Poly(aryl ether oxazole)s with Trifluoromethyl Side Groups

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ABSTRACT: In this paper the synthesis and characterization of four series of poly(aryl ether oxazole)s is described. Four different monomers of the type 2,5-bis(4′-fluorophenyl)oxazole were prepared. They differed in the number and position of trifluoromethyl substituents at the phenyl rings. From these monomers polymers were synthesized by nucleophilic displacement of the fluorine atoms with various bisphenols. The electron-withdrawing property of the oxazole ring in *para*-position of the 4-fluorophenyl rings activates the monomers for nucleophilic displacement reactions. Characterization by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, IR spectroscopy, GPC, DSC, thermogravimetry, and elemental analysis allowed us to determine the effect of the oxazole rings on solubility, glass transition temperature, and decomposition temperature in comparison with other five-membered heteroaromatic rings in polymers known from the literature. The oxazole rings increase solubility, decrease glass transition temperatures, and have no negative effect on the thermal stability. Introduction of trifluoromethyl groups at the phenyl rings improves solubility but has no simple uniform effect on the glass transition temperature.

Introduction

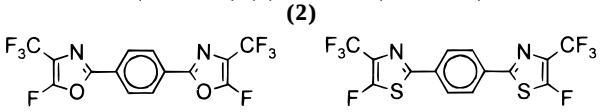
In two preceding papers,[1,2] we described the synthesis, characterization, and properties of two series of poly(aryl ether)s containing oxazole and thiazole rings with trifluoromethyl substituents in the 4-position. With few exceptions, these polymers were amorphous and easily soluble in a number of common organic solvents including THF and chloroform, as well as in more polar amidic solvents such as NMP or DMAc. It was found that the oxazole-containing polymers exhibited surprisingly low thermal stabilities.[1] When the oxazole rings were replaced by thiazole rings, decomposition temperatures in the range of 420−490 °C were observed,[2] which is more close to the values generally found for polymers with five-membered heteroaromatic rings in the main chain.[3] The low decomposition temperature of the polymers with trifluoromethyl-substituted oxazole rings is probably due to a ring scission of the oxazole, which is facilitated by the presence of the trifluoromethyl group in the 4-position. The similarly composed thiazole rings are not destabilized as much by the substituent in 4-position, since the sulfur heteroaromatic systems are known to exhibit a more pronounced aromatic character than their oxygen analogues.[4−6]

The present paper describes the synthesis of another class of oxazole-containing monomers and polymers therefrom. In these monomers, there is no substituent in the 4-position of the oxazole rings. Instead, trifluoromethyl groups are introduced into phenyl rings in order to study their influence on polymer properties and also to allow a comparison with the oxazole polymers of our earlier study.

Synthesis of the Monomers

In our earlier studies[1,2] we investigated poly(aryl ether)s derived from monomers of the following structures (Chart 1).

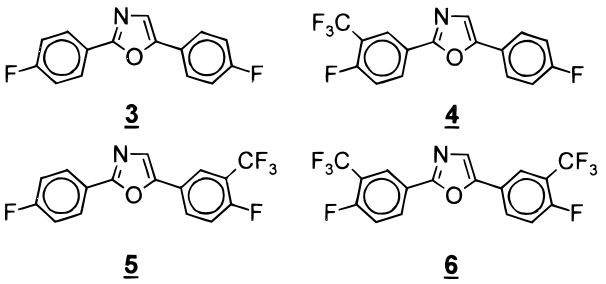
Chart 1. Bis(oxazole) (1) and Bis(thiazole) Monomers (2)



1 **2**

For the present study, we prepared a series of monomers in which the oxazole rings did not have any substituents in the 4-position. Since we wanted to compare the properties of the new poly(aryl ether oxazole)s to those of the polymers prepared from **1** and **2**, we also introduced trifluoromethyl groups in certain positions. Chart 2 shows the monomer structures.

Chart 2. Structures of the Oxazole Monomers 3, 4, 5, and 6



3 **4**

5 **6**

While the polymers derived from monomer **6** with the two trifluoromethyl groups in *ortho*-position to the activated fluorine atoms should be directly comparable to those based on monomers **1** and **2**, the polymers obtained from monomers **3**−**5** should allow some conclusions regarding the influence of the trifluoromethyl groups on the properties of these polymers.

In the literature, numerous methods for the preparation of oxazole rings with various substitution patterns can be found. We chose to synthesize our monomers according to a reaction discovered by Huisgen[7] from the correspondingly substituted benzonitriles and benzoyl chlorides, since the starting materials with the correct

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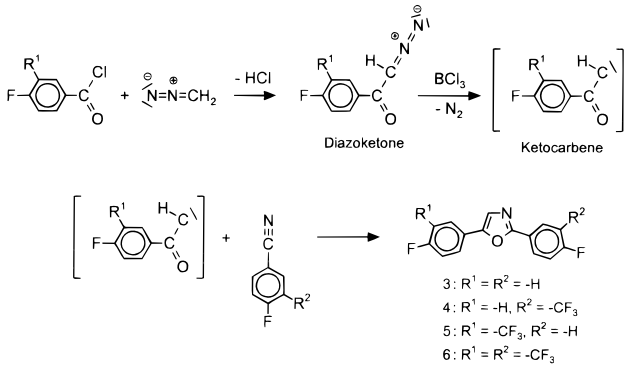
substitution pattern are commercially available. The synthesis involves the preparation of the diazoketone from the corresponding benzoyl chloride and diazomethane in the first step. Subsequently, the diazoketone is reacted with the benzonitrile, using a Lewis acid as a catalyst in a multistep cycloaddition reaction to form the oxazole. The yields after these two steps are fairly high (70%) with respect to the amount of benzoyl chloride used initially. Scheme 1 shows the reaction pathway.[8,9]

Scheme 1. Synthesis of the Oxazole Monomers 3−6



A large excess of the nitrile is required to achieve acceptable yields. However, in our syntheses the nitrile could be recovered easily by vacuum distillation. Therefore, this posed no problem even when the rather expensive 3-(trifluoromethyl)-4-fluorobenzonitrile was used.

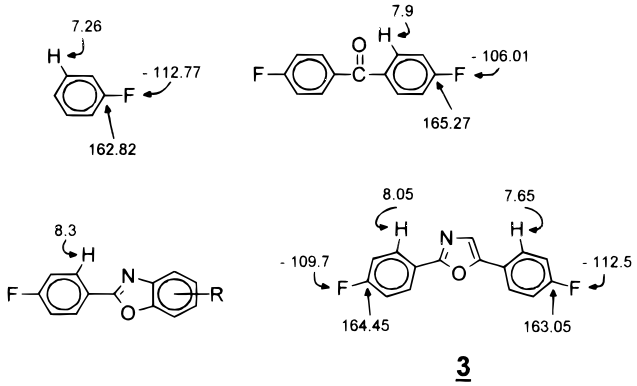
The use of diazomethane is safe, if it is prepared as a solution in diethyl ether from a commercial precursor and reacted immediately with the acid chloride, rather than collected separately. In this case, only a very small amount of diazomethane solution is present at any time. In this way, the hazards connected with the use of diazomethane are minimized. Since the HCl evolving in this reaction also reacts with diazomethane, triethylamine is used to trap HCl in order to avoid the necessity of a 2-fold excess of diazomethane.

The monomers **3**−**6** are crystalline with melting points (T_m) of 143 °C for **3**, 93 °C for **4** and **5**, and 137 °C for **6**. This trend clearly reflects the symmetry of the molecules. The unsubstituted monomer **3** exhibits the highest melting point in this series. With only one trifluoromethyl group added, the melting point drops by 50 °C. The addition of another trifluoromethyl group restores the symmetry somewhat, and therefore increases T_m again by 44 °C.

Reactivity of the Monomers 3−6. Hedrick[10−12] and Carter[13,14] have shown in several papers on poly(heteroaryl ether)s from 4-fluorophenyl-substituted five-membered heterocycles such as 1,3,4-oxadiazole, 1,2,4-triazoles, and benzoxazoles, that the ^{1}H, ^{13}C, and ^{19}F NMR data can give an indication of a new monomer's ability to undergo nucleophilic displacement of the fluorine atoms. However, although monomer **3** is comparable to Hedrick's and Carter's monomers, it does not fit well into this series.

