Poly(aryl ether thiazole)s with Pendent Trifluoromethyl Groups

Gerhard Maier* and Reinhold Hecht

*Lehrstuhl für Makromolekulare Stoffe, Technische Universität München,
Lichtenbergstrasse 4, D-85747 Garching, Germany*

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ABSTRACT: A monomer with two 4-(trifluoromethyl)-5-fluoro-substituted thiazole rings was prepared from terephthalic acid dithioamide and hexafluoroacetone. This monomer was converted to poly(aryl ether thiazole)s by nucleophilic displacement of the fluorine atoms on the thiazole rings with bis(phenol)s or silylated bis(phenol)s. The products obtained by the silyl method exhibit molar masses up to $\bar{M}_w =$ 78 500 g·mol⁻¹. Compared to analogous polymers with oxazole rings in place of the thiazole rings, the thiazole polymers had higher glass transition temperatures and decreased solubilities. This is attributed to the different geometries of the thiazole and oxazole rings. In addition, the decomposition temperatures of the thiazole polymers were at least 100 deg higher than those of the oxazole polymers. This effect is caused by the more pronounced aromatic character of the sulfur heteroaromatic rings as compared to the oxygen-based systems.

Introduction

Heteroaromatic polymers are well-known for their excellent thermooxidative stability in combination with good mechanical properties.[1] A large number of different heteroaromatic structures has already been incorporated into polymers. Rossbach and Oberlein[2] mention polymers based on over 30 different heteroaromatic systems in their review. Among the more popular examples for these structures are benzoxazoles,[3–5] benzothiazoles,[6,7] benzimidazoles,[8,9] oxadiazoles,[10–12] pyrazoles,[13] quinoxalines,[14,15] six-membered nitrogen heteroaromatics,[16–18] and some ladder-type structures such as benzimidazobenzoisoquinoline (BBL) and derivatives.[19,20] Depending on the type of heterocycle, different strategies are used for polymer formation. The classical synthesis of polymers such as poly(benzo-1,3-azole)s, poly(quinoline)s, and poly(quinoxaline)s utilizes the formation of the heteroaromatic system as the polymer-forming reaction. This requires the reaction of difunctional and tetrafunctional monomers, or even the reaction of two tetrafunctional monomers. Despite the problems connected with the required strict control of the reactivities of the various functional groups in these cases, successful processes were developed.[3,6,8,15] However, to obtain high molar mass material, it is necessary to find a very high yielding synthetic method for the preparation of the heterocycle. Otherwise, conversion and hence degree of polymerization will be low. Not all heteroaromatic systems can be prepared by reactions which give sufficiently high yields. An elegant solution for these problems is the use of monomers with preformed heteroaromatic rings.[4,5,7,9–11,13,14,16–18,20,22,23,27,28] This methodology does not require extremely high yields for the preparation of the heterocycle and therefore broadens the types of structures which can be incorporated into polymers.

Rodlike poly(benzobisazole)s[3,6,8] can be spun from lyotropic solutions in poly(phosphoric acid), but if more conventional solvents or melt-processing techniques are to be used, flexibilizing groups within the backbone are important. The most widely used linkage for this purpose is the ether group. It is easy to introduce and has little or no negative effect on the thermooxidative stability. The two most widely used types of heteroaro-

matic monomers contain either two hydroxyphenyl or fluorophenyl groups, which are used for poly(aryl ether formation) with activated aromatic bis(halide)s or bis(phenol)s, respectively.

The polymerization proceeds by nucleophilic replacement of the halogen atoms by phenolate groups. Thus, the halogens must be activated, which is achieved by the presence of an electron-withdrawing group in the *para* position. The most common electron acceptor groups are the carbonyl and sulfone groups. In the heteroaromatic bis(halide) monomers, the heterocycle itself must act as the activating group. If it is electron deficient enough, it will decrease the electron density in the *para* position of adjacent phenyl rings. It will also stabilize the negative charge of the transient Meisenheimer complex during the substitution reaction. 1,3,4-Oxadiazole,[10,14] 1,3,4-thiadiazole,[21] quinoxaline,[14,20,23] and benzoxazole[4] have been used successfully, among others.

Halogen atoms bound directly to the heteroaromatic ring are also strongly activated toward nucleophilic attack. This approach has been used for a number of six-membered heteroaromatic systems such as 2,6-difluoropyridine,[16,17] 2,6-difluoropyrazine,[17] and several halogenated triazine[18,27,28] derivatives. It has also been used with five-membered heteroaromatic systems based on benzothiazole[22–24] **1**, thiophene[25,26] **2**, and oxazole[27–29] **3**, which are shown in Chart 1.

Chart 1. Bis(halide) Monomers with Halogen Atoms Directly Bound to the Heteroaromatic Ring
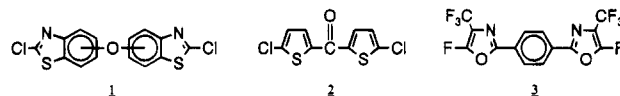

Such systems show much higher reactivity, because the halogen atoms are not separated by phenyl rings from the electron acceptor groups, and therefore activation is maximized. This is evidenced by the observation that **2** yields high molar mass polymers with Bisphenol A, while the analogous phenyl-based compound, 4,4′-dichlorobenzophenone, does not. As we have shown previously, the bis(oxazole) monomer **3** is extremely reactive. It can be converted to high molar mass polymer with various bis(phenol)s under very mild conditions, which are completely unsuitable for 4-fluorophenyl-based monomers. Instead of reaction temperatures of 160–220 °C, which are required for the
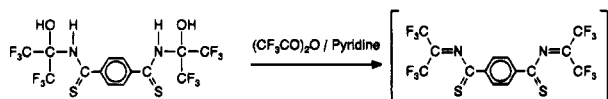
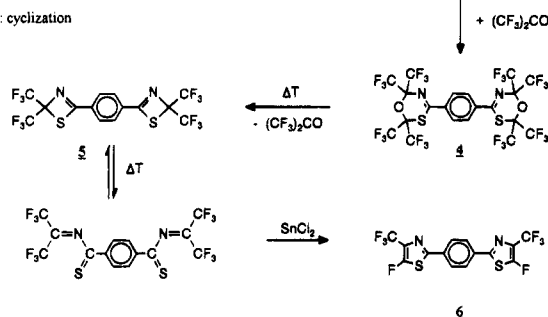**Scheme 1. Synthesis of the Bis(thiazole) Monomer 6**

first step: addition of hexafluoroacetone to the bisthioamide
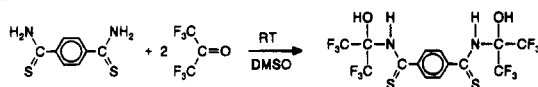
second step: dehydration

third step: cyclization

polymerization of conventional activated bis(fluoride)s with bis(phenol)s, 3 reacts already at 50 °C sufficiently fast and complete.

