When each relative area was multiplied by the molecular weight of the acid, an apparent formula weight of 310 was obtained, which corresponds to a calculated neutralization equivalent of 155.

Oxidative Decarboxylation of Perfluoroglutaric Acid. Perfluoroglutatic acid (1.2 g, 5 mmol) was dissolved in 25 mL of deionized water containing $K_2S_2O_8$ (1.35 g, 5 mmol). The solution was heated to 80 °C with stirring and $FeSO_4{\cdot}7H_2O$ (28 mg, 0.1 mmol) was added. Aliquots recovered after 1 and 2 h showed that 64% and 81% of the peroxydisulfate was gone (by iodimetric titration). After 2 h, a 2-g sample of the solution was treated with an ethereal solution of diazomethane. Gas chromatographic analysis of the esters indicated a 32% conversion of perfluoroglutaric acid to perfluorosuccinic acid (57%) and perfluoromalonic acid (14%). Confirmatory identification of the latter was established by GC–MS analysis. There was no evidence for the formation of C_6-, C_7-, or C_8-perfluorodicarboxylic acids.

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Registry No. $CF_2{=}CF_2$, 116-14-3; $K_2S_2O_8$, 7727-21-1; $FeSO_4$, 7720-78-7; $CuSO_4$, 7758-98-7; $(CF_2)_2(CO)_2O$, 699-30-9; $(CF_2)_3(CO)_2O$, 376-68-1; $(CF_2)_4(CO)_2O$, 22636-86-8; $MeO_2CCF_2CO_2Me$, 379-95-3; $MeO_2C(CF_2)_2CO_2Me$, 356-36-5; $MeO_2C(CF_2)_3CO_2Me$, 1513-62-8; $MeO_2C(CF_2)_4CO_2Me$, 3107-98-0; $MeO_2C(CF_2)_5CO_2Me$, 54404-53-4; $MeO_2C(CF_2)_6CO_2Me$, 2062-20-6; $MeO_2C(CF_2)_7CO_2Me$, 22116-90-1; $MeO_2C(CF_2)_8CO_2Me$, 4590-24-3; $MeO_2C(CF_2)_9CO_2Me$, 22116-91-2; $MeO_2C(CF_2)_{10}CO_2Me$, 84750-88-9; $MeO_2C(CF_2)_{11}CO_2Me$, 84750-89-0; $HO_2C(CF_2)_3CO_2H$, 376-73-8.

References and Notes

(1) Teflon is the trademark of poly(tetrafluoroethylene) from E. I. du Pont de Nemours Co.

(2) Telechelic (from the Greek telos, end, and chele, claw) refers to reactive end groups that have been intentionally introduced.[3]

(3) See: "Kirk-Othmer Encyclopedia of Chemical Technology", 2nd ed.; Wiley: New York, 1970; Vol. 13, p 574.

(4) Mitsch, R. A.; Ogden, P. H.; Stoskoff, A. H. *J. Org. Chem.* **1970**, *35*, 2816.

(5) Haszeldine, R. N. *Nature (London)* **1951**, *167*, 139.

(6) Bedford, C. D.; Baum, K. *J. Org. Chem.* **1980**, *45*, 347.

(7) Berry, K. L.; Peterson, J. H. *J. Am. Chem. Soc.* **1951**, *73*, 5195.

(8) Bier, D. G.; Schäff, R.; Kahrs, K. H. *Angew. Chem.* **1954**, *11*, 285.

(9) Bro, M. I.; Sperati, C. A. *J. Polym. Sci.* **1959**, *28*, 289.

(10) McBee, E. T.; Wiseman, P. A.; Bachman, G. B. *Ind. Eng. Chem.* **1947**, *39*, 415.

(11) Henne, A. L.; Zimmerscheid, W. J. *J. Am. Chem. Soc.* **1945**, *67*, 1235.

(12) Knunyants, I. L.; Dzhi-Yuan, L.; Shokina, V. V. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1961**, 1462.

(13) Owing to the small amounts of tetrafluoroethylene employed in these studies and the relatively large dead volume of the autoclave, yields could not be accurately based on the consumption of monomer.

(14) The reactions described in Table I are intended to be typical but do not necessarily represent optimum conditions for the preparation of the oligomeric fraction WS and the polymeric fraction P of α,ω-perfluorodicarboxylic acids.

(15) See: Weiblen, D. G. In "Fluorine Chemistry"; Simons, J. H., Ed.; Academic Press: New York, 1954; Vol. 2, p 487.

(16) Kauck, E. A.; Diesslin, A. R. *Ind. Eng. Chem.* **1952**, *43*, 2332.

(17) Henne, A. L.; Richter, S. B. *J. Am. Chem. Soc.* **1952**, *74*, 5420.

