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SYNTHESIS OF NEW FLUOROPOLYMERS: TAILORING MACROMOLECULAR PROPERTIES WITH FLUORINATED SUBSTITUENTS

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ABSTRACT

The challenges and opportunities in the preparation of new fluoropolymers are illustrated by the synthesis of fluorinated poly(ether sulfones), polyimides, and polyethers. Synthetic methods used for the preparation of new fluorinated monomers and polymers include anion-radical substitutions of perfluoroalkyl diiodides, nucleophilic additions to fluorinated olefins, perfluoroalkylsulfonyl-mediated nucleophilic substitutions, and direct fluorinations with elemental fluorine. Properly placed fluorinated substituents can have significant effects on the dielectric properties, thermal stability, moisture absorption, permeability, phase transitions, and reactivity of the resulting polymers. In addition, fluorinated groups can enhance nonlinear optical effects and provide a method for chromophore alignment. The special behavior of partially fluorinated substituent groups offers unique tools for tailoring macromolecular properties.

INTRODUCTION

Fluorinated polymers have achieved significant technological importance because of the unique properties imparted by fluorine [1]. In general, substitution of fluorine for hydrogen increases chemical and oxidative stability, weatherability, and melting point, and decreases flammability, adhesion, dielectric constant, and refractive index. In addition, the relatively small size of fluorine permits substitution for virtually every hydrogen in organic polymers, offering the potential for an enormous number of fluorinated polymers.

Many fluorinated polymers have been reported, but the major commercial products are produced by radical polymerization of a few key fluorinated monomers: tetrafluoroethylene, vinylidene fluoride, vinyl fluoride, and chlorotrifluoroethylene. Plastics, elastomers, and ionomers are also produced by copolymerization of these monomers with hexafluoropropylene, ethylene, and perfluoroalkylvinyl ethers.

The highly fluorinated polymers, such as polytetrafluoroethylene, have a unique combination of desirable properties (Table 1), but generally modest mechanical properties and a high specific gravity. They can also be difficult to process into useful shapes. Thus, there have been many investigations on incorporating desirable fluoropolymer-like properties into other classes of polymers by the selective introduction of fluorinated substituents. Of special interest has been the incorporation of fluorinated groups into thermally stable and mechanically-robust condensation polymers such as polyimides, polyamides, and polyesters.

The introduction of fluorinated substituents into or on a polymer backbone poses both challenges and opportunities because of the unique reactivity of fluorocompounds. Synthetic approaches should use few steps and readily available intermediates to provide the best chance for commercial development. With condensation polymers, the challenge often reduces to developing an efficient synthesis of the appropriate difunctional monomers, although solubility and reactivity differences between fluorinated and nonfluorinated groups will often also create problems later in the synthesis.

Another issue in developing fluorinated condensation of polymers is where to place the fluorinated groups. The importance of selecting the correct location of the fluorine to achieve desired properties can be illustrated by two of the commercial fluorinated addition polymers: poly(ethylene-*co*-tetrafluoroethylene) (ETFE) [2] and poly(vinylidene fluoride) (PVDF) [3]. They have isomeric structures, with ETFE having a mostly alternating one-to-one arrangement of monomers. Yet ETFE is a high melting (275°C), nonpolar polymer ($\epsilon = 2.6$), while PVDF has a nearly 100°C lower melting point and is a relatively polar material ($\epsilon = 8.5$).

The features involved in the development of new fluoropolymers will be illustrated in this paper by a description of the syntheses and properties of fluorinated poly(ether sulfones), polyimides, and polyethers. Unique synthetic approaches to these polymers and their monomers include anion-radical substitution reactions of

TABLE 1. Properties of Polytetrafluoroethylene

High thermal stability
Chemical inertness
Low surface energy
Low dielectric constant
Low refractive index
Low moisture absorption
Excellent weatherability
Low flammability

perfluoroalkyl idodides, nucleophilic additions to fluorinated olefins, perfluoroalkylsulfonyl-mediated nucleophilic substitutions, and direct fluorinations with elemental fluorine.

RESULTS AND DISCUSSION

Part I. Fluorinated Poly(Ether Sulfones)

Our first approach to novel fluoropolymers began with perfluoroalkylene diiodides $I(CF_2CF_2)_nI$(n = 1, 2, 3, . . .), readily available from the telomerization of tetrafluoroethylene with iodine [4]. Due to their reverse polarity, perfluoroalkyl iodides do not undergo normal S_N1 or S_N2 substitutions, but will react with selected nucleophiles by an $S_{RN}1$ process (Fig. 1) [5]. When applied to the diiodides, this $S_{RN}1$ substitution affords new difunctional monomers (Fig. 2). Thus, reaction with lithium 2-nitropropionate followed by reduction provides aliphatic diamines **1** and treatment with sodium 4-acetamidothiophenolate followed by removal of the acetamide protecting groups affords aromatic diamines **2** with perfluoroalkylenedithio spacer groups. The latter have been used to prepare novel colorless polyimides [6]. Reaction of the diiodides (n = 2, 4) with sodium 4-fluorobenzenethiolate affords disulfides which are readily oxidized to bis-sulfones **3** in excellent yield.

The perfluoroalkylsulfonyl group is recognized as among the strongest electron-withdrawing groups with a σ_p substituent constant of 1.08 as compared to 0.76 for the more familiar nitro group [7]. Thus, the para fluorines in **3** should be strongly activated toward nucleophilic displacement. In fact, **3** readily polymerizes with bis-phenols under relatively mild conditions to afford fluorinated poly(ether sulfone)s **4** in high yield (Fig. 3). [8].