However, the polymers derived from bis(oxazole) monomer 3 possess only very limited temperature stability. This was attributed to the substitution pattern of the oxazole ring.[27] Therefore, the present study describes the synthesis and characterization of similar polymers, in which the oxazole rings are replaced by thiazole rings.

Synthesis of the Monomers

Starting from dicarboxylic acid dithioamides and hexafluoroacetone, bis(thiazole)s can be prepared in a series of three consecutive reaction steps. This reaction was developed by Burger[30,31] in the late 70s for the synthesis of 4-(trifluoromethyl)-5-fluoro-substituted oxazoles, thiazoles, imidazoles, and selenazoles. Scheme 1 shows the sequence, which is very similar to the one we used earlier for the preparation of 3.[27]

The first step proceeds quantitatively in solution at low temperatures (−10 °C). It is comparable to the first step of the formation of Schiff bases (imines) from ketones and amines. However, non-fluorinated ketones do not add to amides or thioamides. The nitrogen atom in these groups has a very low nucleophilicity, since its lone electron pair is delocalized. The strong negative inductive effect of the two trifluoromethyl groups in hexafluoroacetone decreases the electron density at the carbonyl C atom. Therefore, it is electrophilic enough to react with amide, thioamide, and amidine nitrogen atoms.

During the reaction of hexafluoroacetone with terephthalic acid dithioamide temperatures above −10 °C must be avoided due to the low stability of the addition compound against decomposition into the starting materials. Thus, the addition product cannot be isolated. Instead, it is dehydrated below 0 °C *in situ* by the simultaneous addition of trifluoroacetic anhydride and pyridine. The anhydride acylates the hydroxy groups and converts them into good leaving groups. In the presence of pyridine, the CN double bonds are formed on removal of pyridinium trifluoroacetate, which precipitates.

The dehydration product is a bis(thioacyl imine). Compounds of this type are very powerful dienes. Since the dehydration is carried out in the presence of an excess of hexafluoroacetone, the thioacyl imine groups add hexafluoroacetone in a Diels–Alder reaction. Therefore, the final stable product of the first two steps is 1,4-bis(2,2,6,6-tetrakis(trifluoromethyl)-6H-1,3,5-oxathiazin-4-yl)benzene (4).

The Diels–Alder reaction with hexafluoroacetone is reversible at elevated temperatures. On refluxing in xylene, hexafluoroacetone can be removed, and the bis(thioacyl imine) is regenerated. However, this compound is not stable at room temperature. It undergoes electrocyclic ring closure on cooling to room temperature and forms a bis(thiazete) 5. The equilibrium between bis(thiacyl imine) and bis(thiazete) is temperature dependent.

Treatment of the bis(thiazete) with anhydrous stannous chloride in refluxing toluene regenerates the bis(thioacyl imine), which then reacts with the tin(II) compound under degradation of two trifluoromethyl groups. The result is the formation of the bis(thiazole) 6. The removal of hexafluoroacetone from the bis(oxathiazine) 4 and the reductive cyclization can also be carried out in a one-step procedure. Due to the lability of some of the involved intermediates, the overall yield of bis(thiazole) 6 is only 30%.

A sample of the *meta*-substituted bis(thiazole) 7 (Chart 2), prepared in the same way, was obtained from Prof. Burger's group in Munich.

Chart 2. *m*-Bis(thiazole) 7

7
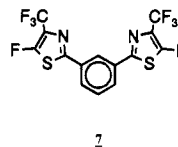
Model Reaction

The results of Burger's[32] studies on monofunctional compounds as well as our studies with the bis(oxazole) monomer 3[27] showed that this monomer exhibits unusually high reactivity toward nucleophiles. Most bis(halide)s such as 4,4′-difluorobenzophenone require complete conversion to the alkali phenoxides by treatment with alkali carbonates and azeotropic removal of the water formed in the acid–base reaction. Even then reaction temperatures between 160 and 220 °C are necessary to obtain high molar mass material in the case of amorphous polymers. Heteroaromatic monomers such as 2,5-bis(4′-fluorophenyl)oxazole or 2,5-bis-(4′-fluorophenyl)-1,3,5-oxadiazole, where the heterocycle acts as an activating group for fluorophenyl substituents, require similar reaction conditions. In contrast to that, the bis(oxazole) 3 yields high molar mass polymer on treatment with bis(phenol)s at temperatures as low as 50 °C.[27] In addition, conversion of the phenol groups to phenoxides is not necessary. This is evidenced by the possibility of using triethylamine as a base, which does not allow us to shift the equilibrium between phenol and phenoxide to the side of the phenoxide.

Therefore, we tried the same mild reaction conditions for the reaction of the bis(thiazole) monomer 6 with phenol, as is shown in Scheme 2.

Conversion above 90% could only be reached after a reaction time of 24 h. The bis(oxazole) 3 yielded more than 90% product already after 2 h. This indicates lower reactivity of the bis(thiazole) 6. However, since

Scheme 2. Model Reaction
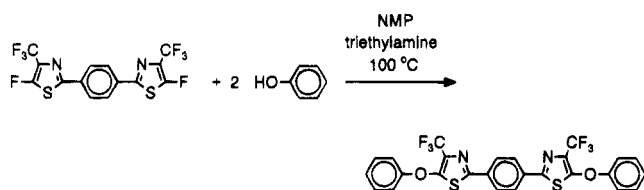
almost quantitative yields could be achieved with the triethylamine reaction, these conditions were employed for several polymerizations.

Polymerization

The monomers **6** and **7** were treated with several bis-(phenol)s in NMP at 100 °C in the presence of triethyl-amine to give the poly(aryl ether thiazole)s **9** and **10**. Scheme 3 and Table 1 show the results.
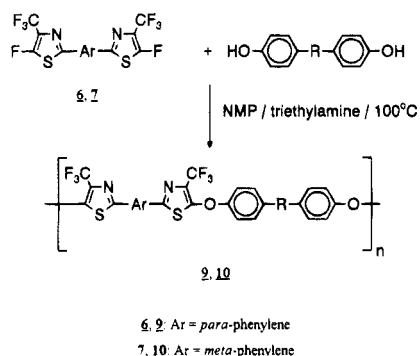
Scheme 3. Synthesis of the Poly(aryl ether thiazole)s 9 and 10

Table 1. Structures and Molar Masses of the Poly(aryl ether thiazole)s 9 and 10

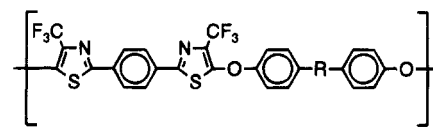| poly-no.	mer	Ar	R	reacn time (h)	$\bar{M}_n{}^a$ (g·mol^{-1})	$\bar{M}_w{}^a$ (g·mol^{-1})
1	9a	*p*-phenylene	$-SO_2-$	24	9200^b	19300^b
2	9b	*p*-phenylene	$-C(CH_3)_2-$	2	2000	3200
3	9b	*p*-phenylene	$-C(CH_3)_2-$	24	4100	6600
4	9c	*p*-phenylene	$-O-$	24	5000	8000
5	10a	*m*-phenylene	$-SO_2-$	24	8400	19200

^{a} GPC in THF, polystyrene calibration. ^{b} GPC in DMAc, polystyrene calibration.

