Poly(aryl ether oxazole)s with Trifluoromethyl Groups

Gerhard Maier*

Lehrstuhl für Makromolekulare Stoffe, TU München, W-8046 Garching, FRG

Reinhold Hecht and Oskar Nuyken

Lehrstuhl für Makromolekulare Chemie I, Universität Bayreuth, W-8580 Bayreuth, FRG

Klaus Burger and Brigitte Helmreich

Institut für Organische Chemie, TU München, W-8046 Garching, FRG

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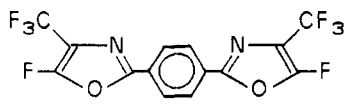
ABSTRACT: Poly(aryl ether oxazole)s with trifluoromethyl groups bound to the oxazole moieties have been synthesized from a bisoxazole monomer containing two activated fluorine atoms by nucleophilic displacement with bisphenols. The poly(aryl ether oxazole)s are completely amorphous with one exception. Their glass transition temperatures are between 136 and 191 °C, depending on the structure of the bisphenol monomer. Due to their amorphous nature they are soluble in a number of common organic solvents. They have been thoroughly characterized by IR and NMR spectroscopy, DSC, GPC, and thermogravimetry. The polymers exhibit an unexpected instability at high temperatures. While other oxazole-containing polymers are stable in air up to more than 450 °C, the new poly(aryl ether oxazole)s already start to lose weight at temperatures of about 310 °C. This is attributed to their special oxazole structure, and a strategy is proposed and studied to overcome this low thermal stability.

Introduction

Many five-membered aromatic heterocycles such as thiazoles,[1] triazoles,[1,9,10] oxadiazoles,[1,7,8] pyrazoles,[1,9,10] and tetrazoles[9] as well as fused five-membered heterocycles such as benzimidazoles,[2,4] benzoxazoles,[3,5,6] and benzothiazoles[3] have been incorporated into polymers already. Except for the tetrazoles, which can decompose in a cycloreversion reaction under elimination of nitrogen,[9] they show good thermooxidative stability. In some cases these polymer structures are soluble in common organic solvents. Among the heteroaromatic polymers the partially sulfonated poly(benzimidazole) shows some of the most remarkable properties. It is commercially available from Hoechst Celanese (pbi-Fiber). It is used as the main component in fire protection suits for jet and space shuttle pilots as well as for race car drivers because of its nonflammability even in atmospheres with increased oxygen content and its low shrinkage and formation of flexible char on exposition to flash fires with temperatures up to 1000 °C.[2] Furthermore, its subjective wear confort, which is similar or superior to cotton,[2] is remarkable.

Trifluoromethyl groups in polymers are known to improve a number of important properties such as solubility, melt viscosity, transparency, color, glass transition temperature, and flame resistance.[11–13,33]

In order to combine the properties of heteroaromatic polymers and trifluoromethyl-containing polymers, we synthesized monomer 1 containing two CF_3-substituted oxazole rings:



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The fluorine atoms of the heterocycles are activated by the electron-withdrawing trifluoromethyl groups and can easily be replaced by nucleophiles in an aromatic nucleophilic substitution reaction.[14] The reaction with bisphenols as difunctional nucleophiles yields heteroaromatic poly(aryl ether)s.

This approach has a major advantage compared to the classical route to heteroaromatic polymers such as poly(benzimidazole) and poly(phenylquinoxazoline). According to the traditional strategy, the formation of the heterocycles itself is the polymer-forming reaction. Usually this involves the reaction of two tetrafunctional monomers (in the case of poly(phenylquinoxaline))[15] or a difunctional and a tetrafunctional monomer (in the case of poly(benzimidazole))[2] in a way which excludes side reactions to 100%. Otherwise, the desired thermal stability of such polymers cannot be reached because of the presence of defect structures along the polymer backbone.

This difficult reaction procedure can be avoided if the heterocyclus is preformed in the monomer. Hergenrother[4,18] and Hedrick[5,6,16,17] have used this approach to synthesize a number of poly(heteroaryl ethers) containing benzoxazole, quinoxaline, and other heteroaromatic moieties. Hergenrother starts from heteroaromatic bisphenols, which are reacted with ketone- or sulfone-activated dihalogen monomers. Hedrick uses heteroaromatics with 4-fluorophenyl substituents which are reacted with common bisphenols. In this case the heterocyclus activates the fluorine replacement in the same way as the keto group does in the synthesis of poly(ether ketone)s.

Surprisingly, there is not much information in the literature concerning the substitution of halogen atoms directly on the heterocyclus by phenoxides in a polymerization reaction despite the unusually high reactivity of such halogen atoms. According to our knowledge, bis(5-chlorothienyl-2) ketone[34,35] and derivatives are the only example for a polycondensation in which a halogen on a five-membered heteroaromatic ring is replaced by a phenoxide.

Synthesis of the Monomer

Although there is a large number of synthetic methods to obtain heterocyclic compounds including oxazoles, there are only very few which allow the introduction of trifluoromethyl groups and fluorine atoms directly from com-

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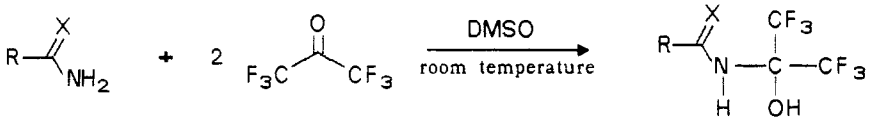
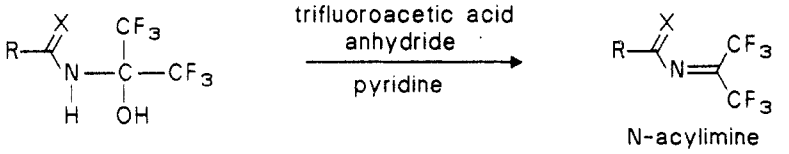
Scheme I

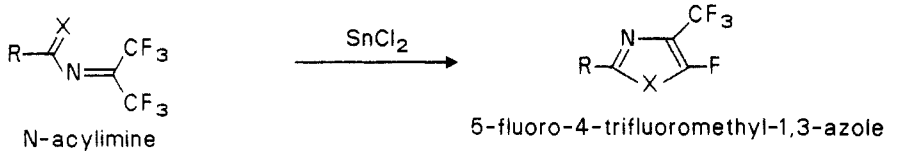
1) Addition of hexafluoroacetone to an aromatic amide or thioamide:



2) Elimination of water:

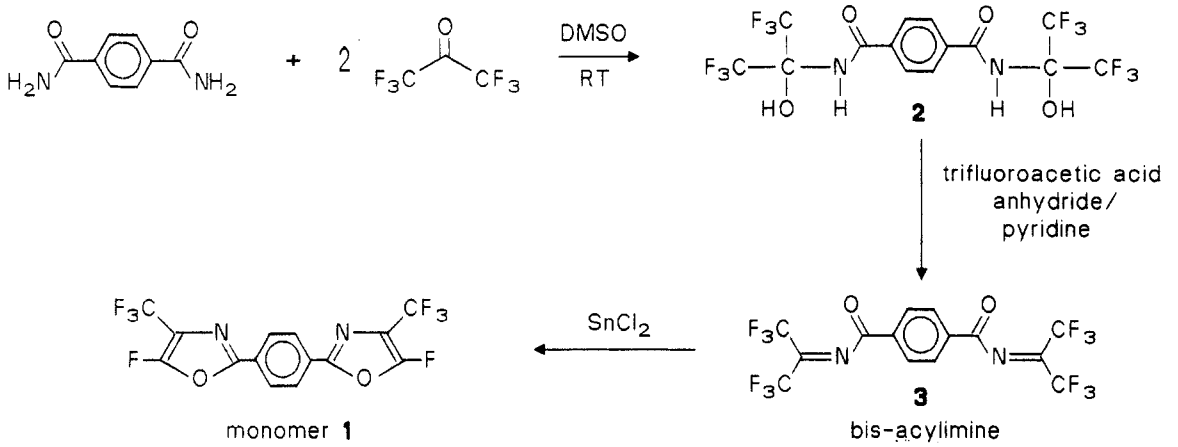


3) Reductive cyclization:



X = O, S ; R = aromatic unit

Scheme II



mercially available starting materials. One of the most versatile routes to CF_3-substituted 1,3-azoles basically consists of the three steps shown in Scheme I.

Starting from aromatic amides or thioamides and hexafluoroacetone, 5-fluoro-4-(trifluoromethyl)oxazoles or -thiazoles can be obtained. The exact reaction mechanism is well examined and has been published earlier.[19]

This reaction sequence allows the conversion of terephthalic acid diamide to monomer 1, as is shown in Scheme II.

Due to the poor solubility of the diamide in common organic solvents, the addition of hexafluoroacetone only takes place in dipolar aprotic solvents like DMSO. Even in this case, the reaction mixture is heterogeneous at the beginning. However, as the reaction proceeds it becomes homogeneous because of the solubility of the product. Quantitative conversion is reached after approximately 2 h at room temperature.

The direct elimination of water in the second step is not possible. Obviously the hydroxyl group is not a good leaving group in this case. Therefore, the simultaneous addition of trifluoroacetic anhydride and pyridine to a solution of the addition product is necessary to convert the two OH groups to trifluoroacetyl groups. Subsequent base-catalyzed elimination of these functions leads to the desired bis(*N*-acylimine) in a one-pot procedure in high yields (≈80%).

Treatment of the bis(*N*-acylimine) with anhydrous stannous chloride yields monomer 1 in a reductive cyclization step under degradation of two of the four trifluoromethyl groups. This is the only poor-yielding step of the monomer synthesis (40–45%).

Model Reaction

In general, inorganic bases such as potassium carbonate or sodium hydroxide are used to generate the phenolates which are necessary for the formation of poly(aryl ether)s via nucleophilic displacement. The water formed by the reaction of the inorganic base with the phenol must be

Scheme III

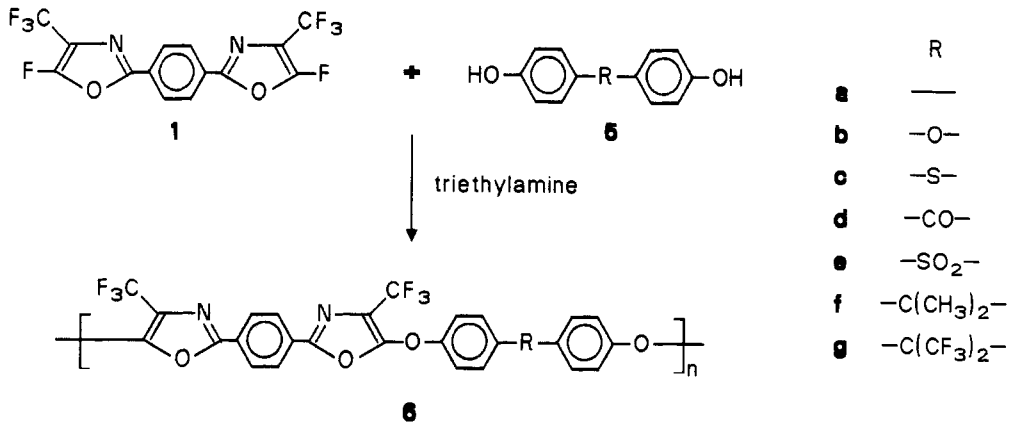


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Table I. Reaction Conditions for the Synthesis of the Polyethers 6

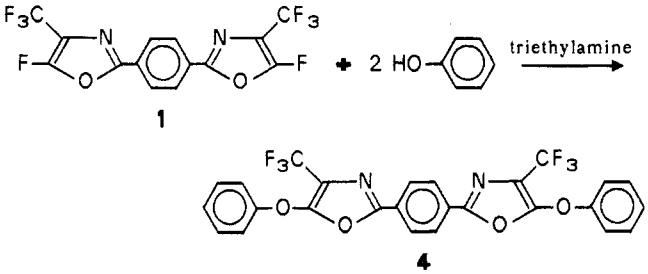
no.	6	R	solvent	time (h)	temp (°C)	$\bar{M}_n$[a]	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$[a]
1	a		DMSO	1	100	oligomers		
2	a		NMP	2	100	18 900	52 200	2.8
3	b	O	NMP	21	50	15 200	44 500	2.9
4	c	S	NMP	2	100	9 000	28 600	3.2
5	d	CO	NMP	7	50	*b*	*b*	*b*
6	e	SO_2	DMSO	2	100	12 700	27 800	2.2
7	e	SO_2	NMP	20	50	18 400	56 300	3.0
8	f	$C(CH_3)_2$	DMAc	20	50	9 500	19 000	2.0
9	f	$C(CH_3)_2$	DMSO	14	80	24 800	76 900	3.1
10	f	$C(CH_3)_2$	DMSO	2	100	26 000	106 000	4.0
11	g	$C(CF_3)_2$	NMP	20	50	18 800	53 300	2.8

[a] GPC in THF, polystyrene calibration. [b] Insoluble in THF.

removed as an azeotrope with an aromatic solvent to shift the equilibrium completely in favor of the phenolate. It is well-known that water (especially in basic conditions) can cause side reactions, e.g., the hydrolysis of the activated halogens. Thus, stoichiometry is lost, and the molar mass of the resulting polymer is limited.

To overcome these problems, we used triethylamine instead of an inorganic base. The major advantage of this method is that the formation of water during the formation of the phenolate is avoided completely.

To prove the ability of monomer 1 to react with nucleophiles to a sufficient conversion under these conditions, 1 was heated to 100 °C in DMSO in the presence of phenol and triethylamine. According to gas chromatography, the conversion was complete after $^1/_2$ h, and no side reactions could be detected. This clearly indicates that monomer 1 is suitable for the synthesis of poly(aryl ether)s.



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Polymerization

The synthesis of amorphous poly(aryl ether)s such as poly(ether sulfone)s usually requires a reaction temperature of at least 160–180 °C to ensure a sufficient reaction rate and degree of polymerization. In contrast to that, the model reaction of monomer 1 with phenol demonstrated the high reactivity of this monomer under mild conditions. Therefore, monomer 1 was reacted with a number of different bisphenols 5 (Scheme III).