The 2- and 5-positions in the oxazole ring are not identical, and therefore the chemical shifts of the signals of the two fluorophenyl groups in **3** are not equal. Scheme 2 shows a comparison of the chemical shifts of certain important atoms in **3** with those in 4,4-difluorobenzophenone, a 4′-fluorophenyl benzoxazole derivative, and fluorobenzene.

Scheme 2. Comparison of Chemical Shifts of the Signals of Certain Important Atoms in the NMR Spectra of Monomer 3, 4,4′-Difluorobenzophenone, 4′-Fluorophenyl Benzoxazole Derivatives, and Fluorobenzene (Shifts in ppm, ^{1}H and ^{13}C NMR Relative to TMS, ^{19}F NMR Relative to $CFCl_3$)



3

While the chemical shifts of the NMR signals of the fluorophenyl group in the 2-position of the oxazole ring indicate a downfield shift similar to the one in 4,4′-difluorobenzophenone, the shifts of the signals of the fluorophenyl group in the 5-position are so close to those in fluorobenzene that one would not expect monomer **3** to be activated sufficiently to allow polymer formation. However, the model reaction between this monomer and phenol in *N*-methylpyrrolidone (NMP), using potassium carbonate as a base and toluene for azeotropic removal of the water formed during the reaction, proceeds with a yield of more than 95%. This clearly indicates that monomer **3** is suitable for polymer formation. The other monomers in this series are more activated than **3** due to their trifluoromethyl groups.

Synthesis of the Polymers

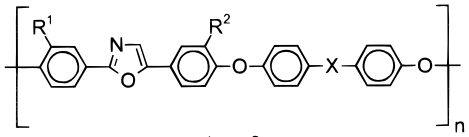
In a previous paper,[15] we reported the optimization of the reaction conditions required to achieve high molar masses by condensation of monomer **3** with Bisphenol A. It was found that although the model reaction proceeded nicely at 160 °C in NMP, rather high reaction temperatures of 200 °C were required for successful polymer synthesis, and when 1,3-dimethylpyrimidin-2-one (DMPU) was used as a solvent, higher molar masses were achieved than in *N*-methylpyrrolidone (NMP), *N*-methylcaprolactam (NMC), or dimethyl sulfoxide (DMSO). Thus, these optimized reaction conditions were chosen for the synthesis of polymers of the types **7**−**10**, with some adjustment of the reaction time to allow for the different nucleophilicities of the bisphenols used.

Characterization of the Poly(aryl ether oxazole)s

Molar Masses. Chart 3 and Table 1 show the structures, molar masses, and molar mass distributions of the polymers obtained from the monomers **3**−**6**.

Gel permeation chromatography (GPC) is a very convenient method for the determination of molar masses. However, since it is related to the hydrodynamic radius of the polymers in solution, it does not yield absolute values. Calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate

Chart 3. Structures of the Poly(aryl ether oxazole)s 7−10 (for X See Table 1)



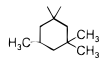
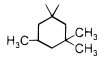
7: $R^1 = R^2 = H$

8: $R^1 = CF_3$, $R^2 = H$

9: $R^1 = H$, $R^2 = CF_3$

10: $R^1 = R^2 = CF_3$

Table 1. Structures and Molar Masses of the Poly(aryl ether oxazole)s 7−10[a]

Polymer	-X-	reaction time	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$
		h	g · mol^{-1}	g · mol^{-1}	
7a	-C(CH$_3$)$_2$-	12	15 000	35 000	2.3
7b	-C(CF$_3$)$_2$-	10	11 000	28 000	2.5
7c	-SO$_2$-	16	15 000	36 000	2.4
7d		16	6 400	12 000	1.9
8a	-C(CH$_3$)$_2$-	10	15 000	70 000	4.7
8b	-C(CF$_3$)$_2$-	8	11 000	34 000	3.1
9a	-C(CH$_3$)$_2$-	10	14 000	67 500	4.8
9b	-C(CF$_3$)$_2$-	8	15 000	57 000	3.8
10a	-C(CH$_3$)$_2$-	2	11 000	37 000	3.4
10b	-C(CF$_3$)$_2$-	2	27 000	87 000	3.2
10c	-O-	3	19 000	47 000	2.5
10d	-CO-	6	39 000	77 000	2.0
10e	-SO$_2$-	6	10 000	19 000	1.9
10f	—	6	22 000	83 000	3.8
10g		9	9 000	19 000	2.1
10h		9	24 000	128 000	5.3

[a] DMPU/toluene/K_2CO_3/200 °C. [b] GPC in THF (polystyrene calibration).

strongly from those of polystyrene. Therefore, we checked the results obtained for polymer **7a** by ^{1}H NMR spectroscopy and by end group titration. A molar mass of $\bar{M}_n = 15\,000$ as indicated by GPC for **7a** corresponds to a degree of polymerization of 67, which is not too high for end group analysis. In the proton NMR spectrum, the signal of the phenol end groups is detected at 9.35 ppm, while the fluorine end group can be seen at −111.2 ppm (relative to $CFCl_3$) in the ^{19}F NMR spectrum. Assuming one phenol and one fluorine end group, the analysis of the proton NMR spectrum results in $\bar{M}_n = 15\,200$, while the end group titration (NaOH in THF solution, phenolphthalein as indicator) yields $\bar{M}_n = 12\,000$. These values prove that, for the class of polymers described in this study, GPC in THF with polystyrene calibration gives a good approximation of the molar masses.

Structure. ^{1}H, ^{13}C, and ^{19}F NMR spectra as well as IR spectra and elemental analysis confirm the structure of the polymers **7**−**10**. The ^{19}F NMR spectrum of polymer **7a** shows only one signal at $\delta = -111.2$ ppm for the fluorine end group. Since the oxazole monomer **3** (as well as the other oxazole monomers used in this study) exhibit two signals (at −109.7 and −112.5 ppm) for its two different fluorine atoms, one could expect to see two different end group signals as well. However, in oxazole rings the 2-position is generally much more activated for nucleophilic reactions than the 5-position. Therefore, the more reactive fluorine group, which is the one in the fluorophenyl ring attached to the oxazole in the 2-position, should react completely and not remain as an end group in the polymer. Consequently, only the signal of the less reactive fluorine atom is observed. In the fluorine NMR spectra of the polymers with trifluoromethyl groups, no end group signal can be detected due to the high intensity of the signals of the trifluoromethyl groups.

In the case of bis(4-chloro-3-trifluoromethyl) sulfone it has been shown[16] that trifluoromethyl groups in an *ortho*-position to the reaction site of the nucleophilic displacement can be degraded under certain reaction conditions. However, in this case very drastic reaction conditions with final temperatures of 280 °C were employed. It was found that the resulting polymers had partially lost the trifluoromethyl groups, which was attributed to hydrolysis by trace amounts of water and subsequent decarboxylation. When the trifluoromethyl groups were in a *meta*-position to the site of the formation of the ether bond, as in bis(4-chloro-2-trifluoromethyl) sulfone, all CF_3 groups were retained. This is clear proof that there is no inherent instability in the trifluoromethyl groups under such reaction conditions. In our previous work[1,2] we showed that trifluoromethyl groups are not degraded even when they are in an *ortho*-position to the reaction site, when mild reaction conditions are employed.

Although reaction temperatures up to 200 °C were routinely used for the preparation of the polymers in the present study, we did not discover any indication for degradation of the trifluoromethyl groups in the polymers derived from monomers **4**, **5**, or **6**. In the case of polymer **10b** the trifluoromethyl groups of the hexafluoroisopropyl group can serve as an internal reference. Thus, in the ^{19}F NMR spectrum of this polymer the signal at −64.5 ppm (hexafluoroisopropyl group) and the group of signals at −62.6 to −63.1 ppm (CF_3 groups at phenyl rings) are of equal intensity, proving the integrity of the trifluoromethyl groups on the phenyl rings. In addition, the elemental analyses of all polymers did not show any discrepancy which could be attributed to loss of fluorine.