The poly(aryl ether thiazole)s **9** and **10** have fairly low molar masses. Even an increase of the reaction time from 2 to 24 h increases the molar mass only from $\bar{M}_n = 2000$ to $\bar{M}_n = 4100$ g·mol^{-1} (entries 2 and 3 in Table 1). Poly(aryl ether oxazole)s prepared from **3** under similar reaction conditions[27] possess molar masses above $\bar{M}_n = 15\,000$ g·mol^{-1}. This clearly indicates the low reactivity of the thiazole system compared to the oxazole system toward nucleophilic attack. Obviously, the thiazole ring is much less electron poor than the oxazole ring. This phenomenon is observed frequently, when oxygen-based heteroaromatic rings are compared with their sulfur analogues.

To obtain high molar mass materials from the bis-(thiazole) monomers **6** and **7**, a different approach was necessary. Kricheldorf[33,34] developed a method based on silylated bis(phenol)s, which allows the preparation of high molar mass materials from aryl halides with relatively low reactivity. In the presence of a fluoride, preferably cesium fluoride, the silyl ether groups are cleaved, and cesium phenoxide and trimethylsilyl fluoride are formed. Trimethylsilyl fluoride is distilled off, and the cesium phenolate reacts with the activated aryl

halide to form the desired ether linkage and regenerate cesium fluoride. Thus, only catalytic amounts of the fluoride are necessary. This method was employed for the synthesis of a number of different poly(aryl ether thiazole)s **9** and **10**. Scheme 4 shows the reaction mechanism. Reaction conditions and molar masses are summarized in Table 2.

Table 2. Reaction Conditions and Molar Masses of Poly(aryl ether thiazole)s Prepared by the Silyl Method (NMP as Solvent, Cesium Fluoride as Catalyst)
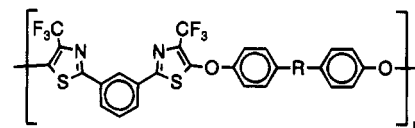
poly-no.	mer	Ar	R	reacn time (h)	reacn temp (°C)	$\bar{M}_n{}^a$ (g·mol^{-1})	$\bar{M}_w{}^a$ (g·mol^{-1})
1	9b	*p*-phenylene	$-C(CH_3)_2-$	1/0.5	50/80	18 900	69 000
2	9c	*p*-phenylene	$-O-$	1/1	50/80	16 900	78 500
3	9d	*p*-phenylene	$-CO-$	1/1	50/100	2 400^b	5 900^b
4	10b	*m*-phenylene	$-CO-$	1/1	50/80	8 900	31 000

It can be seen clearly that the silyl method results in the formation of polymers with much higher molar masses than the triethylamine method. Weight average molar masses of polymers **9** in Table 2 are in the range 69 000–78 500 g·mol^{-1}. The weight average molar masses of the polymers prepared by the silyl method are larger than those of the polymers prepared by the triethylamine method by a factor of 10. This demonstrates clearly the exceptional usefulness of the silyl method for the synthesis of poly(arylene ether)s. The broad molar mass distribution with values for $\bar{M}_w/\bar{M}_n$ up to 4.6 is caused by the presence of oligomers which are probably cyclics (we have shown the cyclic nature of the oligomers in oxazole polymers of similar structures by mass spectroscopy[27]). Polymer **10b** was synthesized from a very small sample (only 330 mg), which is the reason for its relatively low molar mass: the smaller the amount of monomers used for a polycondensation, the larger is the effect of potential errors in weighing, which results in loss of stoichiometry. Anyway, all polymers in Table 2 can be cast into almost colorless, transparent, flexible films.

Determination of molar masses by GPC can be erroneous, if the calibration is based on unsuitable polymer standards. However, since we were able to show for poly(aryl ether oxazole)s that the deviation of the masses determined by GPC in THF with polystyrene calibration from those determined by FAB mass spectroscopy is less than 10%,[27] we believe this method to be fairly accurate for poly(arylene ether)s based on monomers of types **3**, **6**, and **7**.

DSC Measurements

None of the poly(aryl ether thiazole)s **9** and **10** exhibit crystallization or melt transitions in DSC measurements. The glass transition temperatures are sum-

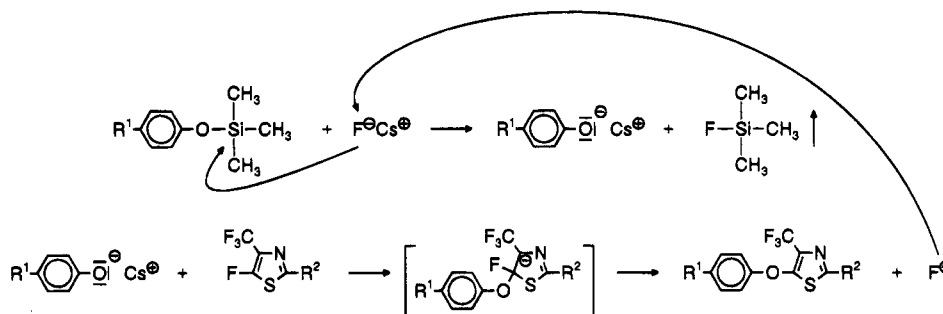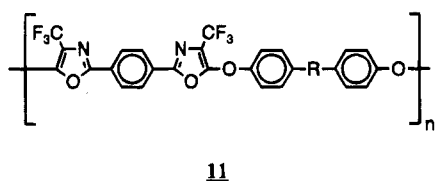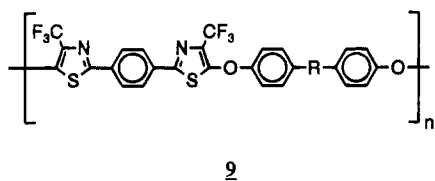**Scheme 4. Synthesis of Poly(aryl ether thiazole)s via the Silyl Method**


Table 3. Comparison of the Glass Transition Temperatures of the Poly(aryl ether thiazole)s with the Analogueous Poly(aryl ether oxazole)s[27] 11

9

11

	9		11		
R	polymer	$T_g{}^a$ (°C)	polymer[b]	$T_g{}^a$ (°C)	ΔT_g
−SO₂−	a	217	a	191	26
−C(CH₃)₂−	b	183	b	151	32
−O−	c	174	c	142	32
−CO−	d	195	d	167 (278)[c]	28

[a] DSC, 20 K/min. [b] Ref 27. [c] Crystallite melt temperature.