Polymers **4** are amorphous white solids with glass transition temperatures ranging from 114 to 165°C, and are soluble in DMAC and some chlorinated solvents. Properties of polymers **4a** and **4b**, prepared from **3** and bisphenol-A, are compared to those of the nonfluorinated polyether sulfone **5** in Table 2 [9]. The fluorine-containing polymers show lower glass transition temperatures due to the presence of the relatively flexible fluoroalkyl chain in their backbones. Notable are

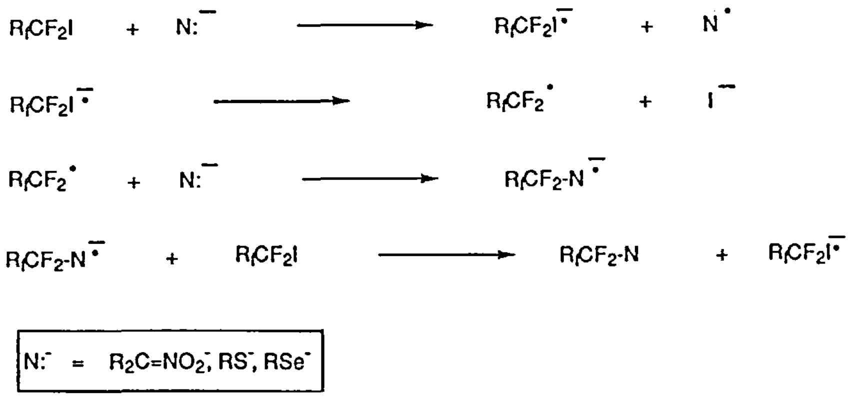


FIG. 1. Mechanism for $S_{RN}1$ substitution reactions of perfluoroalkyliodides.

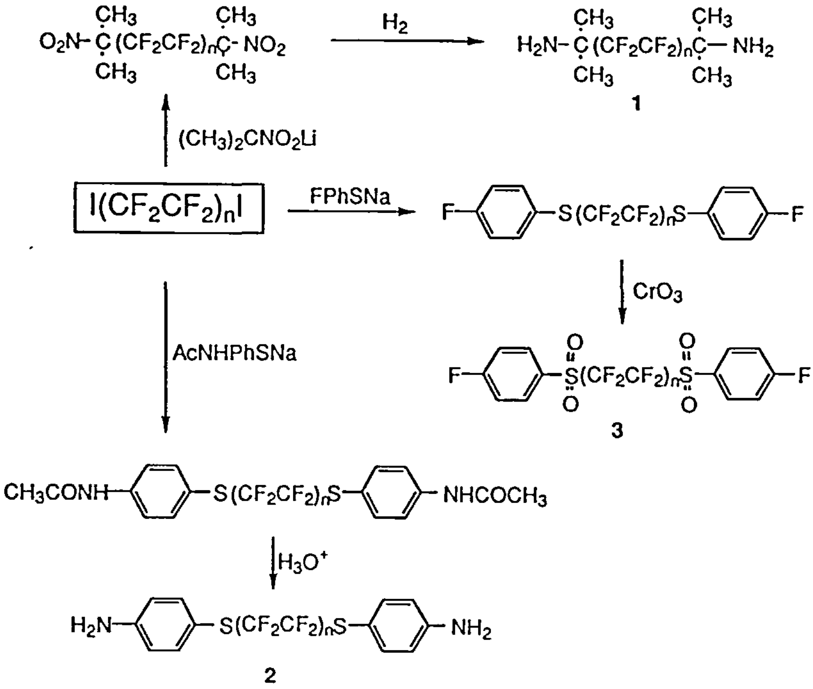


FIG. 2. Synthesis of difunctional fluoromonomers from diiodoperfluoroalkanes.

the lower dielectric constant of **4b**, and its better permeability *and* selectivity in oxygen/nitrogen gas separations as compared to its nonfluorinated analog **5**.

Synthesis of 3-(4-fluorophenylsulfonyl)-1,2,3,3-tetrafluoropropanol (**6**) provides another approach to a fluorinated poly(ether sulfone) [10]. Compound **6** is obtained in excellent yield by conjugate addition of sodium 4-fluorobenzenethiolate

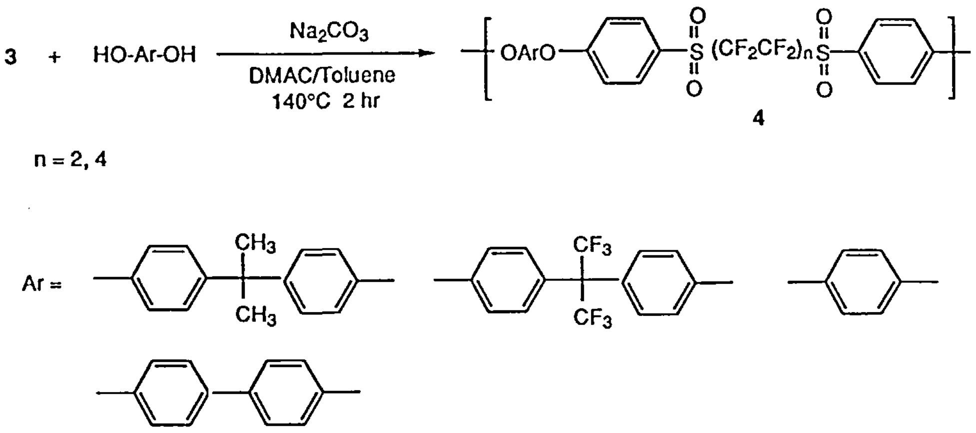
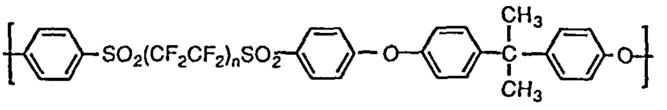


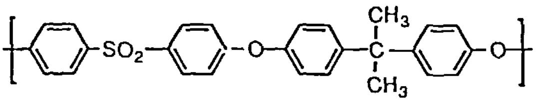
FIG. 3. Synthesis of fluorinated poly(ether sulfone)s.