Solubility. All polymers prepared in this study are soluble up to 30% (w/v) in polar solvents such as NMP, DMPU, THF, and 1,2,4-trichlorobenzene at room temperature. With the exception of **10d**, they are also soluble in chloroform and toluene at 20 °C. On heating, even **10d** is dissolved by these two solvents. Acetone dissolves all polymers **7**−**10** under reflux conditions. The good solubility of these oxazole-containing polymers is in marked contrast to the behavior of other polymers with five-membered heteroaromatic rings. For example, an oxadiazole-containing polymer similar to **7c** has been found[17] to be soluble only in *m*-cresol and sulfuric acid, while others similar to **7a** and **7b** had only "limited solubility"[11] in NMP at room temperature. Polymers with thiadiazole groups[18] are soluble in NMP and chloroform at room temperature (among other solvents) but insoluble in THF, even on heating. A 1*H*-pyrazole ring[19] in place of the oxazole ring in **7c** renders the polymer insoluble in chloroform. All polymers compared here are completely amorphous. The surprisingly good solubility of the poly(aryl ether oxazole)s, in contrast

to the other heteroaromatic poly(aryl ether)s even in solvents of low polarity such as toluene, must obviously be attributed to the various heteroaromatic rings. The geometries of the oxazole and the 1,3,4-oxadiazole rings are very similar. The difference between the catenation angles (132° for the oxazole, 134° for the oxadiazole) is only 2°, which is certainly too small to account for large differences in the physical properties of the corresponding polymers. The real reason is most likely the polarity of the heteroaromatic rings. The value of the dipole moment of the 1,3,4-oxadiazole is 10.14×10^{-30} Cm,[20] which is twice as high as the value for the oxazole, which is only 5.0×10^{-30} Cm.[20] For the 1,3,4-thiadiazole a value of 10.94×10^{-30} Cm[20] can be found in the literature. Although the pyrazole ring itself is less polar (dipole moment 7.37×10^{-30} Cm[20]), the possibility of H-bond formation can certainly account for the insolubility of polymers containing this structure element in nonpolar solvents.

Thermal Properties. In DSC measurements, none of the polymers **7**−**10** displayed any evidence of crystallinity. Only glass transitions could be detected. Considering the angled geometry of the repeating unit, caused by the oxazole ring, we did not expect to find semicrystalline morphologies. This is especially true for those polymers with trifluoromethyl substituents, since the substituents can be expected to disrupt any regular packing and therefore prevent crystallization.

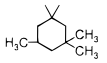
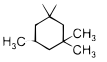
Dynamic thermogravimetry in air showed the relatively good thermal stability of the poly(aryl ether oxazole)s. A weight loss of 5% was detected at 430−470 °C, which is comparable to other polymers with five-membered heteroaromatic units in the backbone.[3] In air, the decomposition takes place in two distinct steps, the second one, starting at approximately 550 °C, being oxidative combustion. In nitrogen, only one step is observed, but the temperature at which a weight loss of 5% occurs is not significantly different from the experiment in air.

In a previous paper,[1] we reported on polymers containing two trifluoromethyl substituted oxazole rings per repeating unit. These polymers exhibited unexpectedly low decomposition temperatures with onsets of weight loss around 310 °C. This was attributed to the substitution pattern with substituents in the 4-position of the oxazole ring.[1] In contrast, the oxazole polymers described in the present paper show much higher decomposition temperatures. This indicates that the oxazole ring in itself is not thermally unstable (or at least not more than other five-membered heteroaromatic rings), but it indeed shows a certain substitution pattern including trifluoromethyl groups in the 4-position of the oxazole, which must be avoided.

Table 2 summarizes the glass transition and the decomposition temperatures of the poly(aryl ether oxazole)s **7**−**10**.

Within each series of polymers the trend of the glass transition temperatures with the nature of the linking group **X** from the bisphenol follows the expectations. Flexible groups result in low T_g's, while strongly polar, stiff, or bulky groups increase the glass transition temperature. More interesting phenomena can be observed when **X** is kept constant, while the number of the trifluoromethyl groups is varied. In the series of polymers with **X** = $-C(CF_3)_2-$, the glass transition temperature rises from 191 °C (**7b**, no CF_3 group) to 195 and 196 °C (**8b** and **9b**, one CF_3 group) and to 205 °C (**10b**, two CF_3 groups). This is to be expected and can be attributed to the chain stiffening, which is caused by the introduction of the trifluoromethyl groups in the *ortho*-position to ether linkages. The rotation of these ether linkages becomes limited due to the bulkiness of the trifluoromethyl groups.

Table 2. Glass Transition and Decomposition Temperatures of the Poly(aryl ether oxazole)s 7−10

Polymer	-X-	T_g[a] °C	T_d[b] °C
7a	$-C(CH_3)_2-$	169	466
7b	$-C(CF_3)_2-$	191	433
7c	$-SO_2-$	195	445
7d		200	440
8a	$-C(CH_3)_2-$	154	430
8b	$-C(CF_3)_2-$	195	430
9a	$-C(CH_3)_2-$	153	428
9b	$-C(CF_3)_2-$	196	447
10a	$-C(CH_3)_2-$	185	443
10b	$-C(CF_3)_2-$	205	441
10c	-O-	180	448
10d	-CO-	195	445
10e	$-SO_2-$	210	441
10f	—	200	460
10g		195	448
10h		220	411

[a] DSC, 20 K/min. [b] 5% weight loss in dynamic thermogravimetry, 10 K/min, air.

However, with **X** = $-C(CH_3)_2-$ the situation is more complicated. In this case, the glass transition temperature first drops from 169 °C (**7a**, no CF_3 group) to 154 and 153 °C (**8a** and **9a**, one CF_3 group), and then rises again to 185 °C (**10a**, two CF_3 groups). There are two effects to be considered, caused by the introduction of the trifluoromethyl groups. First, there is the chain stiffening caused by sterical hindrance and restriction of rotational movements around the ether bonds. This should increase T_g, as was observed indeed for the polymers with **X** = $-C(CF_3)_2-$. Second, each additional substituent also decreases the chain packing density and therefore increases the fractional free volume because of its spatial requirements. Increased free volume enhances main chain movements and therefore decreases T_g. In the case of the polymers **a** with **X** = $-C(CH_3)_2-$, the introduction of one trifluoromethyl group results in a decrease of the glass transition temperature, because the polymer backbone is flexible enough to utilize the additional free volume for additional chain movements. The stiffening caused by sterical hindrance due to the trifluoromethyl group is not strong enough to prevent this. When two trifluoromethyl groups are added, these movements are no longer possible, because the polymer backbone is stiffened too much. T_g is increased by 16 °C on the introduction of two trifluoromethyl groups (**7a**, 169 °C → **10a**, 185 °C).

In contrast, in the series of the polymers **b** (**X** = $-C(CF_3)_2-$), the backbone of the polymers is inherently stiffer due to the presence of the hexafluoroisopropy-

lidene group. Polymer **7b** exhibits a glass transition temperature which is 22 °C higher than that of **7a** (191 vs 169 °C). Thus, in this case the additional free volume introduced by the addition of one trifluoromethyl group (**8b** or **9b**) cannot be used for addition chain motions. Here, the stiffening effect of the CF_3 group always dominates. Introduction of a second trifluoromethyl group further increases the chain stiffness and T_g. The two trifluoromethyl groups increase T_g by 14 °C (**7b**, 191 °C → **10b**, 205 °C).