As is summarized in Table I, the polymerization could be conducted to high molar mass products under very mild reaction conditions; even a temperature of only 50 °C proved to be sufficiently high. However, most polyethers 6 precipitate from DMSO at this low temperature, so that amidic solvents such as DMAc and NMP are favorable. The polymers remain in solution in these solvents even at room temperature.

Entries 1 and 2 of Table I clearly demonstrate the advantage of NMP as solvent in this polymerization. The product precipitates from DMSO at an early stage of the polymerization, resulting in the formation of oligomers rather than polymer. In contrast to that, in NMP high molar mass polymer is produced within 2 h at 100 °C at comparable monomer concentrations. However, good results can be obtained in DMSO when the reaction mixture remains homogeneous, which is the case in the synthesis of polymer **6e**, which is soluble in DMSO at room temperature.

Characterization of the Polymers 6. Cyclic Oligomers. Table I also shows that the ratio of $\bar{M}_w/\bar{M}_n$ is close to 3 in most cases and deviates from the theoretically expected value of $\bar{M}_w/\bar{M}_n = 2$ for ideal polycondensations. GPC diagrams of these polymers reveal the presence of oligomers besides the polymer, which broadens the molar mass distribution. We assumed these oligomers to be macrocycles, which was proved by separation of the oligomeric fraction in one case and obtaining NMR spectra and a FAB mass spectrum (FAB = fast atom bombardment) from this fraction. Neither ^{1}H NMR nor ^{19}F NMR spectroscopy indicated any end groups. The GPC trace and the FAB mass spectrum are shown in Figures 1 and 2, respectively.

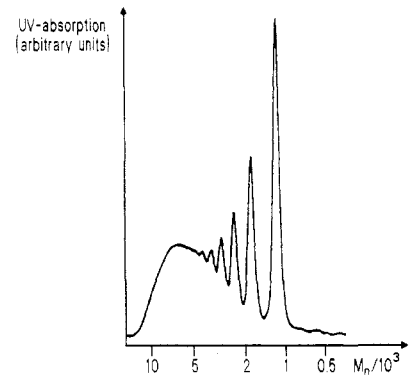


Figure 1. GPC diagram of the oligomer fraction of polymer **6f** (entry 9 in Table I).

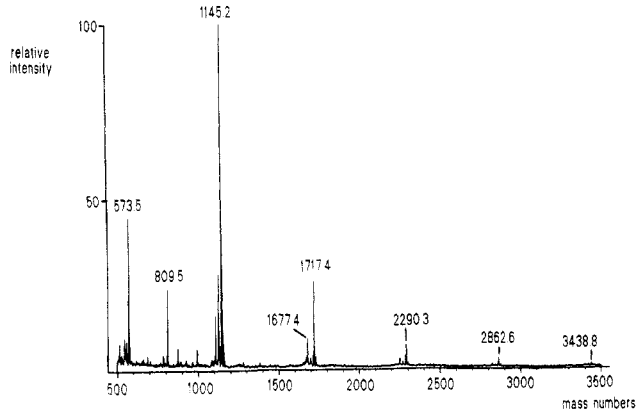


Figure 2. FAB mass spectrum of the cyclic oligomers of **6f** (entry 9 in Table I).

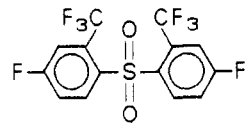
Table II. Calculated and Determined Molar Masses of the Oligomers of 6f

		calcd	
no. of repeat units	determined by MS	without end groups	with -F and -OH end groups
1	573.5	572.5	592.5
2	1145.2	1144.9	1164.9
3	1717.4	1717.4	1737.4
4	2290.3	2289.9	2309.9
5	2862.6	2862.3	2882.3
6	3438.8	3434.8	3454.8

The FAB-ionization method ensures that almost exclusively molecule ions are detected and fractionation is only of very little importance. Therefore, it not only allows the distinction between oligomers of different composition (AB, ABA, BAB, etc.) but also provides reliable information on the presence or absence of end groups. Evaluation of the detected molecule ions (Figure 2) revealed that only oligomers with stoichiometric composition (2:2, 3:3, 4:4, etc.) are present. No oligomers of nonstoichiometric composition (1:2, 2:3, 3:2, etc.) could be detected. Even more important, it showed also that the oligomers have no end groups (-OH and -F). Table II compares calculated and measured masses of the oligomers.

The absence of end groups could also be a consequence of free-radical dehalogenation, a side reaction of the $S_{RN}1$ mechanism, proposed by Percec.[20] However, together with the observations described above concerning the composition of the oligomers, the only possible conclusion is that these oligomers are macrocycles.

Stability of the CF_3 Groups. Trifluoromethyl groups are generally considered as quite inert. However, there are reactions known which attack CF_3 groups on aromatic rings.[21] This has been observed by other authors,[22] who used monomers **7** and **8** for the synthesis of poly(ether sulfone)s.



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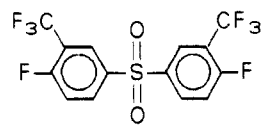

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A solution of monomer **7** or **8** in a dipolar aprotic solvent was added to a preformed solution of a bisphenolate made from the corresponding bisphenol and a stoichiometric amount of NaOH. The reaction temperature was 270 °C.

Polycondensation of **7** proceeded as expected, but the polymers synthesized from **8** showed a markedly decreased fluorine content, and it was not possible to obtain high molar mass polymers from **8**. In analogy to a reaction mechanism proposed by Kobayashi,[21] the process in Scheme IV may occur.

Decarbonylation (A) has been described for aromatic acyl halides, but it needs special catalysts. The most probable pathway is hydrolysis of the CF_3 group to an acid group and subsequent decarboxylation (B) due to (1) the high reaction temperature, (2) the ortho effect (relief of steric strain), and (3) assistance by the ortho ether group via H bonds.

In this reaction sequence protons are released because of the instability of the $-CF_2OH$ function,[23] which leads to deactivation of the phenolate, and the polycondensation stops.

In addition, the high concentration of phenolate during the reaction causes transetherification, which is another starting point for the degradation of the CF_3 groups (Scheme V).