Table 4. Effect of m- and p-Phenylene Rings in the Repeating Unit of Poly(aryl ether thiazole)s

9

10
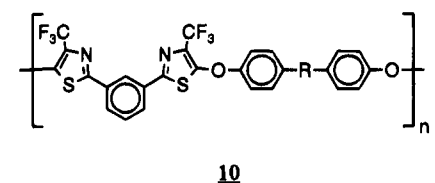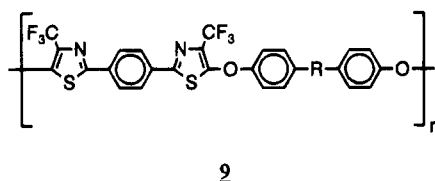
	9		10		
R	polymer	$T_g{}^a$ (°C)	polymer	$T_g a$ (°C)	ΔT_g
−SO₂−	a	217	a	187	30
−CO−	d	195	d	169	26

[a] DSC, 20 K/min.

marized in Tables 3 and 4. Table 3 also contains the T_g values of the analogous poly(aryl ether oxazole)s **11** for comparison, while Table 4 draws a comparison between the *p*- and *m*-phenylene-based poly(aryl ether thiazole)s **9** and **10**.

As Table 3 shows, the glass transition temperatures of the thiazole-containing polymers **9** are about 30 deg

above those of the oxazole polymers **11**. This behavior is caused by the more extended geometry of the thiazole-containing repeating unit. The catenation angle at the thiazole ring is about 153°,[35] while at the oxazole ring it is only about 132°.[36] Consequently, the backbone of the oxazole polymers is less restricted in its mobility, which causes the lower glass transition temperature.

The poly(ether ketone) **11d** proved to be semicrystalline in DSC measurements. In contrast to that, the thiazole-containing poly(ether ketone) **9d** is amorphous, and crystallinity cannot be induced by annealing. A possible explanation can be found in the geometry of the heterocycles. The more linear 1,4-bis(thiazolyl)-benzene structure element may fit less easily into a crystal lattice than the more kinked 1,4-bis(oxazolyl)-benzene group. It is also less flexible and may therefore be less likely to assume a suitable conformation.

As can be expected, the incorporation of a *m*-phenylene ring into the polymer backbone in place of a *p*-phenylene ring decreases the glass transition temperature by 26−30 deg. This is due to the additional rotational degree of freedom, caused by the additional bend in the repeating unit.

Solubility

The poly(aryl ether thiazole)s **9** and **10** show good solubility in a number of common organic solvents. Table 5 summarizes the results of qualitative solubility tests and draws a comparison with the poly(aryl ether oxazole)s **11**. It was attempted to obtain 10%(w/v) solutions of all polymers in several solvents.

All oxazole- and thiazole-based polymers **11**, **9**, and **10** are soluble at room temperature in NMP, with the exception of the poly(aryl ether ketone oxazole) **11d**, which is the only semicrystalline polymer in this series. The poly(aryl ether oxazole) **11a** is more easily soluble than its thiazole analogue **9a**. As mentioned in the discussion of the glass transition temperatures, the thiazole rings result in a more extended geometry of the repeating unit. As a result, the backbones of the thiazole polymers are less flexible than those of the oxazole polymers. This trend is confirmed by the observation that the *m*-phenylene-based polymers **10** show solubility in an even greater range of solvents. The observation that **9d** is more easily soluble than the corresponding oxazole polymer **11d** is not in contradiction with the trend mentioned above, since the oxazole polymer is semicrystalline, while the thiazole polymer is not.

It is somewhat surprising that toluene appears to be a fairly good solvent for these types of polymers, despite its rather low polarity compared to the solvents that are commonly used for poly(arylene ether)s. Polarity in itself does not seem to be a sufficient parameter for the applicability of a solvent. Most polymers in this series

Table 5. Solubility Tests with the Poly(aryl ether thiazole)s 9 and 10 in Comparison with the Poly(aryl ether oxazole)s 11

<u>9</u>: X = S
<u>11</u>: X = O

<u>10</u>
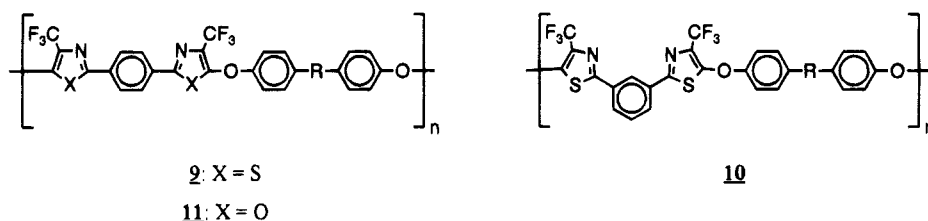
polymer	X	R	NMP	DMAc	DMF	DMSO	THF	acetone	CHCl₃	toluene
11a	—O—	—SO₂—	+	+	+	+	+	−	−	−
9a	—S—	—SO₂—	+	+	o	o	−	−	−	−
10a	—S—	—SO₂—	+	+	+	+	+	+	+	o
11b	—O—	—C(CH₃)₂—	+	+	+	o	+	+	+	+
9b	—S—	—C(CH₃)₂—	+	+	+	o	+	−	+	+
11c	—O—	—O—	+	+	+	o	+	−	o	+
9c	—S—	—O—	+	+	+	o	+	−	+	+
11d	—O—	—CO—	o	o	o	−	−	−	−	−
9d	—S—	—CO—	+	o	o	o	−	−	−	−
10b	—S—	—CO—	+	+	+	o	+	−	+	+

Key: (+) soluble at room temperature; (o) soluble on heating; (−) not completely soluble on refluxing.

Table 6. Decomposition Temperatures of the Poly(aryl ether thiazole)s 9 and 10 in Air

polymer	R	T_{onset}^a (°C)	$T_{10\%}^b$ (°C)
9a	—SO₂—	410	482
9b	—C(CH₃)₂—	417	471
9c	—O—	420	485
9d	—CO—	410	475
10a	—SO₂—	408	474
10b	—CO—	417	470

^{a} First loss of weight in dynamic thermogravimetry, 10 K/min.
^{b} 10% weight loss.

are soluble in DMSO only on heating, while they are soluble in the amide solvents NMP, DMAc, and DMF at room temperature, although these types of dipolar aprotic solvents have similar polarities.