This behavior promises interesting results for example in gas permeability measurements. In the series of the polymers **a**, the introduction of one trifluoromethyl group results in increased free volume, which generally leads to increased permeability coefficients. At the same time, increased chain mobility can be expected to cause a loss in selectivity. Thus, here the usual tradeoff behavior between permeability coefficients and selectivity can be expected. In the series of the polymers **b** the free volume is probably also increased by the addition of one trifluoromethyl group. However, here there are no additional chain movements possible. Therefore, one can expect not only increased permeability coefficients but also increased selectivity. These polymers would deviate from the tradeoff behavior and allow design of permeation properties at least to some degree. Free-standing films can be prepared from all polymers descibed here (except **7d** and **10g**). However, on prolonged drying in a vacuum (50 °C, 1 week) even those prepared from the polymers with relatively high molar masses such as **10b**, **10d**, and **10h** have proved to be too brittle for permeability measurements. The intrinsic viscosity of **7a** was measured to be 0.51 dL/g (at 25 °C in NMP), which is comparable to the values reported by Herick et al.[21] for the corresponding oxadiazole polymer (0.45 at 25 °C in NMP). So far, we have no explanation for the unexpected brittleness of the oxazole polymers. At present, we can only speculate that there are fewer attractive main chain interactions as compared to the oxadiazole polymers, since the oxazole ring is less polar than the oxadiazole ring.

Comparison of the Glass Transition Temperatures with Those for Other Heteroaromatic Polyethers. We have discussed the solubility behavior of our poly(aryl ether oxazole)s in comparison with similar heteroaromatic polyethers based on the polarity and geometry of the heterocycles. These two properties of the heterocycles should also have a pronounced effect on the glass transition temperatures. Table 3 shows a summary of this comparison.

All polymers summarized in Table 3 with a heteroaromatic ring in place of Ar are amorphous, while the *p*,*p*,*p*-terphenyl polymer **11a** is semicrystalline with a very high melting point. The heterocycles induce kinks into the polymer backbone with catenation angles between 132 and 157°, which apparently prevents crystal order. However, heteroaromatic poly(aryl ether)s are not generally amorphous. In particular, when carbonyl groups are introduced, semicrystalline morphologies have been observed.[3,17]

From Table 3 it can also be seen that the introduction of five-membered heterocycles reduces the glass transition temperature considerably in comparison to a 1,4-phenylene ring. The pyrazole ring is an exception to this rule, most probably because of its ability to form hydrogen bonds involving the NH group. It is interesting to note that the oxazole ring decreases T_g much more than the oxadiazole ring, despite the very similar geometry of these two rings. The glass transition temperature of **7c** is 55 °C below the one of **11a**, while the T_g of **11b** is only decreased by 24 °C in comparison to **11a**. Thus, the geometry of the heterocycle cannot be the dominant factor here. The most likely reason for this effect is the difference in polarity between oxazole and oxadiazole rings, as is evidenced by the dipole moments: the dipole moment of the oxadiazole ring is higher than the one of the oxazole ring by a factor of 2. This view is strongly supported by the observation that the introduction of a thiadiazole ring in place of an oxadiazole ring does not change T_g much, despite the much more extended main chain geometry caused by the larger catenation angle of the sulfur heterocycle. While there is a large difference in the geometry of the thiadiazole and the oxadiazole, the dipole moments are very similar. If the glass transition temperatures are dominated by the polarity of the heterocycle, as explained before, this behavior can be easily understood.

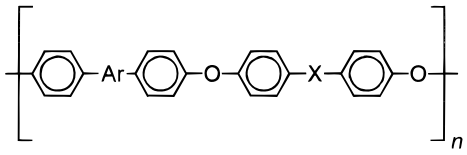


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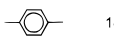
Table 3. Comparison of the Glass Transition Temperatures of Various Poly(heteroaryl ether)s

Polymer No.	Ar: Structure	Ar: catenation angle / degree	Ar: dipole moment[20] / 10^{-30} Cm	X	T_g / °C	T_m / °C	Ref.
11a		180	-	$-SO_2-$	250	400	25)
7c		132[21]	5.0	$-SO_2-$	195	-	this work
11b		134[22]	10.14	$-SO_2-$	226	-	17)
11c		155[23]	7.37	$-SO_2-$	260	-	19)
7a		132	5.0	$-C(CH_3)_2-$	169	-	this work
11d		134	10.14	$-C(CH_3)_2-$	201	-	11)
11e		157[24]	10.94	$-C(CH_3)_2-$	204	-	18)
7b		132	5.0	$-C(CF_3)_2-$	191	-	this work
11f		134	10.14	$-C(CF_3)_2-$	210	-	11)
11g		157	10.94	$-C(CF_3)_2-$	211	-	18)

Conclusions

In this paper we have shown that a noncondensed oxazole ring can be used to activate nucleophilic fluorine displacement in the synthesis of aromatic polyethers. Polymer synthesis was successful, although the oxazole ring is certainly less electron poor than oxadiazole rings, and the oxazole monomers can therefore be expected to exhibit lower reactivity.

The poly(aryl ether oxazole)s described in the present study were amorphous and not only exhibited good solubility in polar solvents such as NMP or DMAc, as is common for poly(aryl ether)s but also were soluble in solvents of rather low polarity, such as toluene. Thus,

the oxazole-containing polymers proved to be much more soluble than their oxadiazole-, thiadiazole-, or pyrazole-containing counterparts, which have been described earlier in the literature.

In comparison with other five-membered heteroaromatic units, the oxazole ring leads to rather low glass transition temperatures. Despite the fact that its geometry is very similar to the one of the oxadiazole ring, oxazole-containing polymers show T_g's approximately 20−30 °C below those of the oxadiazole analogues. This can be attributed to the rather low polarity of the oxazole ring. It shows that in a series of analogous polymers the polarity of the structural units can have a stronger effect on T_g than the geometry.

In the series of polymers discussed here, the number and position of trifluoromethyl groups in the repeating unit was varied. As a result, it was found that the effect of the CF_3 substituents depends strongly on the flexibility of the rest of the polymer chain. With a rather stiff backbone, the introduction of only one trifluoromethyl substituent results in a small increase of T_g, while in a more flexible polymer one additional trifluoromethyl substituent actually caused a decrease in T_g. The addition of two CF_3 groups always increased T_g. The introduction of any substituent in a polymer backbone has two effects: an increase in free volume and a decrease in rotational mobility of the polymer backbone. Both effects are caused by increased sterical demands, yet they are acting against each other, since more free volume tends to cause more chain movements and hence decreases T_g, while hindered chain rotations, e.g., around ether bonds, tend to increase T_g. Which effect dominates apparently depends on the overall rigidity of the backbone. Thus, our conclusions must take into account the position of a substituent and the nature of the rest of the polymer chain as well as the nature of the substituent itself.

Experimental Part

Fourier-transform IR-spectra were recorded on a Bruker IFS 55 spectrometer. For ^1H, ^{13}C, and ^{19}F NMR spectra, a Bruker ARX 300 spectrometer was used with tetramethylsilane as internal reference for ^1H and ^{13}C and $CFCl_3$ as internal reference for ^{19}F. DSC measurements were performed with a Perkin-Elmer DSC 7; for thermogravimetry a Polymer Laboratories STA 1500 H was used. GPC chromatograms were obtained on a system with four columns filled with Ultrastyragel, with 7 μm bead diameter, pore diameters 500, 10^3, 10^4, and 10^5 Å, eluent THF, and polystyrene calibration. Elemental analysis were performed by Ilse Beetz Mikroanalytisches Laboratorium, Postfach 1164, D-96301 Kronach, Germany.

All syntheses were performed under a dry argon atmosphere. 2,2-Bis(4′-hydroxyphenyl)propane and 1,1-bis(4′-hydroxyphenyl)-3,3,5-trimethylcyclohexane were obtained from Bayer AG and were recrystallized from toluene and ethanol/ethyl acetate, respectively. 2,2-Bis(4′-hydroxyphenyl)hexafluoropropane was obtained from Hoechst AG and was used without further purification. All other chemicals were used as obtained from Fluka or Aldrich.

Toluene and THF were dried over K/Na alloy, the chlorinated solvents were dried over CaH_2, and the amidic solvents were dried over P_2O_5. All solvents were distilled freshly before use.