TABLE 2. Properties of Poly(Ether Sulfone)s

Polymer	η_{inh}	T_g, °C	T_d, °C	Dielectic constant	$P(O_2)$	$P(O_2/N_2)$
4a	1.29	124	411		230 cB	4.44
4b	0.95	142	405	2.76	150 cB	6.53
5		185		3.19	100 cB	6.10



4a, n = 4
4b, n = 2



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to tetrafluoroethylene and carbon dioxide (Fig. 4), followed by conventional oxidation of the sulfide to sulfone and reduction of the ester to alcohol. Since 6 contains both the highly electrophilic 4-fluorophenylsulfonyl group and a nucleophilic hydroxyl, it is potentially an AB monomer for condensation polymerization. In fact, the sodium salt of 6 polymerizes under remarkably mild conditions (room temperature in DMAC) to give polymer 8 with an inherent viscosity of 0.41 dL/g. The trimethylsilyl ether 7 also readily polymerizes to 8 in the presence of a catalytic amount of cesium fluoride.

Although the properties of 8 have not been investigated in detail, one surpris-

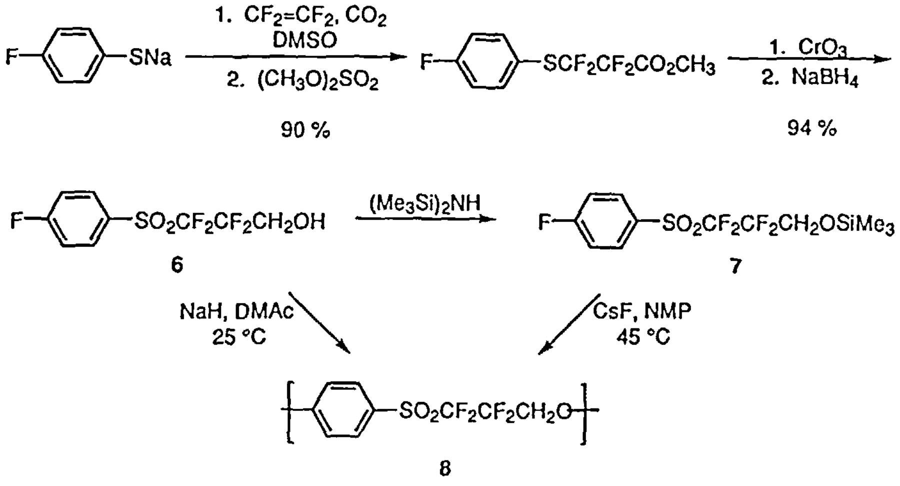


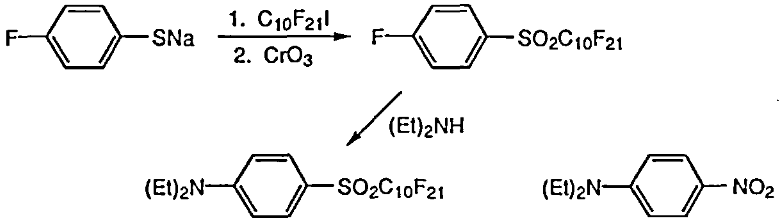
FIG. 4. Synthesis of an aromatic fluoroaliphatic poly(ether sulfone).

ing feature is its crystallinity. In contrast to most aromatic poly(ether sulfone)s which are amorphous, **8** shows a distinct and recoverable melting transition at about 243°C and a glass transition temperature at 85°C. It also has good solubility in a variety of polar organic solvents.

Nonlinear Optical Effects of Aryl Perfluoroalkyl Sulfones

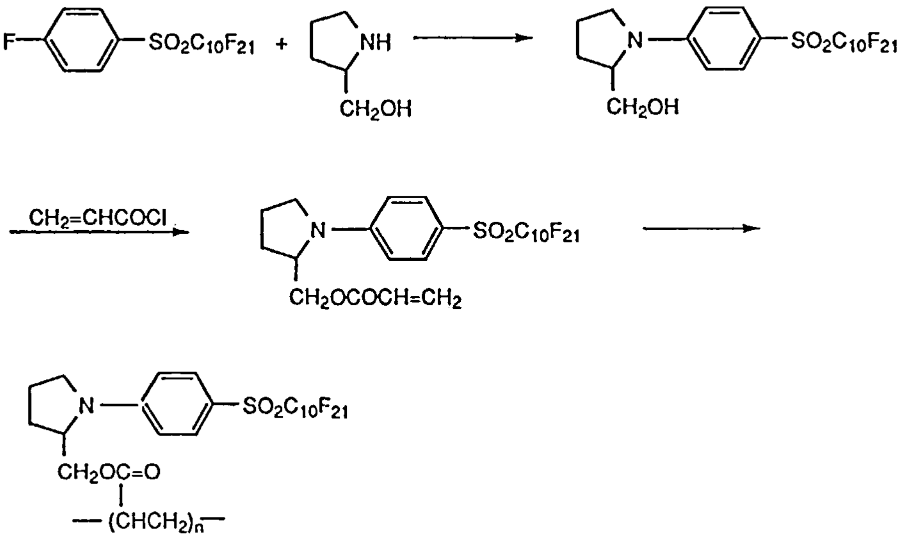
Another potential application of aryl perfluoroalkylsulfones is in the field of nonlinear optics [11]. In the search for organic materials with useful properties for second-order nonlinear optical effects, much attention has focused on donor-acceptor substituted aromatic compounds. The classic examples are variously substituted derivative of 4-nitroaniline. Since the perfluoroalkylsulfonyl substituent is, by some measures, a more powerful acceptor group than nitro, it seemed worthwhile to test appropriately substituted derivatives for this application. Initially, the model compound, 4-(diethylamino)perfluorodecanesulfonylbenzene (**9**) was prepared as shown in Fig. 5. Its hyperpolarizability (β), measured in solution by electric-field-induced second harmonic generation, is nearly as large as that of 4-(diethylamino)nitrobenzene (**10**) measured under the same conditions. More interestingly, the λ_{max} for the fluorinated sulfone is blue shifted from the nitro analog and its dipole moment (μ) is larger. Both are highly desirable features in materials for second harmonic generation, since the former extends the range of wavelengths over which the material could operate and the latter assists in orienting the sample in an electric field.