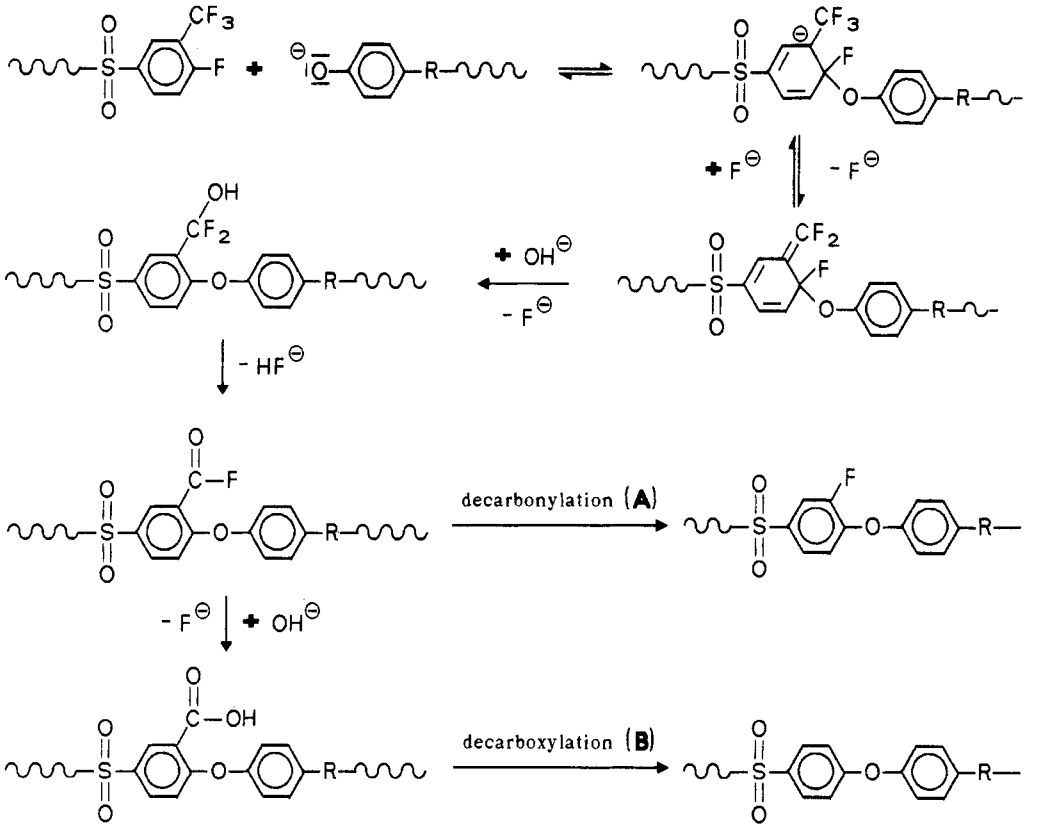
None of these problems can occur in our polycondensation procedure. Firstly, it is completely anhydrous from the beginning because of the use of triethylamine as base. Second, it is conducted at low (equilibrum!) concentrations of phenolate; thus, transetherification is unlikely.

The elemental analyses of the polymers **6** do not indicate any change of the elemental composition. However, the degradation of, e.g., 5% of all CF_3 groups would change the C, H, and N contents only within the range of accuracy of the analysis. Therefore, it is not possible to judge from the elemental analysis whether or not such degradation takes place.

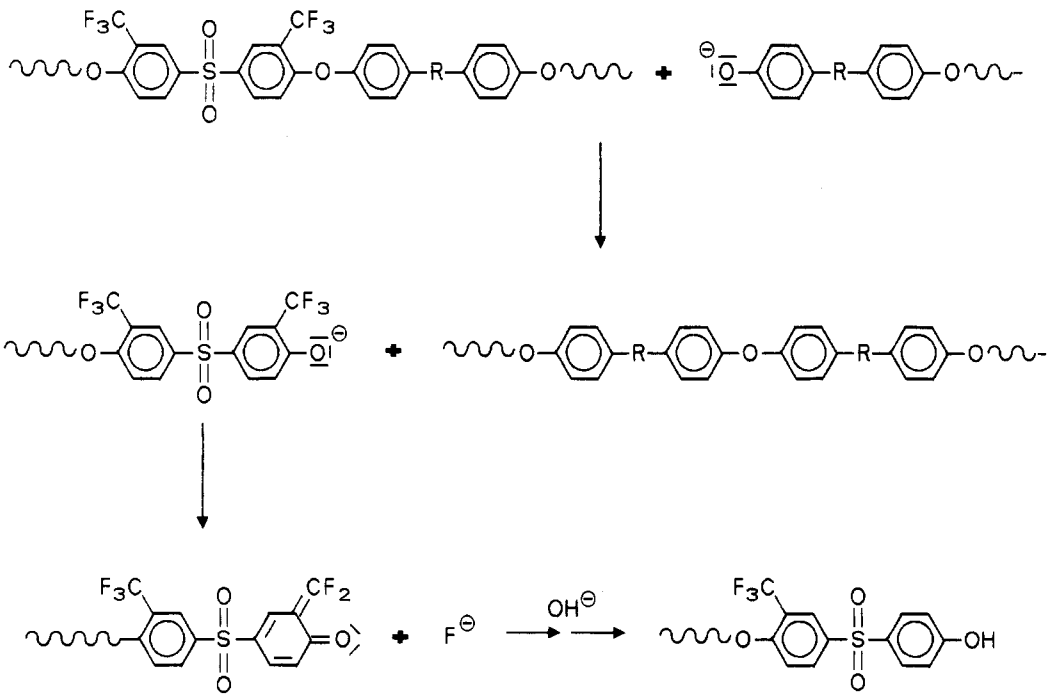
Nevertheless, polymer **6g** contains two different types of CF_3 groups: in addition to those from monomer **1** there are aliphatic trifluoromethyl groups present derived from hexafluorobisphenol A. The ^{19}F NMR of **6g** (Figure 3) shows two singlets of equal intensity for the different CF_3 groups. This indicates that the trifluoromethyl groups at the oxazole rings are not affected (within the accuracy of quantitative NMR spectroscopy).

DSC Measurements of the Polymers 6. The polyethers **6** are amorphous with glass transition temperatures (T_gs) in the range of 136–191 °C, depending on the structure of the bisphenol employed (Table III). The poly(ether ketone) **6d** is an exception, as it is semicrystalline with a melting point of 278 °C and a glass transition temperature of 167 °C. The partial crystallinity of this polymer is not surprising, as it is well-known that carbonyl groups often introduce crystallinity into poly(aryl ether)s. Table II compares the T_g's of the polymers **6** with the T_g's of polymers **9** derived from dichlorodiphenyl sulfone. In

Scheme IV



Scheme V



general, the glass transition temperatures of the polymers **6** are about 45 °C below those of the poly(ether sulfone)s **9**.

The dependence of the glass transition temperatures on the structure of the bisphenol is similar to the observations of other authors. An ether linkage (**6b**) instead of an isopropylidene group (**6f**) lowers T_g by ≈10 °C, while a hexafluoroisopropylidene group (**6g**) increases it by ≈10 °C. The carbonyl group (**6d**) results in a still higher T_g (≈16 °C increase), and the sulfone group (**6e**) causes the highest T_g of this series: ≈40 °C above the glass transition temperature of the polymer with the isopropylidene group (**6f**).

Solubility Tests. Because of their amorphous character, the polyethers **6** are soluble at room temperature in a number of solvents. The only exception is again the semicrystalline poly(ether ketone) **6d**, which is only soluble at temperatures above 50 °C in amidic solvents such as NMP, DMAc, and DMF.

Table IV shows the results of these qualitative solubility tests.