The diazomethane was prepared using a DIAZALD kit from Aldrich with clear, unground glass joints. *Caution!* Diazomethane is very toxic and is a dangerous explosive. Spontaneous explosions have been observed in glass apparatus with ground joints or any sharp edges and on the action of UV light. Care must be taken to minimize the risks connected with the use of diazomethane. Therefore we used a procedure in which the amount of diazomethane present at any given time is minimized.

Synthesis of the Diazoketones (General Procedure). A DIAZALD apparatus (Aldrich), consisting of a Schlenk-tube equipped with an addition funnel and a distillation bridge with dry ice cooler, was used. The addition funnel was charged with 5 g (23 mmol) of *N*-methyl-*N*-nitroso-4-toluenesulfonamide (Diazald, Aldrich) in 50 mL of diethyl ether. A mixture of 4 mL of water, 2.5 g (44.5 mmol) of KOH, 14 mL of 2-ethoxyethanol, and 8 mL of diethyl ether was placed into the Schlenk-tube. The distillation bridge was connected to a flask charged with either a mixture of 2.7 g (17 mmol) of 4-fluorobenzoic acid chloride and 1.83 g (18 mmol) of triethylamine in 10 mL of diethyl ether, or with 1.82 g (7.8 mmol) of 4-fluoro-3-(trifluoromethyl)benzoyl chloride in 10 mL of diethyl ether. This flask was cooled to −20 °C, while the KOH solution in the Schlenk tube was heated to 70 °C. The Diazald solution was added dropwise to the warm KOH solution within 20 min. Diazomethane formed and was distilled off constantly together with diethyl ether from the warm KOH solution, condensed into the precooled reaction flask, and reacted immediately with the acid chloride. Thus, there was never more than a couple of drops of diazomethane solution present at any time in the reaction apparatus.

The diazoketone derived from 4-fluorobenzoyl chloride is soluble in diethyl ether. Therefore, in this case after the end of the reaction, triethylammonium hydrochloride formed by the reaction was filtered off, the solvent was removed under reduced pressure, and 2.74 g (17 mmol) of 4-fluorodiazoacetophenone were obtained as yellow crystalline powder. Further purification was not attempted. The yield was quantitative based on the amount of acid chloride.

The diazoketone derived from 4-fluoro-3-(trifluoromethyl)-benzoyl chloride is insoluble in diethyl ether. Therefore, no triethylamine can be used to trap the hydrogen chloride formed during the reaction, because separation of the desired diazoketone from trimethylammonium hydrochloride would be very difficult. In this case, the hydrogen chloride reacted with additional diazomethane, requiring the use of a 2-fold excess of diazomethane. When the reaction was completed, the solvent was removed under reduced pressure, and 1.8 g (7.8 mmol) of 4-fluoro-3-(trifluoromethyl)diazoacetophenone was obtained as yellow crystalline powder. Again, the yield was quantitative based on the amount of acid chloride.

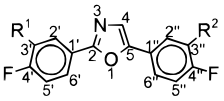
Both diazoketones decompose above 50 °C.

4-Fluorodiazoacetophenone. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3082, 2108, 1602, 1585, 1506, 1413, 1365, 1157, 1099, 1078, 842, 746, 673, 607. ^1H NMR ($CDCl_3$): δ (ppm) = 7.8 (m, H2, 2H), 7.2 (m, H3, 2H), 5.9 (s, −C*H*=N_2, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 183.3 (s, *C*=O), 165.3 (d, $^1J_{C-F}$ = 240 Hz, C4), 132.9 (d, $^4J_{C-F}$ = 3 Hz, C1), 129.8 (d, $^3J_{C-F}$ = 7 Hz, C2), 115.1 (d, $^2J_{C-F}$ = 2 Hz, C3), 54.8 (−*C*H=N_2). ^{19}F NMR ($CHCl_3$): δ (ppm) = −110,3 ppm.

4-Fluoro-3-(trifluoromethyl)diazoacetophenone. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3070, 2118, 1603, 1581, 1505, 1430, 1365, 1157, 1099, 1068, 852, 790, 670. ^1H NMR ($CDCl_3$): δ (ppm) = 8.03 (m, H2, 1H), 7.97 (m, H6, 1H), 7.29 (m, H5, 1H), 5.9 (−C*H*=N_2). ^{13}C NMR ($CDCl_3$): δ (ppm) = 183.3 (*C*=O), 162.3 (C4), 133.0 (C1), 132.6 (C6), 126.3 (−*C*F_3), 122.1 (C2), 117.7 (C3), 117.4 (C5), 54.8 (−*C*H=N_2). ^{19}F NMR ($CHCl_3$): δ (ppm) = −110.3 (F4), −65.3 (−C*F*$_3$).

Synthesis of the Monomers (General Procedure). A mixture of 163 mmol of the nitrile (4-fluorobenzonitrile or 4-fluoro-3-(trifluoromethyl)benzonitrile) and 7 mL of BF_3·Et_2O in 200 mL of dry dichloromethane was cooled to 0 °C. Then a solution of 16.3 mmol of the diazoacetophenone (4-fluorodiazoacetophenone or 4-fluoro-3-(trifluoromethyl)diazoacetophenone) in 20 mL of dry dichloromethane was added dropwise within 30 min. After the evolution of nitrogen stopped, 100 mL of 20% aqueous NaOH was added, and the resulting mixture was extracted three times with 50 mL of diethyl ether each. The ether extracts were combined and the solvent was removed under reduced pressure, and from the resulting oil, the excess nitrile was removed at 0.1 mmHg and 80 °C (4-

fluorobenzonitrile) or 100 °C (4-fluoro-3-(trifluoromethyl)-benzonitrile). The resulting crude product was recrystallized from dichloromethane/hexane (1:1, v/v) and sublimed at 180 °C and 0.01 mmHg. The yield was 70% based on the diazoketone employed.



Monomer 3 ($R^1 = R^2 = H$). Fp: 145 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3110, 1600, 1502, 1491, 1244, 1232, 1224, 1215, 950, 931, 738, 732, 505. ^1H NMR ($CDCl_3$): δ (ppm) = 8.05 (m, H2′), 7.65 (m, H2″), 7.33 (s, H4), 7.14 (m, H3′ and H3″). ^{13}C NMR ($CDCl_3$): δ (ppm) = 164.5 (d, C4′, $^1J_{C-F}$ = 249 Hz), 163.1 (d, C4″, $^1J_{C-F}$ = 249 Hz), 160,7 (C2), 150.9 (C5), 128.7 (d, C2′, $^3J_{C-F}$ = 8 Hz), 126.4 (d, C2″, $^3J_{C-F}$ = 8 Hz), 124.8 (C1′), 124.3 (C1″), 123.5 (C4), 116.4 (d, C3′, $^2J_{C-F}$ = 22 Hz), 116.3 (d, $^2J_{C-F}$ = 22 Hz). ^{19}F NMR ($CHCl_3$): δ (ppm) = −109.7 (F4′), −112.5 (F4″). Anal. Calcd for $C_{15}H_9F_2NO$, 257.24 g·mol^{-1}: C, 70.04; H, 3.53. Found: C, 69.8; H, 3.5.

Monomer 4 ($R^1 = -CF_3$, $R^2 = H$). Fp: 93 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3117, 1610, 1512, 1480, 1225, 1205, 930, 738, 732, 525. ^1H NMR ($CDCl_3$): δ (ppm) = 8.22 (m, H6′), 8.15 (m, H2′), 7.58 (m, H2″), 7.2 (m, H5′), 7.05 (m, H4 and H3″). ^{13}C NMR ($CDCl_3$): δ (ppm) = 163.4 (d, C4″, $^1J_{C-F}$ = 251 Hz), 161.2 (d, C4′, $^1J_{C-F}$ = 261 Hz), 159.3 (C2), 151.7 (C5), 132.1 (d, C2″, $^3J_{C-F}$ = 9 Hz), 130.9 (m, C6′), 126.7 (m, C2′), 125.7 (C1″), 124.4 (C1′), 123.7 (C4), 119.8 (q, C3′, $^2J_{C-F}$ = 33 Hz), 118.2 (d, C5′, $^2J_{C-F}$ = 21 Hz), 116.7 (d, C3″ $^2J_{C-F}$ = 22 Hz), -CF_3 (R^1) cannot be assigned because of overlapping signals. ^{19}F NMR ($CHCl_3$): δ (ppm) = −111.6 (F4′), −111.9 (F4″), −62.1 (−CF_3). Anal. Calcd for $C_{16}H_8F_5NO$, 325.24 g·mol^{-1}: C, 59.09; H, 2.48. Found: C, 58.8; H, 2.5.