A high β is not sufficient, however, for a material to have useful second-order activity in real optical devices. Since second-order nonlinearity is a vector effect, the collection of molecules with the desired chromophore must be appropriately oriented in the macroscopic sample and must maintain this orientation over the useful life of a device. In this connection, an additional advantage of the perfluoroalkylsul-



	9	**10**
λmax (nm)	314	376
μ (10^{-18} esu)	7.3	6.4
β (10^{-30} esu)	9.0	12.0

FIG. 5. Synthesis and properties of perfluoroalkylsulfonyl- and nitro-substituted aromatics with nonlinear optical activity.



11

FIG. 6. Synthesis of a polymer with a pendant NLO active group.

fonyl substituent over the more traditional nitro or cyano acceptors may emerge since the fluoroalkyl group may be tailored or functionalized to help with orientation.

Since materials for nonlinear optics must have also useful mechanical properties and a high degree of optical clarity, the chromophore is often incorporated into polymers. We have prepared polymer **11** (Fig. 6) in which the amino-4-perfluoroalkylsulfonylbenzene group is attached as a side chain to a polyacrylate [12]. This polymer provides well-behaved monolayers when spread on water from a chloroform solution, and multilayers can be deposited on a substrate by the usual Langmuir–Blodgett techniques. Not unexpectedly, however, the polymer undergoes Y-type deposition, leading to a centrosymmetric multilayer structure which is devoid of second-order activity.

A solution to this problem was found through alternation of polymer **11** with a buffer polymer of appropriate structure. After some investigation, polymer **12** (Fig. 7) was identified as a suitable spacer material. This polymer is prepared by reaction of 4-hydroxyphenyloxazoline with the fluorinated olefin **13** (a readily available trimer of hexafluoropropylene), giving monomer **14**. Cationic polymerization of **14** provided amorphous polymer **12**.

Polymers **11** and **12** could be transferred alternatively from air–water interfaces to a glass substrate using connected troughs. As illustrated by the cartoon in Fig. 8, this process provides multilayers with the nonlinear optical groups properly aligned. The ordering of the side chains is maintained in at least up to 80 monolayers as determined by a linear relationship of the second harmonic signal to the number of layers. The orientational order also exhibits excellent long-term stability, in excess of 2 years, at room temperature. This system has recently been used to study

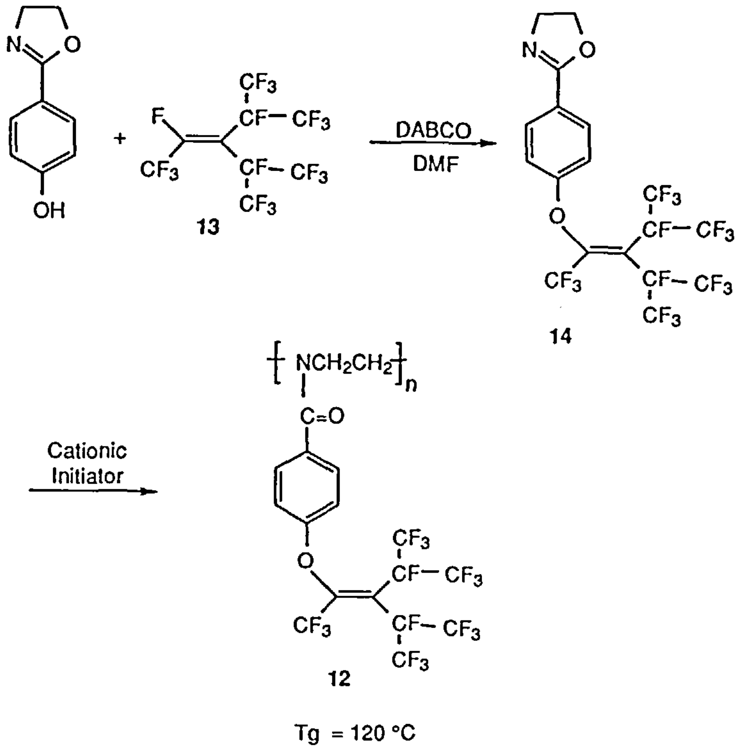


FIG. 7. Synthesis of a spacer polymer.