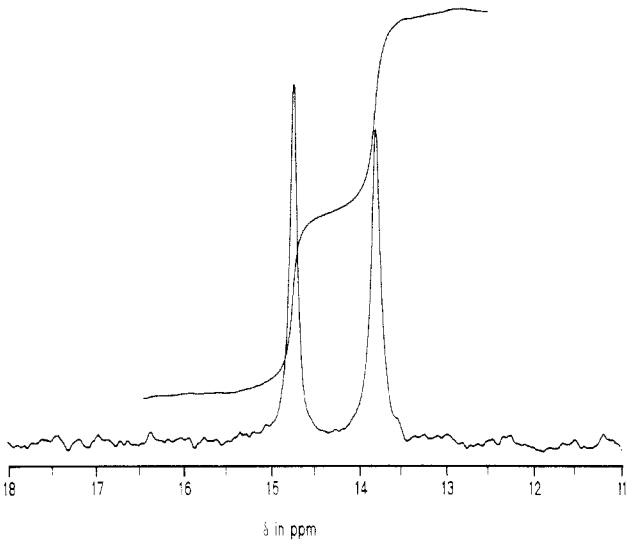
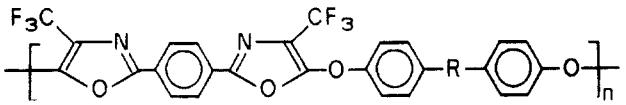


Figure 3. ^{19}F NMR of 6g.



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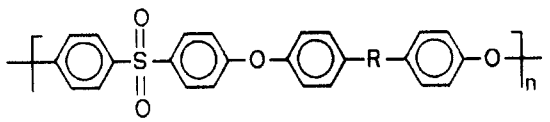
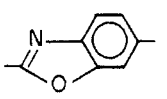


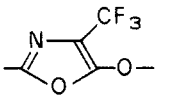
9

Among the amorphous polyethers the flexibility rather than the polarity of the linkage R seems to control the solubility of the polymer. **6a** has the least flexible backbone, and it is soluble only in DMAc, NMP, and THF at room temperature as well as in DMF at higher temperature. **6b**, with R being an ether group, is soluble not only in DMAc, NMP, and THF but also in DMF and toluene at room temperature. In addition, it is dissolved by DMSO and $CHCl_3$ at elevated temperatures. **6c** with the sulfide group in its backbone shows a very similar solubility. The sulfone group of **6e** instead of the sulfide results in decreased flexibility and decreased solubility. Polyether **6f**, derived from bisphenol A, is soluble in all solvents tested (see Table IV), including acetone and $CHCl_3$. Replacement of the isopropylidene group of **6f** by a hexafluoroisopropylidene group (**6g**) results in insolubility in acetone and $CHCl_3$. The reason seems to be the increased rigidity of the hexafluoroisopropylidene group containing backbone, which is caused by the increased van der Waals radius of the trifluoromethyl group, compared to the methyl group. Therefore, the rotation of the two phenyl rings neighboring the hexafluoroisopropylidene group is more hindered than in the case of the isopropylidene group.

Thermal Stability. Dynamic thermogravimetry reveals that the thermal stability of the heteroaromatic polyethers **6** is lower than expected. Poly(benzoxazole)s[3] and poly(aryl ether benzoxazole)s[5,6] exhibit decomposition temperatures of up to 500 °C in air (beginning of weight loss at a heating rate of 5 K/min). In contrast to that, the polyethers **6** decompose at 300–320 °C in air as well as in nitrogen atmosphere, independent of the nature of the bisphenol moiety. This suggests that the unstable part of these polymers is the trifluoromethylated oxazole ring:



benzoxazole unit
thermally stable



oxazole unit
thermally less stable

Since the thermogravimetric analysis was carried out with dry samples (powder or film), hydrolytic degradation of the heterocyclus is unlikely (oxazoles are somewhat more stable against acidic or basic hydrolysis than furanes and somewhat less stable than pyridines).[25] This is confirmed by the observation that the onset of degradation is not affected by the presence or absence of residual acidic nonsolvent (MeOH/HCl) in the sample. Therefore, the polymer shows equal thermal stability in neutral as well as in acidic environment.

The source of the instability of the trifluoromethylated oxazole ring in the polymers **6** can be found by studying the synthetic routes to oxazoles. Besides the classical condensation reactions, oxazoles can be obtained by a cycloaddition reaction according to Scheme VI.[30,31]

The reaction between the ketocarbene and the nitrile directly yields an oxazole, without the necessity of any subsequent modification or aromatization. Cycloaddition reactions are known to be reversible at high temperatures, and therefore oxazoles may be subject to this kind of decomposition reaction, provided they fulfill certain structural criteria.

The aromatic electron sextet is destroyed by the cycloreversion reaction in oxazole as well as in benzoxazole derivatives. However, in benzoxazoles, the aromaticity of the phenyl ring is destroyed as well (B), as can be seen in Scheme VII. On the other hand, one of the three most important mesomeric structures of the ketocarbene analogon A is strongly stabilized by an inductive effect. It contains a negative charge on the carbon atom next to the trifluoromethyl group. Both facts allow us to conclude that the activation energy for the cycloreversion of the trifluoromethylated oxazole is lower than that for the cycloreversion of the benzoxazole, and hence the decomposition of the CF_3-substituted oxazoles starts at lower temperatures.

It is well-known that, despite the aromatic behavior oxygen-containing five-membered heteroaromatics show in substitution reactions,[26] they can still react as dienes. Furanes and oxazoles, for instance, can undergo a Diels–Alder reaction with powerful dienophiles like arynes,[27] although the aromatic electron sextet of the heterocyclus must be broken in this reaction.

In contrast to that, thiophenes and thiazoles are not able to react in this way.[28,29] This is attributed to the more pronounced aromaticity of the sulfur heteroaromatics compared to their oxygen analogues. Assuming that the cycloreversion reaction described above is indeed the reason for the low thermal stability of the polyethers **6** and assuming that thiazoles are more aromatic than

Table III. Glass Transition Temperatures

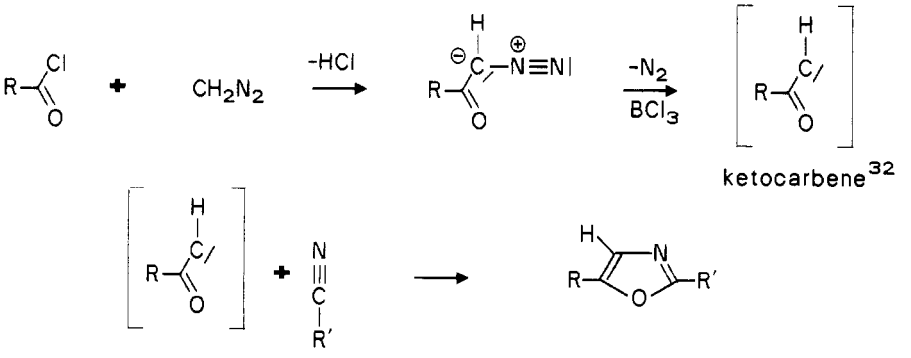
		T_g (°C)	
	R	6	9
a	—	185	230[24]
b	O	142	180[25]
c	S	136	175[25]
d	CO	167	205[25]
e	SO_2	191	245[25]
f	$C(CH_3)_2$	151	195[25]
g	$C(CF_3)_2$	160	205[25]

Table IV. Solubility of the Polyethers 6[a]