Thermal Stability

In many cases heteroaromatic polymers exhibit outstanding thermooxidative stability. In a previous paper we reported surprisingly low decomposition temperatures of the poly(aryl ether oxazole)s 11.[27] The initial weight loss of these polymers is observed at about 310 °C, which is at least 100 deg lower than one expects for such polymer structures. This instability was attributed to the substitution pattern of the oxazole rings. The trifluoromethyl group in the 4-position stabilizes the transition state of a ring-opening reaction. Thus, the activation energy of this decomposition reaction is lowered sufficiently for weight loss to start at 310 °C.

The thiazole polymers 9 and 10 do not show this remarkable instability at high temperatures. It is well-known that sulfur heteroaromatic rings exhibit more pronounced aromaticity than their oxygen analogues. Furan and oxazole for instance are able to undergo Diels—Alder reactions as dienes, while thiophene and thiazole do not react under similar conditions.[37—39] Therefore, the thiazole polymers can be expected to possess higher decomposition temperatures than oxazole polymers of similar compositions. Table 6 summarizes the decomposition temperatures of polymers 9 and 10 in air, as determined by dynamic thermogravimetry.

The poly(aryl ether thiazole)s exhibit an initial weight loss at temperatures which are 100 deg higher than the corresponding poly(aryl ether oxazole)s 11. Their ther-
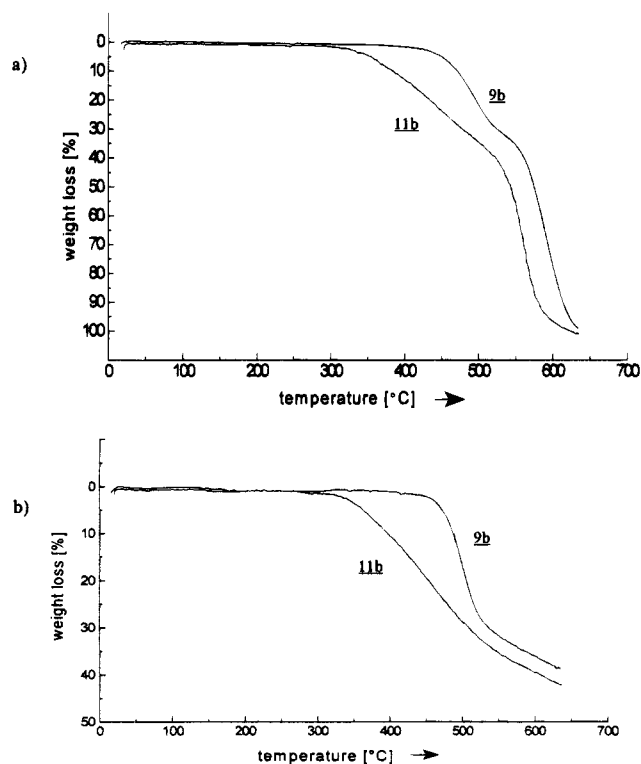

Figure 1. Thermogravimetry curves of 9b and 11b (a) in air and (b) in nitrogen.

mal stabilities, expressed as the temperature at which a weight loss of 10% occurs in air, are between 470 and 485 °C. This is in the range of decomposition temperatures that can be expected from heteroaromatic polymers. The thermal stability of polymers 9 and 10 in nitrogen is very similar to the results obtained in air. Figure 1 shows the thermogravimetry curves of polymers 9b and 11b in air and nitrogen as examples.

Spectroscopy

All spectroscopic data from IR, ¹H-NMR, ¹³C-NMR, and ¹⁹F-NMR spectroscopy support the structure of the poly(aryl ether thiazole)s 9 and 10. These characterization methods, as well as elemental analysis, do not indicate any degradation of trifluoromethyl groups or

the thiazole rings themselves during polymerization. The exact data are listed in the Experimental Part.

Conclusions

Monomers with two thiazole rings with the 4-(trifluoromethyl)-5-fluoro substitution pattern can be prepared from aromatic bis(thioamide)s and hexafluoroacetone in a sequence of three reaction steps. The fluorine atoms on the thiazole rings are much less activated for nucleophilic displacement than fluorine atoms in similar oxazole rings. High molar mass polymers with $\bar{M}_w$ up to 78 500 g·mol⁻¹ can be prepared from the bis(thiazole) monomers **9** and **10** with silylated bis(phenol)s and cesium fluoride catalysis under very mild reaction conditions.

The resulting poly(aryl ether thiazole)s are amorphous with glass transition temperatures between 169 and 217 °C, depending on the exact structure of the repeating unit. The additional angle which is introduced by replacement of the *p*-phenylene ring in polymers **9** with a *m*-phenylene ring in polymers **10** decreases T_g by 26−30 deg. A comparison with poly(aryl ether oxazole)s having similar structures reveals the effect of the thiazole ring on glass transition temperature, solubility, and thermal stability. The thiazole ring introduces a catenation angle of 153°, while the same angle at the oxazole ring is 132°. Therefore, the T_g's of the thiazole polymers are 26−32 deg higher than those of the corresponding oxazole polymers. In addition, the thiazole polymers are in general soluble only in a range of solvents smaller than for the oxazole polymers.

The thiazole ring exhibits a much higher decomposition temperature than the oxazole ring. It has been shown that the trifluoromethyl group in the 4-position destabilizes the oxazole ring. This effect is absent in the thiazole ring. The most probable reason for this increased stability is the more pronounced aromatic character of sulfur heteroaromatic rings as compared to oxygen-based systems.

Experimental Part

Instruments. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AC 250 spectrometer (250 MHz for protons, 62.5 MHz for carbon-13; reference, TMS). For ¹⁹F-NMR spectra a JEOL FX 90Q was used (84.26 MHz; external reference, pure trifluoroacetc acid). IR spectra were obtained with a Digilab FTS-40 instrument. GPC was performed with a Waters ALC 200, RI and UV (254 nm) detection, four columns with PL-Gel 5 μm with pore sizes 500, 1000, 10⁴, and 10⁵Å, THF as eluent, and polystyrene calibration. DSC measurements were made on a Perkin-Elmer DSC 7 instrument at 20 K/min under nitrogen. For thermogravimetry a Netzsch STA 409 was used at a heating rate of 10 K/min. Elemental analysis was performed by Ilse Beetz, Mikroanalytisches Laboratorium, D-96317 Kronach, Germany.

Starting Materials. 2,2-Bis(4-hydroxyphenyl)propane (Bisphenol A, Bayer AG) was recrystallized from toluene. All other bis(phenol)s (Hoechst AG) were used without further purification. Hexafluoroacetone (Hoechst AG) was received as sesquihydrate and was dehydrated as described below. Phenol (Riedel-de-Haën), pyridine (Merck), cesium fluoride (Fluka), and trifluoroacetic anhydride (Fluka) are commercial products and were used as received. THF and toluene were refluxed over Na/K alloy to remove water and distilled freshly before use. NMP (Fluka) was distilled twice from P₂O₅ under reduced pressure. Triethylamine was stirred over KOH pellets, filtered, and distilled. The boiling point of the fraction which was used for the polymerizations was 87−88 °C. The *m*-bis(thiazole) monomer **7** was received from Dr. B. Helmreich (Technical University of Munich) and used without further purification.