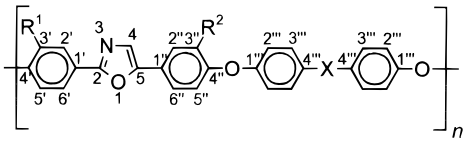
Monomer 5 ($R^1 = H$, $R^2 = -CF_3$). Fp: 93 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3120, 1610, 1512, 1480, 1225, 930, 738, 525. ^1H NMR ($CDCl_3$): δ (ppm) = 8.12 (m, H2″), 8.05 (m, H6″), 7.84 (m, H2′), 7.25 (m, H5″), 7.05 (m, H4 and H3′). ^{13}C NMR ($CDCl_3$): δ (ppm) = 163.2 (d, C4′, $^1J_{C-F}$ = 249 Hz), 160.8 (d, C4″, $^1J_{C-F}$ = 255 Hz), 159.2 (C2), 151.9 (C5), 132.0 (d, C2′, $^3J_{C-F}$ = 8 Hz), 131.5 (m, C6″), 126.9 (m, C2″), 125.7 (C1′), 124.4 (C1″), 123.7 (C4), 120.0 (q, C3″, $^2J_{C-F}$ = 31 Hz), 118.2 (d, C5″, $^2J_{C-F}$ = 21 Hz), 117.4 (d, C3′ $^2J_{C-F}$ = 20 Hz), −CF_3 (R^2) cannot be assigned because of overlapping signals. ^{19}F NMR ($CHCl_3$): δ (ppm) = −111.6 (F4′), −111.9 (F4″), −62.0 (−CF_3). Anal. Calcd for $C_{16}H_8F_5NO$, 325.24 g·mol^{-1}: C, 59.09; H, 2.48. Found: C, 58.9; H, 2.55.

Monomer 6 ($R^1 = R^2 = -CF_3$). Fp: 137 °C. IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3125, 1627, 1499, 1440, 1325, 1249, 1129, 687, 534. ^1H NMR ($CDCl_3$): δ (ppm) = 8.35 (m, H2′), 8.29 (m, H6′), 7.29 (m, H2″), 7.88 (m, H6″), 7.48 (m, H5″), 7.35 (s, H4), 7.32 (m, H5′). ^{13}C NMR ($CDCl_3$): δ (ppm) = 161.3 (d, C4′, $^1J_{C-F}$ = 262 Hz), 159.9 (d, C4″, $^1J_{C-F}$ = 257 Hz), 159.5 (C2), 150.2 (C5), 132.2 (d, C6″, $^3J_{C-F}$ = 9 Hz), 129.9 (d, C6′, $^3J_{C-F}$ = 9 Hz), 122.6 (q, −CF_3), 125.9 (m, C2′), 125.0 (C4), 124.4 (dq, C3″, $^2J_{C-F}$ = 41 Hz, $^2J_{C-F3}$ not determined), 124.3 (dq, C3′, $^2J_{C-F}$ = 41 Hz, $^2J_{C-F3}$ not determined), 120.1 (m, C1′), 119.7 (m, C1″), 118.4 (d, C5′, $^2J_{C-F}$ = 23 Hz), 118.3 (d, C5″, $^2J_{C-F}$ = 22 Hz). ^{19}F NMR ($CHCl_3$): δ (ppm) = −113.7 (F4′), −110.8 (F4″), −62.1 (−CF_3). Anal. Calcd for $C_{17}H_7F_8NO$, 393.24 g·mol^{-1}: C, 51.93; H, 1.79. Found: C, 51.6; H, 1.9.

Model Reaction. A 1.47 g (5.7 mmol) sample of 2,5-bis-(4,4′-fluorphenyl)oxazole and 1.4 g (15 mmol) of phenol were dissolved in a mixture of 20 mL of DMPU and 10 mL of toluene in a round-bottom flask with a nitrogen inlet and a Dean−Stark trap. Then 2.76 g (20 mmol) of K_2CO_3 was added, and the reaction mixture was heated to reflux. After 6 h, the toluene was distilled off and removed through the Dean−Stark trap. The reaction was continued for another 12 h and then cooled to room temperature. Then the mixture was extracted between water and chloroform (20 mL each), The organic phase was separated, dried over Na_2SO_4, and evaporated. The model compound was obtained as white, crystalline powder with a melting point of 120 °C (yield: 1.24 g; 95% based on the oxazole monomer).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1587, 1498, 1259, 1236, 831, 750, 690. ^1H NMR ($CDCl_3$): δ (ppm) = 8.05 (m, H2′), 7.65 (m, H2″), 7.37 (m, H2‴ and H2^{iv}), 7.34 (s, H4), 7.15 (m, H4‴ and H4^{iv}), 7.05 (m, H3′, H3″, H3‴, and H3^{iv}). ^{13}C NMR ($CDCl_3$): δ (ppm) = 160.6 (C2), 159.5 (C1‴), 157.6 (C1^{iv}), 156.7 (C4′), 150.7 (C5), 129.95 (C2′), 129.88 (C2″), 128.0 (C3‴), 125.8 (C3″), 124.1 (C4‴), 123.75 (C4^{iv}), 123.2 (C1′), 122.65 (C4), 122.35 (C1″), 119.65 (C3′), 119.25 (C3″), 119.05 (C2‴), 118.45 (C2^{iv}). Anal. Calcd for $C_{27}H_{19}NO$, 405.45 g·mol^{-1}: C, 74.47; H, 4.86. Found: C, 74.8; H, 4.75.

Polymerization (General Procedure). Equimolar amounts (2.5 mmol each) of oxazole monomer and Bisphenol were dissolved in 20 mL of DMPU and 10 mL of toluene under an inert atmosphere in a round-bottom flask with reflux condenser, nitrogen inlet, and a Dean−Stark trap. Potassium carbonate was added (0.75 g, 5.1 mmol), and the mixture was refluxed for 3 h at 180 °C oil bath temperature. During this time the toluene was replaced twice with fresh, dry toluene. Finally, the temperature of the oil bath was raised to 220 °C, while the toluene was removed through the Dean−Stark trap. After 4−16 h (depending on the oxazole monomer and the Bisphenol) 1 mL of acetic acid was added to neutralize the phenoxide, and the mixture was filtered hot to remove salts. After the reaction was cooled to ambient temperature, the polymer was precipitated by pouring the mixture into a mixture of 450 mL of methanol and 50 mL of water. The polymer was filtered off, washed with water and methanol, and dried under reduced pressure. Yields were quantitative.



Polymer 7a: $R^1 = R^2 = H$; X = $-C(CH_3)_2-$. Conditions: oxazole monomer **3**, 643.1 mg; Bisphenol A, 570.7 mg; reaction time, 12 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2965, 1599, 1493, 1238, 1170, 1013, 833. ^1H NMR ($CDCl_3$): δ (ppm) = 8.0 (m, H2′), 7.65 (m, H2″), 7.32 (s, H4), 7.25 (m, H3′ and H3″), 7.05 (m, H3‴), 6.95 (m, H2‴), 1.7 (s, −CH_3). ^{13}C NMR ($CDCl_3$): δ (ppm) = 162.0 (C2), 159.8 (C4′), 157.8 (C4″), 154.6/154.1 (C1‴), 151.6 (C5), 146.3 (C1′), 146.0 (C1″), 129.1 (C3‴), 128.9 (C2′), 126.0 (C2″), 123.7/122.8 (C4‴), 123.4 (C4), 119.3 (C2‴), 118.5 (C3′), 118.3 (C3″), 42.3 (−C(CH$_3$)$_2$−), 31.1 (−C(CH_3)$_2$−). Anal. Calcd for $(C_{30}H_{23}NO_3)_n$, (445.51 g·mol^{-1})$_n$: C, 80.88; H, 5.20. Found: C, 81.5; H, 4.90.