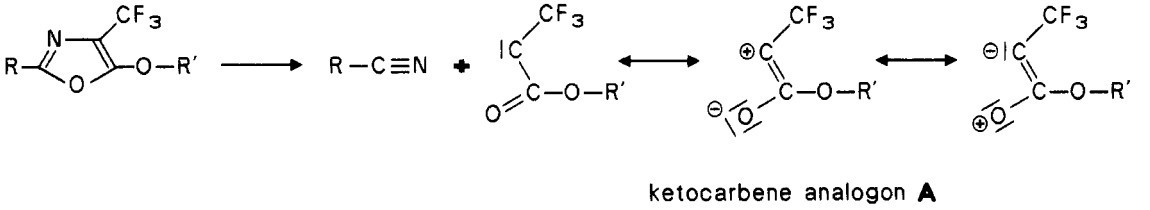
6	R	NMP	DMAc	DMF	DMSO	THF	toluene	$CHCl_3$	acetone
a		+	+	o	–	+	–	–	–
b	O	+	+	+	o	+	+	o	–
c	S	+	+	+	o	+	o	o	–
d	CO	o	o	o	–	–	–	–	–
e	SO_2	+	+	+	+	+	–	–	–
f	$C(CH_3)_2$	+	+	+	o	+	+	+	+
g	$C(CF_3)_2$	+	+	+	o	+	+	–	–

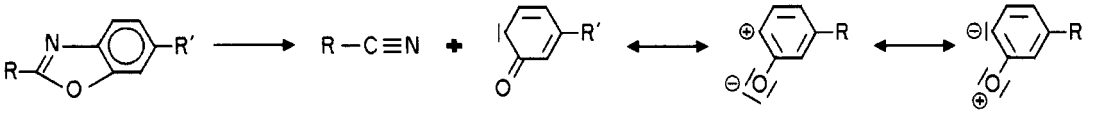
[a] +, soluble at room temperature to give a solution of at least 20% by weight; o, soluble above 50 °C to give a solution of at least 20% by weight; –, insoluble.

Scheme VI

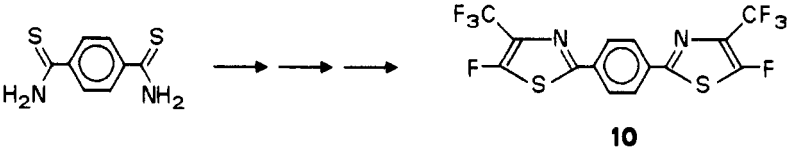


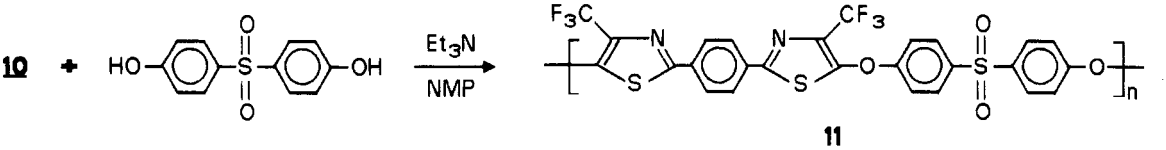
Scheme VII





Scheme VIII





oxazoles, polyethers with a structure similar to 6 but having thiazole rings instead of the oxazole rings must exhibit a considerably higher decomposition temperature. To test this assumption, we synthesized the bisthiazole monomer **10** and converted it to the poly(ether sulfone) **11** by polycondensation with 4,4'-dihydroxydiphenyl sulfone (Scheme VIII).

The glass transition temperature of polyether **11** is T_g = 203 °C, which is 12 °C above the T_g of the analogous polyether **6e**. This increase of the glass transition temperature is probably due to the different geometry of the oxazole and the thiazole ring:

Dynamic thermogravimetry indeed shows a considerably higher thermal stability of **11** compared to **6e**: the onset

of weight loss of 11 is 410 °C (air, 10 K/min) and 440 °C (nitrogen, 10 K/min), while it is only 319 °C (air, 10 K/min) for **6e**. The synthesis of trifluoromethylated thiazole polymers will be described in detail in a future paper.

Conclusion

The reaction of the diamides or dithioamides of dicarboxylic acids with hexafluoroacetone yields bis(1,3-azoles) with reactive fluorine atoms in a sequence of three steps. Such compounds are suitable for polyether synthesis by nucleophilic displacement of halogen atoms under very mild conditions. The incorporation of trifluoromethyl groups in the ortho position to aryl ether groups is possible, provided the polymerization conditions are mild enough. In the case of the oxazoles, the trifluoromethyl groups reduce the decomposition temperature of the polymer. However, trifluoromethyl groups do not have a similar effect on the thermal stability of analogous thiazole polymers. We are continuing our research to investigate the effect of the position and number of trifluoromethyl groups in heterocyclic polymers on properties such as glass transition temperature, crystallinity, melt temperature, solubility, and thermal stability.

Experimental Part

Instruments. For ^{1}H NMR and ^{13}C NMR spectra a Bruker AC 250 (250 MHz for protons, 62.5 MHz for carbon-13; internal standard, $CDCl_3$) was used, and for ^{19}F NMR, a JEOL FX 90Q (84.26 MHz for fluorine; external standard, trifluoroacetic acid). IR spectra were recorded on a Digilab FTS-40 FTIR spectrometer. GPC diagrams were obtained with a Waters ALC 200, RI and UV (254 nm) detection, four columns of 500, 1000, 10^4, and 10^5 Å (5 μm PL-gel), THF as eluent, and polystyrene calibration. DSC measurements were conducted with a Perkin-Elmer DSC 7 at 20 K/min. Thermogravimetry was measured with a Netzsch STA 409 in air or nitrogen at 10 K/min. Elemental analyses were performed by Ilse Beetz, Mikroanalytisches Laboratorium, W-8640 Kronach, Germany.

Starting Materials. 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A, Bayer AG), was recrystallized from toluene. All other bisphenols (Hoechst AG) were used without further purification. Hexafluoroacetone (Hoechst AG) was received as sesquihydrate and was dehydrated as described below. Phenol (Riedel-de-Haen), pyridine (p.a., Merck), and trifluoroacetic acid anhydride (Fluka) are commercial products and were used as received. Diethyl ether and toluene were refluxed over a K/Na alloy to remove water and freshly distilled before use. NMP (Fluka) and DMAc (Merck) were distilled twice from P_2O_5 under reduced pressure. DMSO (Merck) was stirred over a molecular sieve (4 Å), filtered, and distilled under reduced pressure. Triethylamine was stirred over KOH pellets, filtered, and distilled. The boiling point of the fraction used for the polymerizations was 87–88 °C.