Synthesis of the Monomers. Terephthalic Acid Dithioamide. In a 500 mL round-bottom flask with gas inlet, 10 g (78 mmol) of terephthalic acid dinitrile (Fluka, 98+%) is dispersed in a mixture from 400 mL of pyridine and 11 mL of triethylamine. Hydrogen sulfide is passed through this dispersion at room temperature under vigorous stirring for 3 h. During this time, a yellow solution is formed initially, which changes its color to dark green with time. After completion of the reaction, the mixture is poured onto 1000 mL of deionized water. The product (yellow) precipitates, is filtered out, washed thoroughly with deionized water, and dried under vacuum in a desiccator over P₂O₅. Yield: 14.2 g (93%). Melting point: 257−258 °C (lit.: 260 °C). ¹H-NMR (DMSO-d_6): δ (ppm) 7.85 (s, 4H, H$_{ar}$), 9.60 (s, 2H, NH), 10.0 (s, 2H, NH). IR (KBr): $\tilde{\nu}$ 3277, 3127 (NH), 1641, 1429, 1314, 1271 cm⁻¹.

1,4-Bis(2,2,6,6-tetrakis(trifluoromethyl)-6H-1,3,5-oxathiazin-4-yl)benzene (4). In a 250 mL three-neck round-bottom flask with gas inlet, 7.05 g (36 mmol) of terephthalic acid dithioamide is dispersed in 150 mL of dry THF. The flask is equipped with a CO₂ reflux condenser and two addition funnels, one charged with 10.5 mL (75.5 mmol) of trifluoroacetic anhydride, the other one with 12.8 mL (158.3 mmol) of pyridine. The slurry is stirred vigorously and cooled to 0 °C by an ice bath. Then 250 mL of concentrated sulfuric acid is placed in a two-neck round-bottom flask equipped with a dropping funnel and gas outlet, which is connected to the gas inlet of the flask with the terephthalic dithioamide. The sulfuric acid is heated to 80 °C under slow stirring, and hexafluoroacetone sesquihydrate (about 35 mL) is added very slowly through the dropping funnel. This removes the water from the hydrate, and gaseous hexafluoroacetone evolves, which is transferred to the slurry of terephthalic acid dithioamide. When the absorption of hexafluoroacetone into this slurry starts, the rate of addition of hexafluoroacetone sesquihydrate is adjusted in a way that all gaseous hexafluoroacetone is absorbed completely as it evolves. The end of the reaction is indicated by refluxing hexafluoroacetone at the CO₂ reflux condenser, and the addition of hexafluoroacetone sesquihydrate to the sulfuric acid is stopped. At this point, a clear yellow solution is obtained, as the product is soluble in THF. While hexafluoroacetone is refluxing, the pyridine and trifluoroacetic anhydride are added slowly (about 30 min) and simultaneously. During all operations, a temperature of 0 °C should not be exceeded. After that, the mixture is stirred for another 4 h at room temperature. The whole apparatus is flushed with nitrogen to remove unreacted hexafluoroacetone prior to opening. The pyridinium salt is filtered off, and the THF is removed under vacuum. The product is washed with water and dried under vacuum in a desiccator over P₂O₅. Yield: 22.2 g (75%). Melting point: 166−168 °C (lit.: 171 °C). ¹H-NMR (acetone-d_6): δ (ppm) 8.38 (s, H$_{ar}$). IR (KBr): $\tilde{\nu}$ 1630 (C=N), 1330−1200 (CF₃) cm⁻¹.

1,4-Bis(5-fluoro-4-(trifluoromethyl)thiazol-2-yl)benzene (6). 4 (22.0 g, 26.6 mmol) and 11.15 g (58.8 mmol) of anhydrous SnCl₂ (Sigma, 99%) are refluxed in 150 mL of xylene under argon for 48 h. After cooling, the insoluble parts are filtered off, and the toluene is removed under vacuum. Since toxic hexafluoroacetone is generated in this reaction, care should be taken to remove and collect it before opening the flask. The crude product is purified by chromatography on silica gel with chloroform as eluent. The first, yellow fraction is collected. Repeated recrystallization from chloroform yields colorless needles, which are dried under vacuum. Yield: 3.3 g (30%). Melting point: 154−155 °C (lit.: 171 °C).[40]
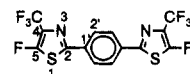
¹H-NMR (CDCl₃): δ (ppm) 7.90 (s, H$_{ar}$). ¹⁹F-NMR (CDCl₃): δ (ppm) 13.3 (d, 6F, $^4J_{F-F}$ = 12 Hz, CF₃), −60.8 (q, 2F, $^4J_{F-F}$ = 12 Hz, CF). ¹³C-NMR (CDCl₃): δ (ppm) 119.7 (dq, $^1J_{C-F}$ = 269 Hz, $^3J_{C-F}$ = 4 Hz, CF₃), 126.8 (C2'), 126.9 (dq, $^2J_{C-F}$ = 38 Hz, $^2J_{C-F}$ = 5 Hz, C4), 134.4 (C1'), 155.8 (d, $^3J_{C-F}$ = 8 Hz, C2), 161.8 (dq, $^1J_{C-F}$ = 312 Hz, $^3J_{C-F}$ = 2 Hz, C5). Anal. Calc for

$C_{14}H_4F_8N_2S_2$ (416.3 g·mol^{-1}): C, 40.39; H, 0.97; N, 6.73; S, 15.40. Found: C, 40.42; H, 1.05; N, 6.72; S, 15.49.

Silylated Bis(phenol)s. General Procedure. A two-neck round-bottom flask with an argon inlet is charged with a solution of 50 mmol of bis(phenol) and 16.7 mL (120 mmol) of triethylamine in 320 mL of dry THF. Chlorotrimethylsilane (Merck, 99+%) (15.2 mL, 120 mmol) is added under stirring within 15 min. The precipitation of triethylammonium chloride starts immediately. The mixture is stirred for an additional 2 h under reflux. After cooling to room temperature, the precipitated salt is filtered off and THF removed under vacuum. The crude product, a brown oil, is purified by distillation under reduced pressure.

2,2-Bis(4-(trimethylsiloxy)phenyl)propane (Silylated Bisphenol A). Yield: 14.9 g (80%). Boiling point: 130−131 °C/0.1 mbar.