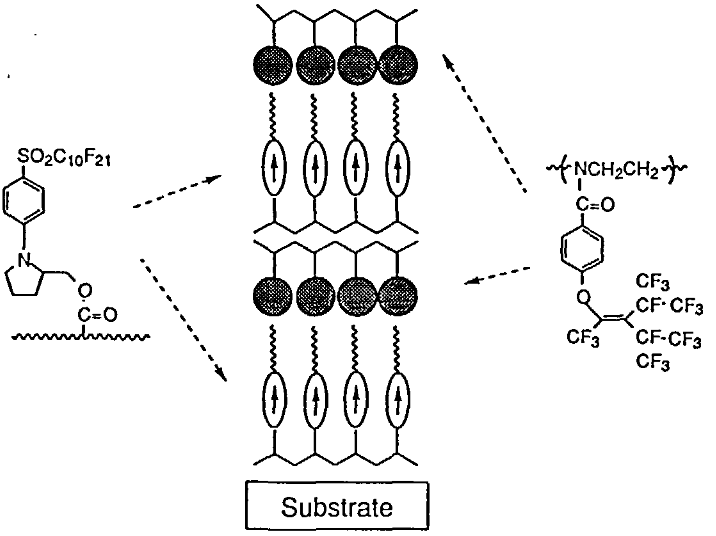


FIG. 8. Alternating Langmuir-Blodgett bilayer films.

the disordering process which occurs when the system is heated above the glass transition temperatures of its polymeric components [13].

Summary

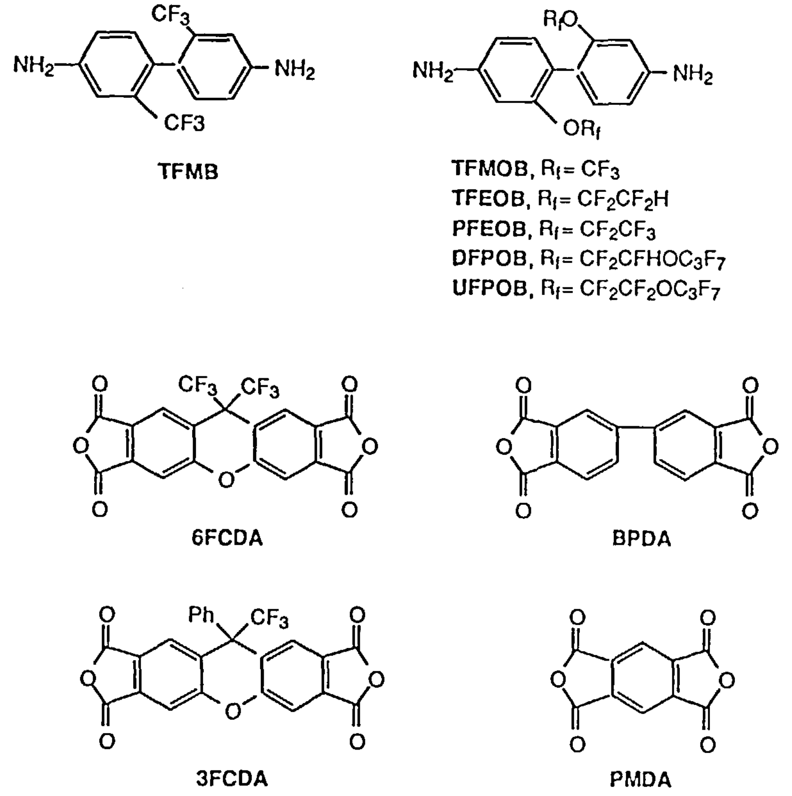
The perfluoroalkylsulfonyl group is readily introduced into monomers by the $S_{RN}1$ substitution of perfluoroalkyl iodides or by nucleophilic additions to tetrafluoroethylene, followed by oxidation. Its powerful electronegativity strongly activates nucleophilic substitution on appropriately substituted aromatic rings, leading to efficient polymerizations. The fluorinated chains in the resulting polymers can have a significant impact on thermal properties, permeability, and dielectrics. In addition, the perfluoroalkylsulfonyl substituent has potential in the development of materials with nonlinear optical properties.

Part II. Fluoroalkoxy-Substituted Polyimides

The impact of different fluorinated substituents on the properties of aromatic polyimides will now be considered. Polyimides are widely used as films, coatings, adhesives, and matrix resins due to their excellent electrical and mechanical properties, high thermal and chemical stability, and dimensional stability [14]. Incorporation of fluorinated substituents into the polyimide structure may lead to lower moisture pickup and dielectric constant, properties of special importance in electrical or electronics applications. The 2,2′-bis(trifluoromethyl)benzidine monomer (TFMB) (Fig. 9) has been of special interest recently since it combines fluorinated substituents with a rigid backbone [15]. The latter feature, when combined with appropriate dianhydrides, also provides polyimides with a desirable low coefficient of thermal expansion.

We considered that a further tailoring of polymer properties might be achieved by replacing the trifluoromethyls of TFMB with fluoroalkoxy substituents, especially trifluoromethoxy. The CF_3O group is very chemically and thermally stable and is significantly less electron withdrawing than CF_3, so the diamine should be more reactive. Thus, the novel fluoroalkoxy monomers TFMOB, TFEPB, PFEOB, DFPOB, and UFPOB were prepared and polymerized with the dianhydrides shown in Fig. 9 [16].

TFMOB is prepared in good yield by reduction of readily available 3-nitrotrifluoromethoxybenzene [17] to the corresponding hydraazo derivative, followed by benzidine rearrangement (Fig. 10). The remaining fluoroalkoxy monomers are prepared in similar fashion from the corresponding 3-fluoroalkoxynitrobenzenes. The latter compounds are obtained from 3-nitrophenol as shown in Fig. 11. Compounds **15** and **16** are prepared using the facile addition of phenols to the fluoromonomers tetrafluoroethylene and perfluoropropylvinyl ether, respectively, again illustrating the utility of nucleophilic additions to fluorinated olefins [18]. Preparations of the perfluorinated analogs **17** and **18** require different procedures. Compound **17** was best obtained by reaction of the phenyl trifluoroacetate with sulfur tetrafluoride. When this reaction is run in the presence of excess hydrogen fluoride, the product is obtained in excellent yield. Compound **18** is obtained by preparing the addition-elimination product from 3-nitrophenoxide and perfluoropropylvinyl ether, followed by a selective fluorination of the double bond using elemental fluorine [19].