(18) Padburg, J. J.; Kropa, E. L. *U.S. Patent* 2 502 478, 1950.

(19) Hauptschein, M.; Stokes, C. S.; Nodiff, E. A. *J. Am. Chem. Soc.* **1952**, *74*, 4005.

(20) Compare with related acyclic perfluoro anhydrides listed by: Lovelace, A. M.; Rausch, D. A.; Postelnak, W. "Aliphatic Fluorine Compounds"; Reinhold Publishing Co.: New York, 1958; ACS Monogr. Ser., No 138.

(21) From PCR Research Chemicals, Inc.

(22) (a) In this analysis it was assumed that all of the oligomeric acids were completely converted to methyl esters by treatment with diazomethane. [Compare: Eisenbaum, E. J.; Norris, R. N.; Adolphen, G. *J. Chem. Educ.* **1970**, *47*, 710.] In our hands, we found that 99% of perfluoroglutaric acid, 98% of perfluorosuccinic acid, and 90% of perfluoromalonic acid can be accounted for by this method. (b) Typical calculations are given in the Experimental Section.

(23) The chromatograms also show the presence of minor byproducts, which remain unidentified.

(24) For example, see ref 9 for a discussion of the problem.

(25) House, D. A. *Chem. Rev.* **1962**, *62*, 185.

(26) Behrman, E. J.; McIssac, S. E. "Annual Report on Mechanism of Reactions of Sulfur Compounds; Intra-Science Research Foundation"; Santa Monica, CA, 1968; Vol. 2, p 235.

(27) Wilmarth, W. K.; Haim, A. "Peroxide Reaction Mechanisms"; Edwards, J. O., Ed.; Wiley: New York, 1962; p 175ff.

(28) Walling, C.; Camaioni, D. M.; Kim, S. S. *J. Am. Chem. Soc.* **1978**, *100*, 4814.

(29) Although the formation of HO· from $SO_4^{-}\cdot$ and hydroxide is fast ($k = 6.5 \times 10^7$ M^{-1} s^{-1}), the corresponding reaction with water has an upper limit of $k < 3 \times 10^3$ M^{-1} s^{-1}. See: Hayon, E.; Treinin, A.; Wilf, J. *J. Am. Chem. Soc.* **1972**, *94*, 47. Thus its importance in this system may be questionable.

(30) Perfluoro alcohols are known to be hydrolytically unstable. See: Hauptschein, M.; Stokes, C. S.; Grosse, A. V. *J. Am. Chem. Soc.* **1952**, *74*, 1974. Kellogg, K. B.; Cady, G. H. *Ibid.* **1948**, *70*, 3986.

(31) (a) Perfluoroalkyl sulfates like the corresponding alcohols[30] should be hydrolytically unstable. (b) Some sulfate esters may also be formed by cross coupling of perfluoroalkyl radicals with $SO_4^{-}\cdot$ and/or induced decomposition of peroxydisulfate.

(32) The relative amounts of the various even-numbered oligomeric acids also do not appear to be consistent with a wholly coupling mechanism.

(33) The catalytic role of the metal promoter is especially required where the temperature of the reaction is substantially lower than that required for the first-order homolysis of the peroxydisulfate to proceed at comparable rates (i.e., $T > 100$ °C).[34]

(34) For the purely thermal reaction of peroxydisulfate with tetrafluoroethylene, compare entry 2 in Table I. The *increase* in pressure noted may be tentatively ascribed to the formation of XCF_2CF_2X, and hence, oxalic acid, which is known to afford CO_2 with peroxydisulfate [Po, H. N.; Allen, T. L. *J. Am. Chem. Soc.* **1968**, *90*, 1127]. It is noteworthy that no or little insoluble polymeric material was formed.

(35) For a review, see: (a) Kochi, J. K. "Free Radicals"; Wiley: New York, 1973; Vol. I, Chapter 11; (b) Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: London, 1974; p 305ff. (c) Such a facile oxidation of perfluoroalkyl radicals by iron(III) species is interesting and merits further study.

(36) Tanner, D. D.; Osman, S. A. A. *J. Am. Chem. Soc.* **1968**, *90*, 6572.

(37) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 1651. For a discussion, see also ref 35a, p 651ff.

(38) The absence of perfluorsuberic, -pimelic, or -adipic acids in the oxidative decarboxylation of perfluoroglutaric acid in eq 4 suggests that radical coupling does not compete with radical oxidation in these systems. It is also possible that some hypervalent iron species can lead to carboxy radicals in eq 11. Compare: Groves, J. T.; Van De Puy, M. *J. Am. Chem. Soc.* **1975**, *97*, 7118.

(39) Hamilton, J. M. *Ind. Eng. Chem.* **1953**, *45*, 1347.

(40) From J & W Scientific, Inc.