4,4′-Bis(trimethylsiloxy)diphenyl Ether (Silylated Dihydroxydiphenyl Ether). Yield: 12.6 g (73%). Melting point: 65−66 °C.

4,4′-Bis(trimethylsiloxy)benzophenone (Silylated Dihydroxybenzophenone). Yield: 13.8 g (77%). Boiling point: 152−153 °C/0.1 mbar.

Model Reaction: Synthesis of 8. A 15 mL pressure resistant Pyrex tube with a Teflon screw cap and an argon inlet is charged with 327.5 mg (0.79 mmol) of bis(thiazole) **6** and 148.1 mg (1.58 mmol) of phenol. The tube is evacuated and filled with argon three times to remove oxygen. Then 4 mL of dry NMP and 0.24 mL (1.72 mmol) of triethylamine are added under argon. The tube is sealed tightly and heated for 24 h to 100 °C (oil bath). After cooling to room temperature, the mixture is poured onto 100 mL of deionized water, and the aqueous fraction is extracted twice with 150 mL of diethyl ether. The organic phases are combined and dried over sodium sulfate, and the solvent is evaporated. The brown crude product is purified by chromatography on silica with chloroform as eluent. The first, yellow fraction is collected. Recrystallization from hexane yields colorless needles. Yield: 0.4 g (90%). Melting point: 148−149 °C.
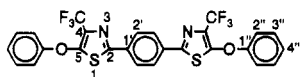

^{1}H-NMR (CDCl$_3$): δ (ppm) 7.20 (m, 6H, H$_{ar}$), 7.45 (m, 4H, H$_{ar}$), 7.85 (m, 4H, H$_{ar}$). ^{19}F-NMR (CDCl$_3$): δ (ppm) 13.9 (s, CF$_3$). ^{13}C-NMR (CDCl$_3$): δ (ppm) 118.8 (C2″), 121.8 (q, $^{1}J_{C-F}$ = 270 Hz, CF$_3$), 126.7 (C4″), 127.3 (C2′), 130.2 (q, $^{2}J_{C-F}$ = 37 Hz, C4), 131.2 (C3″), 135.5 (C1′), 157.6 (C1″), 159.7 (C2), 160.2 (q, $^{3}J_{C-F}$ = 2 Hz, C5). IR (KBr): $\tilde{\nu}$ 3100−3040 (CH$_{aromatic}$), 1547, 1489, 1389, 1185−1100 (CF$_3$) cm^{-1}. Anal. Calcd for $C_{26}H_{14}F_6N_2O_2S_2$ (564.5 g·mol^{-1}): C, 55.32; H, 2.50; N, 4.96; S, 11.36. Found: C, 55.29; H, 2.49; N, 5.12; S, 11.54.

Polymerizations. Triethylamine Method. A 15 mL pressure resistant Pyrex tube with an argon inlet is charged with equimolar amounts of bis(thiazole) **6** or **7** and the bis(phenol) (about 1 mmol each). The tube is sealed, and oxygen is replaced by argon by three evacuation/venting cycles. Dry NMP is added under argon to give a solution with 20% solids content, and 2.2 mmol of dry triethylamine is added (10% molar excess). The tube is sealed tightly and heated to 100 °C for the time given in Table 1. After cooling to room temperature, 5 mL of THF is added to dilute the mixture, and the polymer is precipitated by slow addition of the reaction mixture to 150 mL of methanol. The polymer is filtered off, washed with water, and dried at 80 °C under reduced pressure.

Silyl Method. A 10 mL Pyrex tube with an argon inlet is charged with equimolar amounts of bis(thiazole) **6** or **7** and the bis(phenol) (about 1 mmol each). The tube is flushed with argon, and NMP is added to give a solution of 20% solids. Cesium fluoride (1% (w/w)) is added as catalyst. The tube is equipped with a reflux condenser under argon, and reacted under the conditions given in Table 2 in a continuous flow of argon. Evolution of gas starts at 50 °C and indicates the onset of the reaction. After cooling to room temperature, 5 mL of THF is added to dilute the mixture, and the polymer is recovered by precipitation from 150 mL of methanol. The

polymer is filtered off, washed with water, and dried at 80 °C under reduced pressure.

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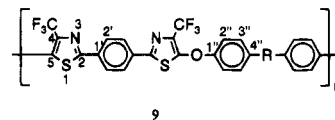
Polymer 9a (Table 1, entry 1): 476.3 mg (1.14 mmol) of bis(thiazole) **6**; 286.3 mg (1.14 mmol) of 4,4′-dihydroxydiphenyl sulfone; 0.35 mL (2.51 mmol) of triethylamine/3 mL NMP; R = −SO$_2$−. ^{1}H-NMR (DMSO-d_6, 60 °C): δ (ppm) 7.45−8.10 (m, 8H, H2″, H3″), 8.00 (s, 4H, H2′). ^{19}F-NMR (DMSO-d_6): δ (ppm) 13.2 (s, CF$_3$). IR (KBr): $\tilde{\nu}$ 3100−3040 (CH$_{aromat}$), 1587, 1551, 1487, 1384, 1245−1100 (CF$_3$) cm^{-1}. Anal. Calc for $(C_{26}H_{12}F_6N_2O_4S_3)_n$ (626.6 g·mol^{-1})$_n$: C, 49.84; H, 1.93; N, 4.47; S, 15.35. Found: C, 49.70; H, 2.00; N, 4.61; S, 15.48.

Polymer 9b (Table 2, entry 1): 447.0 mg (1.07 mmol) of bis(thiazole) **6**; 400.1 mg (1.07 mmol) of 2,2′-bis(4-(trimethylsiloxy)phenyl)propane; 8.5 mg (0.056 mmol) of cesium fluoride/3.3 mL NMP; R = −C(CH$_3$)$_2$−. ^{1}H-NMR (THF-d_8): δ (ppm) 1.7 (s, 6H, CH$_3$), 7.15−7.4 (m, 8H, H2″, H3″), 7.95 (s, 4H, H2′). ^{19}F-NMR (DMSO-d_6): δ (ppm) 13.2 (s, CF$_3$). ^{13}C-NMR (THF-d_8): δ (ppm) 31.3 (−C(CH$_3$)$_2$−), 43.3 (−C(CH$_3$)$_2$−), 118.3 (C2″), 121.8 (q, $^{1}J_{C-F}$ = 269 Hz, CF$_3$), 127.3 (C2′), 129.6 (C3″), 130.2 (q, $^{2}J_{C-F}$ = 36 Hz, C4), 135.3 (C1′), 149.0 (C4″), 157.4 (C2), 157.7 (C1″), 160.2 (q, $^{3}J_{C-F}$ = 2 Hz, C5). IR (KBr): $\tilde{\nu}$ 3100−3040 (CH$_{aromat}$), 2960 (CH$_{aliph}$), 1551, 1503, 1387, 1245−1130 (CF$_3$) cm^{-1}. Anal. Calc for $(C_{29}H_{18}F_6N_2O_2S_2)_n$ (604.6 g·mol^{-1})$_n$: C, 57.61; H, 3.00; N, 4.63; S, 10.61. Found: C, 57.77; H, 3.07; N, 4.90; S, 10.51.