Polymer 7b: $R^1 = R^2 = H$; X = $-C(CF_3)_2-$. Conditions: oxazole monomer **3**, 643.1 mg; 2,2-bis(4′-hydroxyphenyl)-hexafluoropropane, 840.5 mg; reaction time, 10 h.

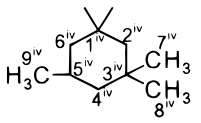
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1604, 1496, 1247, 1174, 1010, 968, 952, 831. ^1H NMR ($CDCl_3$): δ (ppm) = 8.0 (m, H2′), 7.6 (m, H2″), 7.3 (s, H4), 7.25 (m, H3′ and H3″), 7.2 (m, H3‴), 6.9 (m, H2‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 162.2 (C2), 159.8 (C4′), 157.9 (C4″), 156.8/156.4 (C1‴), 151.6 (C5), 146.3 (C1′), 146.0 (C1″), 132.1 (C4‴), 129.4 (C3‴), 128.9 (C2′), 125.1 (q, $^1J_{C-F}$ = 280 Hz, −C(CF$_3$)$_2$−), 126.0 (C2″), 123.4 (C4), 119.0 (C2‴), 118.5 (C3′), 118.5 (C3′), 118.3 (C3″), 64.9 (m, −C(CF$_3$)$_2$−). Anal. Calcd for $(C_{30}H_{17}F_6NO_3)_n$, (553.47 g·mol^{-1})$_n$: C, 65.11; H, 3.10. Found: C, 65.3; H, 3.30.

Polymer 7c: $R^1 = R^2 = H$; X = $-SO_2-$. Conditions: oxazole monomer **3**, 643.1 mg; 4,4′-dihydroxydiphenyl sulfone, 625.7 mg; reaction time, 16 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1614, 1587, 1490, 1420, 1240, 1150, 1012, 968, 950, 834. ^1H NMR ($CDCl_3$): δ (ppm) = 8.0 (m, H2′), 7.8 (m, H3′ and H3″), 7.65 (m, H2″), 7.3 (s, H4), 7.2 (m, H3‴), 6.95 (m, H2‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 162.3 (C2), 161.9 (C1‴), 158.2 (C4′), 156.4 (C4″), 151.5 (C5), 138.3 (C1′), 138.2 (C1″), 130.9 (C4‴), 129.6 (C3‴), 127.0 (C2′), 126.6 (C2″), 123.7

(C4), 120.3 (C3′), 119.6 (C3″), 116.2 (C2‴). Anal. Calcd for $(C_{27}H_{17}NO_5S)_n$, (467.50 g·mol^{-1})$_n$: C, 69.37; H, 3.67. Found: C, 69.0; H, 3.70.

Polymer 7d: $R^1 = R^2 = H$; X =



Conditions: oxazole monomer **3**, 643.1 mg; 1,1-bis(4′-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 766.0 mg; reaction time, 16 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3002, 1600, 1499, 1258, 1160, 1010, 833. ^{1}H NMR ($CDCl_3$): δ (ppm) = 7.95 (m, H2′), 7.55 (m, H2″), 7.3 (s, H4), 7.2 (m, H3′ and H3″), 7.0 (m, H3‴), 6.95 (m, H2‴), 2.6/2.4 (H2^{iv}), 1.9 (d, H6^{iv}), 1.37 (m, H5^{iv}), 1.1/0.8 (m, H4^{iv}), 0.9 (s, H7^{iv} and H8^{iv}), 0.4 (s, H9^{iv}). ^{13}C NMR ($CDCl_3$): δ (ppm) = 162.1 (C2), 159.7 (C4′), 158.1 (C4″), 156.8/155.6 (C1‴), 150.3 (C5), 148.3 (C1′), 147.7 (C1″), 145.6/139.3 (C4‴), 129.4/127.8 (C3‴), 128.9 (C2′), 126.2 (C2″), 123.6 (C4), 118.8 (C3′), 118.3 (C3″), 115.4/115.2 (C2‴), 67.8 (1^{iv}), 49.2 (C2^{iv}), 48.3 (C6^{iv}), 46.7 (C4^{iv}), 34.7 (C5^{iv}), 26.5/25.8 (C7^{iv} and C8^{iv}), 25.5 (C3^{iv}), 22.2 (C9^{iv}). Anal. Calcd for $(C_{36}H_{33}NO_3)_n$, (527.67 g·mol^{-1})$_n$: C, 81.95; H, 6.30. Found: C, 80.0; H, 5.9.

Polymer 8a: $R^1 = -CF_3$; $R^2 = H$; X = $-C(CH_3)_2-$. Oxazole monomer **4**: 813.1 mg; Bisphenol A: 570.7 mg; reaction time: 10 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2960, 1599, 1493, 1238, 1172, 1013, 968, 950, 830. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.2 (m, H6′), 8.1 (m, H2′), 7.6 (m, H2″), 7.3 (s, H4), 7.25 (m, H3″), 7.05 (m, H5′ and H3‴), 6.95 (m, H2‴), 1.7 ($-C(CH_3)_2-$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 161.2 (C2), 158.4/157.3 (C1‴), 157.1 (q, $^3J_{C-F}$ = 4.5 Hz, C4′), 154.1 (C4″), 149.4 (C5), 132.0/131.9 (C4‴), 129.1/128.9 (C3‴), 128.8 (C6′), 128.5 (C2″), 124.3 (C4), 124.0 (C1″), 123.85 (q, $^3J_{C-F}$ = 2 Hz, C2′), 123.2 (C1′), 122.9 (C3″), 122.7 (q, $^2J_{C-F}$ = 30 Hz, C3′), 119.5 (C5′), 118.5/118.4 (C2‴), 42.3 ($-C(CH_3)_2-$), 31.1 ($-C(CH_3)_2-$). ^{19}F NMR ($CHCl_3$): δ (ppm) = −62.1 (R^1). Anal. Calcd for $(C_{31}H_{22}F_3NO_3)_n$, (513.51 g·mol^{-1})$_n$: C, 72.51; H, 4.32. Found: C, 71.6; H, 4.1.

Polymer 8b: $R^1 = -CF_3$; $R^2 = H$; X = $-C(CF_3)_2-$. Conditions: oxazole monomer **4**, 813.1 mg; 2,2-bis(4′-hydroxyphenyl)hexafluoropropane, 840.5 mg; reaction time, 8 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1604, 1496, 1247, 1174, 1010, 968, 952, 831. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.2 (m, H6′), 8.1 (m, H2′), 7.6 (m, H2″), 7.3 (s, H4), 7.25 (m, H3″), 7.2 (m, H5′ and H3‴), 7.0 (m, H2‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 161.2 (C2), 158.2/157.1 (C1‴), 157.0 (q, $^3J_{C-F}$ = 4 Hz, C4′), 154.1 (C4″), 149.3 (C5), 132.4/132.0 (C4‴), 129.1/128.6 (C3‴), 128.5 (C6′), 128.4 (C2″), 124.3 (C4), 124.0 (C1″), 123.8 (q, $^3J_{C-F}$ = 2 Hz, C2′), 123.2 (C1′), 122.9 (C3″), 122.7 (q, $^2J_{C-F}$ = 30 Hz, C3′), 119.5 (C5′), 118.7/118.6 (C2‴), 62.9 (s, $^2J_{C-F}$ = 25 Hz, $-C(CF_3)_2-$); the signals of the trifluoromethyl groups R^1 and $-C(CF_3)_2-$ could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −62.5 (R^1), −64.4 ($-C(CF_3)_2-$). Anal. Calcd for $(C_{31}H_{16}F_9NO_3)_n$, (621.46 g·mol^{-1})$_n$: C, 59.91; H, 2.60. Found: C, 59.3; H, 2.3.