Monomer Synthesis. *N,N'*-Bis[1-hydroxy-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]terephthalic Acid Diamide (2). Terephthalic acid diamide (16.4 g, 0.1 mol) and 250 mL of DMSO are placed in a 500-mL two-neck round-bottomed flask equipped with a CO_2 reflux condenser (−78 °C) and a gas inlet tube. This slurry is stirred vigorously. Concentrated sulfuric acid is placed in another 500-mL two-neck round-bottomed flask equipped with a dropping funnel and a gas outlet, which is connected to the inlet of the flask with the reaction slurry. The sulfuric acid is heated to 80 °C, and hexafluoroacetone sesquihydrate (100 mL) is added *slowly* via the dropping funnel to the sulfuric acid. This removes the water from the hydrate, and gaseous hexafluoroacetone (bp −28 °C) evolves and is transferred to the reaction slurry. When the absorption of the hexafluoroacetone starts, the addition of the hexafluoroacetone sesquihydrate to the sulfuric acid is adjusted to result in complete absorption of the evolved hexafluoroacetone. The end of the absorption is indicated by refluxing hexafluoroacetone. By this time, the reaction mixture has become homogeneous due to the solubility of the product in DMSO.

The whole apparatus is flushed with dry nitrogen to remove unreacted hexafluoroacetone before opening. The solution is poured into 300 mL of distilled water. The colorless product precipitates quantitatively. It is collected on a filter, carefully washed with water to remove DMSO, and dried under reduced pressure over P_2O_5.

It should be noted that hexafluoroacetone is toxic, and its sesquihydrate is very corrosive. Care should be taken to absorb the unreacted hexafluoroacetone in water by flushing the apparatus with nitrogen before opening. It is also very important to exclude moisture during the reaction, because in the presence of moisture hexafluoroacetone monohydrate (mp 43–45 °C) forms and blocks the gas inlet, which results in overpressure within the apparatus. Yield: quantitative. Decomposition temperature: 265 °C. IR (KBr): 3258 (ν(N–H)), 3100–3040 (ν(C–H$_{arom}$)), 1643 (ν(C=O)), 1553, 1425, 1320–1160 (several sharp peaks of high intensity: CF_3), 1145, 1042, 976 cm^{-1}. ^{19}F NMR (DMSO-d_6): δ −2.6 (s). ^{1}H NMR (DMSO-d_6): δ 7.88 (s, 4 H, phenyl ring), 9.34 (s, 2 H, N*H*), 9.71 (s, 2 H, O*H*) ^{13}C NMR (DMSO-d_6): δ 83.6 (sept, J = 33 Hz, $C(CF_3)_2$), 121.7 (q, J = 289 Hz, CF_3), 128.5, 136.9, 168.7 (C=O).

***N,N'*-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-terephthalic Acid Diamide (3; Bisacylimine).** The addition product **2** (15 g, 30 mmol) is dissolved in dry diethyl ether (250 mL) and cooled to 0–5 °C in an ice bath. The trifluoroacetic acid anhydride (8.4 mL, 60 mmol) and pyridine (9.8 mL, 120 mmol) are added simultaneously under stirring within 1 h. The precipitation of pyridinium trifluoroacetate starts immediately. After an additional hour of stirring the precipitated salt is filtered off and the ether is removed under reduced pressure. The resulting residue is extracted three times with 50 mL of hexane. The hexane extracts are combined and cooled to −30 °C to crystallize the desired product in colorless needles. Yield: 78%. Mp: 77–78 °C. IR (KBr): 3100–3040 (ν)(C–H$_{arom}$)), 1738 (ν-(C=N)), 1701 (ν(C=O)), 1543, 1333–1160 (several sharp peaks of high intensity: CF_3), 1043, 1012, 981, 700 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 10.5 (s). ^{1}H NMR ($CDCl_3$): δ 7.93 (s). ^{13}C NMR ($CDCl_3$): δ 116.1 (q, J = 282 Hz; CF_3), 129.6, 134.4, 143.7 (sept, J = 38 Hz; $C(CF_3)_2$), 171.9 (C=O).

1,4-Bis[5-fluoro-4-(trifluoromethyl)-2-oxazolyl]benzene (1). The bisacylimine **3** (6.9 g, 15 mmol) is dissolved in dry toluene (70 mL). Anhydrous stannous chloride (5.7 g, 30 mmol) is added, and the resulting heterogeneous mixture is heated to reflux for 48 h. Then it is cooled to room temperature, the insoluble parts are removed by filtration, and the solvent is removed under reduced pressure. The crude product is purified by filtration over a silica column (Merck Kieselgel 60, length 20 cm, eluent $CHCl_3$) and recrystallized from $CHCl_3$. Yield: 40%. Mp: 148–149 °C. IR (KBr): 3130–3075 (ν(C–H$_{arom}$)), 1689, 1583, 1437, 1333, 1171–1140 (several sharp peaks of high intensity: CF_3), 1074, 1055 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ −39.95 (q, J = 9 Hz, 2 F), 15.85 (d, J = 9 Hz, 6 F). ^{1}H NMR ($CDCl_3$): δ 8.05 (s). ^{13}C NMR ($CDCl_3$): δ 106.2 (dq, $^2J_{C-F}$ = 42 Hz, $^2J_{C-F}$ = 7 Hz, oxazole C4), 119.6 (dq, $^3J_{C-F}$ = 5 Hz, $^1J_{C-F}$ = 266 Hz; CF_3), 126.8, 127.9, 151.4 (d, $^3J_{C-F}$ = 6 Hz; oxazole C2), 155.0 (dq, $^1J_{C-F}$ = 294 Hz, $^3J_{C-F}$ = 3 Hz; oxazole C5). Elem anal. Calcd for $C_{14}H_4F_8N_2O_2$ (384.19): C, 43.76; H, 1.05; N, 7.29. Found: C, 43.80; H, 1.12; N, 7.38.

Model Reaction. A Pyrex glass tube with a Teflon screw cap and nitrogen inlet is charged with monomer **1** (748.8 mg, 1.95 mmol), phenol (366.8 mg, 3.9 mmol), dry NMP (5 mL), and dry triethylamine (0.6 mL, 4.29 mmol) under an argon atmosphere. The tube is closed tightly and heated to 100 °C for 2 h. A deep red solution forms. After the reaction has ended, the solution is cooled to room temperature and poured into 100 mL of distilled water to remove the water-soluble parts, especially the NMP. The water fractions is extracted with diethyl ether. The organic phases are combined and dried over Na_2SO_4, and the solvent is removed under reduced pressure. The crude product is purified by filtration over a short silica column (Merck Kieselgel 60, length 20 cm, eluent $CHCl_3$) and recrystallized from $CHCl_3$. Yield: quantitative. Mp: 161–162 °C. IR (KBr): 3100–3040 (ν(C–H$_{arom}$)), 1665, 1489, 1423, 1413, 1160–1128 (several sharp peaks of high intensity: CF_3), 1076, 1041, 754 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 15.2 (s). ^{1}H NMR ($CDCl_3$): δ 7.15 (m, 4 H), 7.25 (m, 2 H), 7.4 (m, 4 H), 8.05 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 113.4 (q, $^2J_{C-F}$ =

41 Hz), 116.9, 120.4 (q, $^1J_{C-F}$ = 266 Hz), 125.4, 126.6, 128.1, 130.2, 152.9 (q, $^3J_{C-F}$ = 3 Hz), 153.7, 155.7. Elem anal. Calcd for $C_{26}H_{14}F_6N_2O_4$ (532.37): C, 58.65; H, 2.65; N, 5.26. Found: C, 58.72; H, 2.65; N, 5.35.