Polymer 9c (Table 2, entry 2): 362.2 mg (0.87 mmol) of bis(thiazole) **6**; 301.5 mg (0.87 mmol) of 4,4′-bis(trimethylsiloxy)diphenyl ether; 6.6 mg (0.043 mmol) of cesium fluoride/2.6 mL NMP; R = −O−. ^{1}H-NMR (THF-d_8): δ (ppm) 7.05−7.45 (m, 8H, H2″, H3″), 7.97 (s, 4H, H2′). ^{19}F-NMR (DMSO-d_6): δ (ppm) 13.2 (s, CF$_3$). ^{13}C-NMR (CDCl$_3$): δ (ppm) 119.4 (C2″), 120.2 (C3″), 120.5 (q, $^{1}J_{C-F}$ = 269 Hz, CF$_3$), 126.6 (C2′), 129.8 (q, $^{2}J_{C-F}$ = 37 Hz, C4), 134.4 (C1′), 154.3 (C4″), 154.5 (C1″), 156.6 (C2), 158.9 (q, $^{3}J_{C-F}$ = 2 Hz, C5). IR (KBr): $\tilde{\nu}$ 3100−3040 (CH$_{aromat}$), 1551, 1489, 1387, 1240−1130 (CF$_3$) cm^{-1}. Anal. Calc for $(C_{26}H_{12}F_6N_2O_3S_2)_n$ (578.5 g·mol^{-1})$_n$: C, 53.98; H, 2.09; N, 4.84; S, 11.08. Found: C, 54.30; H, 2.29; N, 5.10; S, 11.04.

Polymer 9d (Table 2, entry 3): 388.2 mg (0.93 mmol) of bis(thiazole) **6**; 334.4 mg (0.93 mmol) of 4,4′-bis(trimethylsiloxy)benzophenone; 7.2 mg (0.047 mmol) of cesium fluoride/2.8 mL NMP; R = −CO−. ^{1}H-NMR (THF-d_8): δ (ppm) 7.35−8.00 (m, 8H, H2″, H3″), 8.05 (s, 4H, H2′). ^{19}F-NMR (DMSO-d_6): δ (ppm) 12.8 (s, CF$_3$) (NMR data for THF-soluble fraction only). IR (KBr): $\tilde{\nu}$ 3100−3040 (CH$_{aromat}$), 1661, 1601, 1551, 1499, 1383, 1245−1130 (CF$_3$) cm^{-1}. Anal. Calc for $(C_{27}H_{12}F_6N_2O_3S_2)_n$ (590.5 g·mol^{-1})$_n$: C, 54.91; H, 2.05; N, 4.75; S, 10.86. Found: 54.49; H, 1.96; N, 4.63; S, 10.45.

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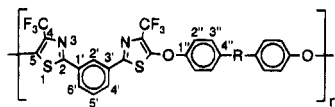
Polymer 10a (Table 1, entry 5): 609.0 mg (1.46 mmol) of bis(thiazole) **7**; 366.1 mg (1.46 mmol) of 4,4′-bis(trimethylsiloxy)diphenyl sulfone; 0.45 mL (3.23 mmol) of triethylamine/3.8 mL NMP; R = −SO$_2$−. ^{1}H-NMR (THF-d_8): δ (ppm) 7.60 (m, 4H, H$_{ar}$), 7.80 (m, 1H, H$_{ar}$), 8.25 (m, 6H, H$_{ar}$); 8.60 (m, 1H, H$_{ar}$). ^{19}F-NMR (THF-d_8): δ (ppm) 12.8 (s, CF$_3$). ^{13}C-NMR (THF-d_8): δ (ppm) 118.5 (C2″); 121.4 (q, $^{1}J_{C-F}$ = 270 Hz, CF$_3$), 123.9 (C5′), 129.4 (C4′, C6′), 131.1 (C2′), 132.7 (q, $^{2}J_{C-F}$ = 37 Hz, C4), 134.5 (C1′, C3′), 139.7 (C4″), 156.6 (C2), 160.1 (q, $^{3}J_{C-F}$ = 2 Hz, C5), 162.5 (C1″). IR (KBr): $\tilde{\nu}$ 3100−3040 (CH$_{aromat}$), 1587, 1553, 1489, 1385, 1250−1130 (CF$_3$) cm^{-1}. Anal. Calc for $(C_{26}H_{12}F_6N_2O_4S_3)_n$ (626.6 g·mol^{-1})$_n$: C, 49.84; H, 1.93; N, 4.47; S, 15.35. Found: C, 49.74; H, 2.07; N, 4.61; S, 15.30.

Polymer 10b (Table 2, entry 4): 328.7 mg (0.79 mmol) of bis(thiazole) **7**; 283.1 mg (0.79 mmol) of 4,4'-bis(trimethylsiloxy)benzophenone; 0.45 mL (3.23 mmol) of triethylamine/3.8 mL NMP; R = $-$CO$-$. ¹H-NMR (THF-d_8): δ (ppm) 7.40 (m, 4H, H$_{ar}$), 7.60 (m, 1H, H$_{ar}$), 7.90 (m, 4H, H$_{ar}$), 8.05 (m, 2H, H$_{ar}$), 8.42 (m, 1H, H$_{ar}$). ¹⁹F-NMR (THF-d_8): δ (ppm) 12.9 (s, CF$_3$). ¹³C-NMR (THF-d_8): δ (ppm) 117.2 (C2''), 121.5 (q, $^1J_{C-F}$ = 269 Hz, CF$_3$), 123.9 (C5'), 129.2 (C4', C6'), 131.0 (C2'), 132.1 (q, $^2J_{C-F}$ = 37 Hz, C4), 133.2 (C3''), 134.6 (C1', C3'), 135.5 (C4''), 157.6 (C2), 159.4 (q, $^3J_{C-F}$ = 2 Hz, C5), 162.5 (C1''), 193.1 (C=O). IR (KBr): $\tilde{v}$ 3100$-$3040 (CH$_{aromat}$), 1661 (C=O), 1603, 1555, 1501, 1388, 1255$-$1130 (CF$_3$) cm^{-1}. Anal. Calc for (C$_{27}$H$_{12}$F$_6$N$_2$O$_3$S$_2$)$_n$ (590.5 g·mol^{-1})$_n$: C, 54.91; H, 2.05; N, 4.75; S, 10.86. Found: C, 55.04; H, 2.33; N, 5.59; S, 10.66.

References and Notes

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