TFMB

TFMOB, $R_f = CF_3$
TFEOB, $R_f = CF_2CF_2H$
PFEOB, $R_f = CF_2CF_3$
DFPOB, $R_f = CF_2CFHOC_3F_7$
UFPOB, $R_f = CF_2CF_2OC_3F_7$

6FCDA

BPDA

3FCDA

PMDA

FIG. 9. Fluorinated diamine and dianhydride monomers for polyimides.

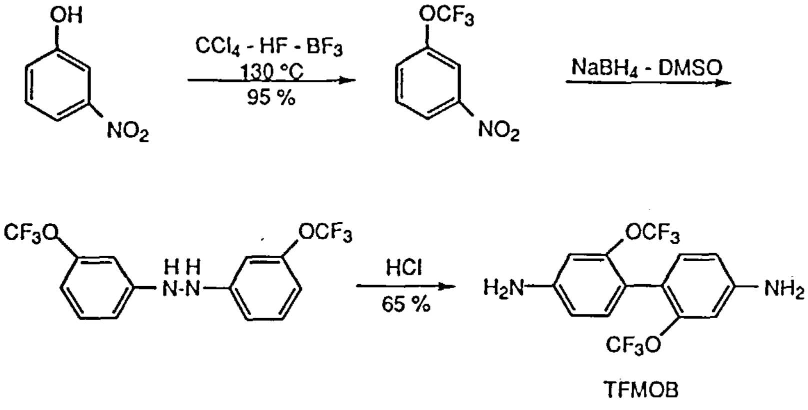


FIG. 10. Synthesis of TFMOB.

However, subjecting these nitrocompounds to the reduction and benzidine rearrangement gives surprising results. The trifluoromethoxy compound gives a single benzidine, the desired, 4,4′-diamino isomers, whose structure was confirmed by x-ray crystallography. The other compounds, however, give a mixture of benzidine derivatives (Fig. 12) with the isomer ratio appearing to be a sensitive function of the size of the fluorinated substituent. Fortunately, the desired isomer can be isolated by fractional crystallization from the mixture. The fluorinated diamines can be polymerized with the dianhydrides in Fig. 9 using standard conditions, generally by formation of the intermediate amic acid in NMP, followed by spin coating and thermal imidization.

Properties of polyimides from pyromellitic dianhydride (PMDA) and the fluorinated diamines are shown in Tables 3 and 4 with comparison data for the commercially available polyimide from PMDA and oxydianiline (ODA). In general, the mechanical properties of films from TFMB, TFMOB, and TFEOB are similar and show the higher tensile strength and modulus and low coefficients of thermal expansion (CTE) expected from the rigid polymer backbone. In contrast, the polyimides incorporating the longer fluoroalkoxy chains showed significantly lower mechanical properties and a notably high CTE, despite maintenance of the rigid backbone. Moisture absorption of these fluorinated polyimides is quite low, with the trifluoromethoxy derivatives showing superior performance to the trifluoromethyl analog. The highly fluorinated polymer from DFPOB has an extremely low moisture absorption, more typical of a fluoropolymer than of a polyimide. Dielectric constants are also lower with the fluorinated polymers, with the exception of TFEOB. In this case the presence of the lone hydrogen may create a strong dipole which increases the dielectric constant despite the presence of fluorine in the polymer. The same

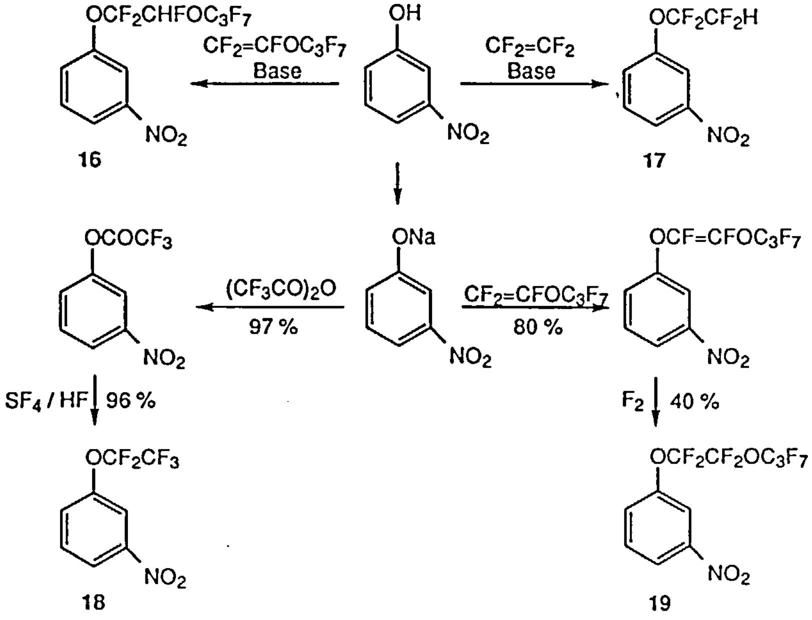
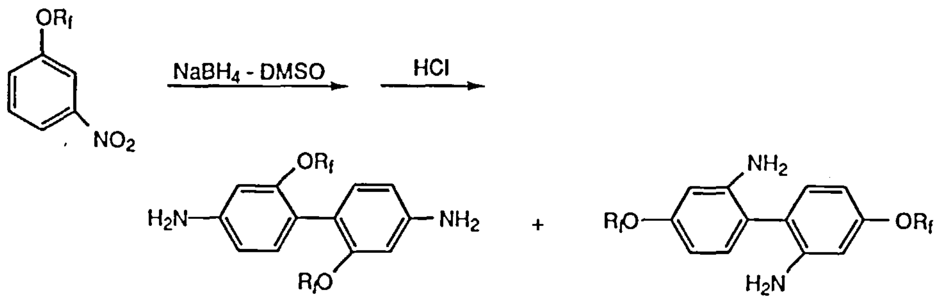