Polymerization Behavior of 7,7,8,8-Tetrakis(ethylsulfonyl)quinodimethane with Donor Monomers

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ABSTRACT: It was found from the charge-transfer transition with hexamethylbenzene that 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane (TESQ) (EA = 1.17 eV) is much lower in electron affinity than 7,7,8,8-tetracyanoquinodimethane (TCNQ) (EA = 2.84 eV). TESQ and styrene underwent spontaneous alternating copolymerization in nitromethane, but when *p*-dioxane or dichloromethane was used instead of nitromethane, the copolymer obtained was not alternating and the styrene unit content was greater than 50 mol %, supposedly indicating that cationic polymerization of styrene takes place simultaneously. Additionally, when the TESQ fraction was above about 0.4, no copolymer was produced, and only 1:1 adduct was obtained in high yield. It was found that TESQ is able to induce the cationic oligomerization of isobutyl vinyl ether, *n*-butyl vinyl ether, 2-chloroethyl vinyl ether, and phenyl vinyl ether. However, reaction with vinyl acetate did not take place at all. Hydrogen-transfer reactions of TESQ and some alcohols, e.g., cinnamyl alcohol, 1-phenyl-1-propanol, and 1-phenylethanol, were attempted. Dehydration of the alcohols took place in addition to the intended hydrogen-transfer reaction, especially in the case of the latter two alcohols. It is pointed out that TESQ behaves more like an acidic compound than TCNQ although TESQ is much weaker in electron-accepting character than TCNQ.

So far the polymerization behavior of some quinodimethane derivatives with electron-accepting character has been studied. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) can be copolymerized in an alternating fashion in acetonitrile with so-called donor monomers such as styrene (St),[1] 2-chloroethyl vinyl ether (CEVE),[2] phenyl vinyl ether (PhVE),[2] and vinyl acetate (VAc)[2] and is able to induce the cationic polymerizations of *n*-butyl vinyl ether (*n*-BVE) and isobutyl vinyl ether (*i*-BVE) in acetonitrile.[2,3] The mode of polymerization between TCNQ and CEVE was found to change from the alternating copolymerization to the cationic polymerization of CEVE upon replacement of the solvent from acetonitrile, with a low dielectric constant, to ethylene carbonate, with a high dielectric constant.[4] 7,7,8,8-Tetrakis(methoxycarbonyl)quinodimethane (TMCQ) can be copolymerized in an alternating amphoteric fashion; it reacts as an acceptor monomer with donor monomers such as St, VAc, PhVE, CEVE, and *i*-BVE while it reacts as a donor monomer with the very powerful electron-accepting monomer TCNQ.[5] 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$) can be copolymerized in an alternating fashion not only with donor monomers such as St, PhVE, and VAc but also with so-called acceptor monomers with small positive *e* values such as methyl methacrylate and methyl acrylate.[6] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) is copolymerized alternatingly with St and induces the cationic polymerization of *i*-BVE and CEVE.[7] These interesting and unusual polymerization behaviors had not been found in conventional vinyl polymerizations.

In a series of studies of quinodimethane compounds at the Experimental Station of the du Pont Co. in the 1960's, 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane (TESQ) was reported by Hertler and Benson,[8] but its polymerization behavior has not been described yet. In Hammett substituent constants,[9] the ethylsulfonyl group ($\sigma_p = 0.68$) is as electron withdrawing as the cyano group ($\sigma_p = 0.66$), indicating a similar electron-withdrawing inductive effect, so TESQ was expected to be similar to TCNQ in its polymerization behavior as an acceptor monomer. Thus it seemed interesting to study in detail its polymerization behavior, as an acceptor monomer.

In this paper we study the spontaneous reactions between TESQ and donor monomers such as St, *n*-BVE, *i*-BVE, CEVE, PhVE, and VAc. In addition, we study the hydrogen-transfer reaction and dehydration of some alcohols with TESQ in connection with some unusual phenomena in the above reactions.

Experimental Section

Materials. TESQ (mp 190 °C dec) and $\alpha,\alpha,\alpha',\alpha'$-tetrakis(ethylsulfonyl)-*p*-xylene ($TESQH_2$) (mp 257–258 °C) were prepared according to the method of Hertler and Benson.[8] TCNQ and *p*-phenylenedimalononitrile ($TCNQH_2$) were obtained by the process of Acker and Hertler.[10] TCNQ was purified by recrystallization from ethyl acetate and sublimation (twice) (mp 293.5–296 °C). PhVE was prepared from phenol and dibromomethane (bp 51.5–52.0 °C (17 mmHg)).[11] St (bp 58 °C (32 mmHg)), *n*-BVE (bp 92.5 °C), *i*-BVE (bp 81 °C), CEVE (bp 109

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