Polymerizations (General Procedure). Stoichiometric quantities of monomer 1 and a bisphenol (usually 1.6 mmol of each monomer) are placed in a Pyrex glass tube with a Teflon screw cap and nitrogen inlet. Dry dipolar aprotic solvent (see Table I for the solvent; the amount of solvent is adjusted to give a solution of a solid content of approximately 20% by weight) and the corresponding amount of triethylamine (usually 3.5 mmol, 10% excess over the calculated amount) are added under an argon atmosphere. The reaction times and temperatures are listed in Table I. After the reaction has ended, the solution is diluted with 10 mL of dry THF (dry NMP in the case of polymer **6d**). The polymer is recovered by precipitation into 100 mL of methanol, collected on a filter, washed with water, and dried under reduced pressure at 80 °C to constant weight.

Characterization of the Polymers 6. Polymer 6a. IR (KBr): 3100–3040 (ν(C-H_{arom})), 1660, 1599, 1493, 1421, 1245–1130 (several sharp peaks of high intensity: CF_3), 1060, 1041 cm^{-1}. ^{19}F NMR (THF-d_6): δ 16.4 (s). ^{1}H NMR ($CDCl_3$): δ 7.4–8.0 (m, 8 H), 8.3 (s, 4 H). Elem anal. Calcd for $(C_{26}H_{12}F_6N_2O_4)_n$ (530.36)$_n$: C, 58.88; H, 2.28; N, 5.28. Found (Table I, entry 2): C, 59.00, H, 2.31, N, 5.12.

Polymer 6b. IR (KBr): 3100–3040 (ν(C-H_{arom})), 1662, 1492, 1240–1130 (several sharp peaks of high intensity: CF_3), 1076, 1058, 1040, 850 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 15.3 (s). ^{1}H NMR ($CDCl_3$): δ 7.2–7.45 (m, 8 H), 8.2 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 113.4 (q, $^2J_{C-F}$ = 41 Hz), 119.4, 121.1, 121.7 (q, $^1J_{C-F}$ = 266 Hz), 127.4, 129.2, 152.6, 154.2 (q, $^3J_{C-F}$ = 3 Hz), 154.7, 155.0. Elem anal. Calcd for $(C_{26}H_{12}F_6N_2O_5)_n$ (546.36)$_n$: C, 57.17; H, 2.21; N, 5.12. Found (Table I, entry 3): C, 57.33; H, 2.14; N, 5.08.

Polymer 6c. IR (KBr): 3100–3040 (ν(C-H_{arom})), 1662, 1583, 1485, 1421, 1245–1130 (several sharp peaks of high intensity: CF_3), 1076, 1058, 1041, 1012, 850 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 15.2 (s). ^{1}H NMR ($CDCl_3$): δ 7.3–7.6 (m, 8 H), 8.2 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 114.0 (q, $^2J_{C-F}$ = 41 Hz), 118.7, 121.6, (q, $^1J_{C-F}$ = 266 Hz), 127.9, 129.2, 133.4, 133.9, 153.6 (q, $^3J_{C-F}$ = 3 Hz), 155.0, 156.4. Elem anal. Calcd for $(C_{26}H_{12}F_6N_2O_4S)_n$ (562.42)$_n$: C, 55.52; H, 2.15; N, 4.98; S, 5.70. Found (Table I, entry 4): C, 55.49; H, 2.27; N, 5.03; S, 5.62.

Polymer 6d. IR (KBr): 3100–3040 (ν(C-H_{arom})), 1662, 1597, 1500, 1423, 1411, 1245–1130 (several sharp peaks of high intensity: CF_3), 1059, 1041, 928 cm^{-1}. Elem anal. Calcd for $(C_{27}H_{12}F_6N_2O_5)_n$ (558.37)$_n$: C, 58.07; H, 2.16; N, 5.01. Found (Table I, entry 5): C, 58.27; H, 2.17; N, 5.19.

Polymer 6e. IR (KBr): 3100–3040 (ν(C-H_{arom})), 1662, 1587, 1489, 1421, 1327, 1245–1130 (several sharp peaks of high intensity: CF_3), 1076, 1058, 1043, 1014, 832, 732 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 15.0 (s). ^{1}H NMR ($CDCl_3$): δ 7.5–8.2 (m, 8 H), 8.25 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 114.9 (q, $^2J_{C-F}$ = 41 Hz), 118.2, 121.4, (q, $^1J_{C-F}$ = 266 Hz), 127.6, 129.2, 131.4, 140.0, 152.5 (q, $^3J_{C-F}$ = 3 Hz), 155.5, 160.1. Elem anal. Calcd for $(C_{26}H_{12}F_6N_2O_6S)_n$ (594.41)$_n$: C, 52.23; H, 2.03; N, 4.71; S, 5.39. Found (Table I, entry 7): C, 52.60; H, 2.13; N, 4.64; S, 5.33.

Polymer 6f. IR (KBr): 3085–3020 (ν(C-H_{arom})), 1662, 1504, 1424, 1250–1130 (several sharp peaks of high intensity: CF_3), 1040 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 15.0 (s). ^{1}H NMR ($CDCl_3$): δ 1.7 (s, 6 H), 7.1–7.4 (m, 8 H), 8.1 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 30.6, 42.9, 113.5 (q, $^2J_{C-F}$ = 44 Hz), 116.8, 121.5, (q, $^1J_{C-F}$ = 269 Hz), 127.1, 128.9, 129.1, 148.2, 153.8 (q, $^3J_{C-F}$ = 3 Hz), 154.4, 154.7. Elem anal. Calcd for $(C_{29}H_{18}F_6N_2O_4)_n$ (572.43)$_n$: C, 60.85; H, 3.17; N, 4.90. Found (Table I, entry 8): C, 61.13; H, 3.20; N, 5.23. Found (Table I, entry 9): C, 61.23; H, 3.25; N, 5.28. Found (Table I, entry 10): C, 60.82; H, 3.21; N, 5.25.

Polymer 6g. IR (KBr): 3100–3040 (ν(C-H_{arom})), 1664, 1604, 1510, 1415, 1250–1130 (several sharp peaks of high intensity: CF_3), 1043 cm^{-1}. ^{19}F NMR ($CDCl_3$): δ 14.7 (s, 6 F), 13.8 (s, 6 F). ^{1}H NMR ($CDCl_3$): δ 7.25–7.65 (m, 8 H), 8.15 (s, 4 H). ^{13}C NMR ($CDCl_3$): δ 64.9 (sept, $^2J_{C-F}$ = 25 Hz), 114.7 (q, $^2J_{C-F}$ = 44 Hz), 117.5, 121.6 (q, $^1J_{C-F}$ = 266 Hz), 125.2 (q, $^1J_{C-F}$ = 285 Hz), 127.6, 129.3, 130.8, 133.2, 153.1 (q, $^3J_{C-F}$ = 3 Hz), 155.4, 157.4. Elem anal. Calcd for $(C_{29}H_{12}F_{12}N_2O_4)_n$ (680.39)$_n$: C, 51.19; H, 1.78; N, 4.11. Found (Table I, entry 11): C, 51.35; H, 2.27; N, 4.18.

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