FIG. 11. Synthesis of 3-(fluoroalkoxy)nitrobenzenes.



$R_f = CF_3$	~ 100		
$R_f = CF_2CF_2H$	~ 67	:	33
$R_f = CF_2CF_3$	~ 42	:	58
$R_f = CF_2CHFOC_3F_7$	~ 30	:	70
$R_f = CF_2CF_2OC_3F_7$	~ 26	:	74

FIG. 12. Synthesis of fluoroalkoxy-substituted benzidines.

effects may be operative in the DFPOB case, but they are much diluted by the higher levels of fluorine.

Thus, properties of these polyimides are readily tailored by changing the structure of the fluorinated side chain with, perhaps, the best combination afforded by the OCF_3 substituted materials. Polyimides with extremely low moisture absorption can be obtained by selecting the longer fluoroalkyl side chains but at a price in mechanical properties. Also of interest is the effect on properties of a lone hydrogen in an otherwise perfluorinated group; an effect which will show up more strongly in the polymers described in the next section.

TABLE 3. Thermal and Mechanical Properties of Fluorinated Polyimides

Monomers	TGA 5% weight loss (air)	Tensile strength, MPa	Modulus, GPa	Elongation, %
PMDA/TFMB	592	374	7.4	28
PMDA/TFMOB	591	378	7.2	18
PMDA/TFEOB	549	333	6.9	14
PMDA/PFEOB	543	233	6.7	10
PMDA/DFPOB	496	226	3.1	24
PMDA/UFPOB	535	177	2.5	28
PMDA/ODA	565	168	1.3	82

TABLE 4. Properties of Fluorinated Polyimides

Monomers	% Fluorine	CTE, ppm	% Water absorption, 85% RH	Dielectric constant, dry, 1 MHz
PMDA/TFMB	22.7	−3	1.9	2.6
PMDA/TFMOB	21.3	−3	0.7	2.6
PMDA/TFEOB	25.4	−7	1.6	3.3
PMDA/PFEOB	30.0	16		2.6
PMDA/DFPOB	40.8	81	<0.05	2.5
PMDA/UFPOB	43.3	129		2.4
PMDA/ODA	0	31	3.5	3.2

Part III. Poly- and Perfluorinated Polyethers

The final example of the synthesis and properties of new fluorinated polymers will come from the family of fluorinated polyethers. In contrast to the polymers discussed above, these materials have low glass transition temperatures and little or no crystallinity due to their aliphatic structures and the presence of in-chain oxygens. The perfluorinated polyethers exhibit high thermal stability, excellent chemical resistance, and low surface energy, leading to applications as lubricants, elastomers, and heat transfer fluids under demanding conditions. Currently they are prepared by ring-opening polymerization of hexafluoropropylene oxide [20], by randon copolymerization of tetrafluoroethylene and/or hexafluoropropylene with oxygen under ultraviolet irradiation [21], or by ring-opening polymerization of 2,2,3,3-tetrafluorooxetane, followed by fluorination [22]. A few examples have also been prepared by fluorination of alkyl polyethers although this requires exceptional care to avoid chain cleavage or other side reactions [23].

We have found an alternative approach to fluorinated polyethers with well-defined structures involving polymerization of fluorinated vinyl ether alcohols, followed by fluorination of the intermediate, partially-fluorinated structures [24]. Polymerization involves ionic addition of OH groups to the trifluorovinyl ether moity, a reaction used above to prepare monomers but not previously used for polymerizations. Thus, reduction of the ester vinyl ether 20 (Fig. 13), a readily

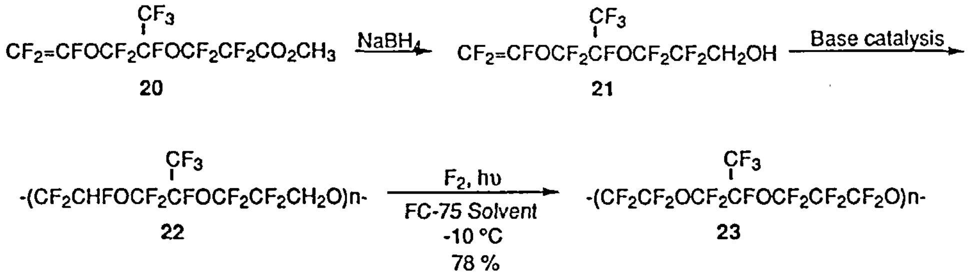


FIG. 13. Synthesis of poly- and perfluorinated polyethers.

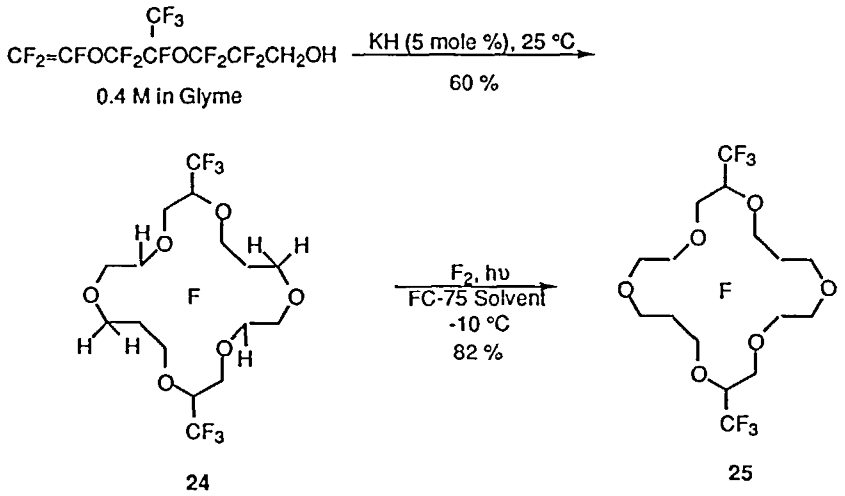
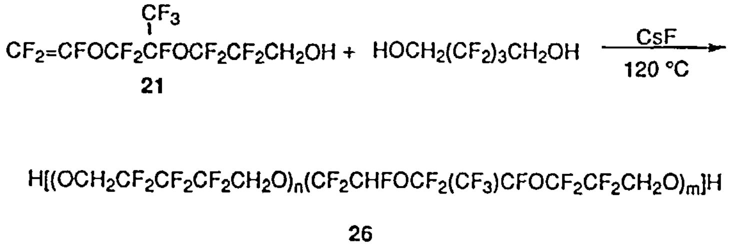


FIG. 14. Synthesis of fluorinated crown ethers.

available intermediate used in the production of Nafion ion-exchange resins [25], affords the hydroxy vinyl ether **21** in good yield without need for protection of the double bond. Treatment of **21** with basic catalysts such as potassium or cesium carbonates or cesium fluoride in the absence of solvent at about 120°C affords the partially fluorinated polyethers **22** in excellent yield. Polymers with weight-average molecular weights as high as 65,000 are obtained. Subsequent reaction of **22** with elemental fluorine under UV irradiation in an inert perfluorinated solvent affords the perfluorinated analogs **23**. Since polymers **22** are already mostly fluorinated, this fluorination requires no special precautions and proceeds in excellent yield with little chain cleavage.

On the other hand, if the reaction of **21** with a catalytic amount of base is conducted at moderate dilution in a polar, aprotic solvent, the major product is the cyclic ether dimer **24** (Fig. 14). This material is readily isolated in yields of up to 60% with the remaining products mostly higher cyclic oligomers. The cyclic ether **24** is readily photofluorinated to the perfluorinated cyclic ether **25** in excellent yield. This procedure affords a remarkably high yield route to the interesting perfluori-



$$CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2CH_2OH + HOCH_2(CF_2)_3CH_2OH \xrightarrow[120\ ^\circ C]{CsF} H[(OCH_2CF_2CF_2CF_2CH_2O)_n(CF_2CHFOCF_2(CF_3)CFOCF_2CF_2CH_2O)_m]H$$

FIG. 15. Synthesis of fluorinated telechelic polyethers.

TABLE 5. Proton NMR Chemical Shifts of $-(CF_2CH^aFOCF_2CF(CF_3)OCF_2CF_2CH^b_2O)n-$

Solvent	δH^a	δH^b
Benzene	5.17	3.77
Chloroform	5.96	4.32
Acetonitrile	6.34	4.56
Methanol	6.61	4.52
Acetone	6.79	4.72
DMSO	7.10	4.69

nated crown ethers in a few steps without requiring high dilution or other special precautions.

A further useful variation on the ionic polymerization of hydroxy trifluorovinyl ethers is illustrated by reaction of **21** in the presence of a calculated amount of a fluorinated diol (Fig. 15) [26]. This provides telechelic macrodiols **26** with excellent difunctionality which can be used for the preparation of segmented block copolymers [27].

The dramatic effects of a few hydrogens in otherwise perfluorinated polymers are illustrated by a comparison of the properties of **22** and **23**. As expected, the perfluorinated material is soluble only in perfluorinated solvents. In contrast, **22** is soluble in many common organic solvents. Proton NMR chemical shifts of the CHF and CF_2CH_2O protons in **22** are highly solvent dependent, with the shifts in the direction expected from hydrogen bond interactions with donor solvents (Table 5). A further indication of these interactions is the formation of complexes of the cyclic species with *anions*. Thus **24** forms a 2:1 complex with tetrabutylammonium chloride.

CONCLUSIONS

Several families of fluorine-containing polymers have been used in this report to illustrate the unique reactivity of fluorinated compounds leading to novel monomers and polymerization processes for control of molecular architecture. Reactions include the $S_{RN}1$ substitutions of perfluoroalkyl diiodides leading to various monomers for condensation polymers and the activation of aromatic nucleophilic substitutions by perfluoroalkylsulfones. Nucleophilic additions to fluorinated olefins can be used to prepare both monomers and polymers, and direct fluorinations can be used to prepare highly fluorinated monomers and polymers in selected cases.

In addition, we have illustrated the ability of fluorinated groups to modify the thermal stability, phase transitions, dielectric properties, moisture sensitivity, and permeability of various polymers. Fluorinated groups can help to organize multilayers and improve nonlinear optical properties. Finally, it is noted that a few hydrogens in a fluorinated chain can have dramatic effects on properties due to strong interactions with their environment. These features are likely to lead to increasing interest in the preparation and properties of novel fluorinated polymers.

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