Polymer 9a: $R^1 = H$; $R^2 = -CF_3$; X = $-C(CH_3)_2-$. Conditions: oxazole monomer **5**, 813.1 mg; Bisphenol A, 570.7 mg; reaction time, 10 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2960, 1599, 1493, 1238, 1172, 1013, 968, 950, 830. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.15 (m, H6″), 8.0 (m, H2″), 7.6 (m, H2′), 7.3 (s, H4), 7.2 (m, H3′), 7.1 (m, H5′ and H3‴), 6.95 (m, H2‴), 1.7 ($-C(CH_3)_2-$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 161.2 (C2), 158.3/157.1 (C1‴), 156.0 (q, $^3J_{C-F}$ = 4 Hz, C4″), 154.1 (C4′), 149.4 (C5), 132.0/131.9 (C4‴), 129.1/128.9 (C3‴), 128.0 (C6″), 127.5 (C2′), 124.6 (C1″), 124.3 (C4), 123.9 (q, $^3J_{C-F}$ = 3 Hz, C2″), 123.6 (C1″), 123.2 (C3′), 121.0 (q, $^2J_{C-F}$ = 35 Hz, C3″), 119.5 (C5′), 118.5/118.4 (C2‴), 42.3 (-$C(CH_3)_2$-), 31.1 ($-C(CH_3)_2-$); the signal of the trifluoromethyl group R^2 could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −62.1 (R^2). Anal. Calcd for $(C_{31}H_{22}F_3NO_3)_n$, (513.51 g·mol^{-1})$_n$: C, 72.51; H, 4.32. Found: C, 71.5; H, 4.2.

Polymer 9b: $R^1 = H$; $R^2 = -CF_3$; X = $-C(CF_3)_2-$. conditions: oxazole monomer **5**, 813.1 mg; 2,2-bis(4′-hydroxyphenyl)hexafluoropropane, 840.5 mg; reaction time, 8 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1615, 1480, 1255, 1164, 1010, 970, 955, 835. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.15 (m, H6″), 8.0 (m, H2″), 7.6 (m, H2′), 7.3 (s, H4), 7.2 (m, H5′ and H3‴), 7.0 (m, H2‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 162.0 (C2), 158.2/157.1 (C1‴), 157.0 (q, $^3J_{C-F}$ = 3 Hz, C4″), 154.1 (C4′), 149.3 (C5), 132.4/132.0 (C4‴), 129.1/128.6 (C3‴), 128.9 (C6″), 128.0 (C2′), 124.3 (C4), 124.0 (C1′), 123.8 (q, $^3J_{C-F}$ = 3 Hz, C2″), 123.6 (C1″), 122.8 (C3′), 122.7 (q, $^2J_{C-F}$ = 30 Hz, C3″), 119.5 (C5″), 118.8/118.6 (C2‴), 62.9 (s, $^2J_{C-F}$ = 25 Hz, $-C(CF_3)_2-$); the signals of the trifluoromethyl groups R^2 and $-C(CF_3)_2-$ could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −62.5 (R^2), −64.4 ($-C(CF_3)_2-$). Anal. Calcd for $(C_{31}H_{16}F_9NO_3)_n$, (621.46 g·mol^{-1})$_n$: C, 59.91; H, 2.60. Found: C, 58.7; H, 2.2.

Polymer 10a: $R^1 = R^2 = -CF_3$; X = $-C(CH_3)_2-$. Conditions: oxazole monomer **6**, 983.1 mg; Bisphenol A, 570.7 mg; reaction time, 2 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2970, 1620, 1599, 1481, 1422, 1240, 1155, 1010, 960, 952, 830. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.2 (m, H2′), 8.0 (m, H6′), 7.8 (m, H2″), 7.6 (m, H6″), 7.1 (m, H4, H5″ and H3‴), 6.8 (m, H5′ and H2‴), 1.7 (s, $-C(CH_3)_2-$). ^{13}C NMR ($CDCl_3$): δ (ppm) = 160.2 (C2), 157.6 (C4′), 155.9 (C4″), 153.3 (C1‴), 150.1 (C5), 131.0 (C4‴), 128.9 (C6′), 128.7 (C6″), 128.5/128.4 (C3‴), 125.6 (q, $^3J_{C-F}$ = 4 Hz, C2″), 124.9 (q, $^3J_{C-F}$ = 4 Hz, C2′), 123.7 (C1″), 123.3 (C4), 122.4 (C1′), 121.8 (q, $^2J_{C-F}$ = 27 Hz, C3″), 121.4 (q, $^2J_{C-F}$ = 26 Hz, C3′), 119.7/119.3 (C2‴), 119.2 (C5′), 118.7 (C5″), 42.5 ($-C(CH_3)_2-$), 31.0 ($-C(CH_3)_2-$); the signals of the trifluoromethyl groups R^1 and R^2 could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.5 (R^1 and R^2). Anal. Calcd for $(C_{32}H_{21}F_6NO_3)_n$, (581.52 g·mol^{-1})$_n$: C, 66.10; H, 3.64. Found: C, 66.0; H, 3.7.

Polymer 10b: $R^1 = R^2 = -CF_3$; X = $-C(CF_3)_2-$. Conditions: oxazole monomer **6**, 983.1 mg; 2,2-bis(4′-hydroxyphenyl)hexafluoropropane, 840.5 mg; reaction time, 2 h.

^{1}H NMR ($CDCl_3$): δ (ppm) = 8.4 (m, H2′), 8.2 (m, H2″), 8.0 (m, H6″), 7.8 (m, H6′), 7.45 (H5″), 7.4 (m, H4 and H3‴), 7.1 (m, H5′ and H2‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 159.9 (C2), 156.8/156.4 (C1‴), 156.2 (C4″), 154.4 (C4′), 150.0 (C5), 132.1 (C4‴), 131.3 (C6″), 129.4 (C3‴),129.0 (C6′), 124.2 (C4), 123.9 (q, $^1J_{C-F}$ = 273 Hz, $-CF_3$ (all)), 123.5 (C2″), 123.4 (C1″), 123.3 (q, $^2J_{C-F}$ = 30 Hz, C3″), 122.6 (C2′), 122.3 (q, $^2J_{C-F}$ = 30 Hz, C3′), 122.2 (C1′), 120.7 (C5″), 119.8 (C5′), 119.0/118.6 (C2‴); the signal of $-C(CF_3)_2-$ could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.0 (R^1 and R^2), −64.2 ($-C(CF_3)_2-$). Anal. Calcd for $(C_{32}H_{15}F_{12}NO_3)_n$, (689.46 g·mol^{-1})$_n$: C, 55.75; H, 2.19. Found: C, 55.0; H, 2.0.

Polymer 10c: $R^1 = R^2 = -CF_3$; X = $-O-$. Conditions: oxazole monomer **6**, 983.1 mg; 4,4′-dihydroxydiphenyl ether, 505.52 mg; reaction time, 3 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1604, 1580, 1480, 1455, 1220, 1100, 1020, 980, 958, 834. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.35 (m, H2′), 8.22 (m, H2″), 8.0 (m, H6″), 7.8 (m, H6′), 7.4 (m, H5″), 7.34 (s, H4), 7.1 (m, H5′), 6.8 (m, H2‴ and H3‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 159.9 (C2), 156.2 (C4″), 154.4 (C4′), 153.3/151.6 (C1‴), 152.9 (C4‴), 150.5 (C5), 131.1 (C6″), 129.1 (C6′), 123.6 (C2″), 123.5 (C4), 123.4 (C1″), 123.0 (q, $^2J_{C-F}$ = 25 Hz, C3″), 122.4 (C2′), 122.1 (q, $^2J_{C-F}$ = 25 Hz, C3′), 121.4 (C1′), 119.8 (C5′), 119.5 (C5″), 119.2 (C2‴ and C3‴); the signals of the trifluoromethyl groups R^1 and R^2 could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.3 (R^1 and R^2). Anal. Calcd for $(C_{29}H_{15}F_6NO_4)_n$, (555.44 g·mol^{-1})$_n$: C, 62.71; H, 2.72. Found: C, 61.8; H, 2.5.

Polymer 10d: $R^1 = R^2 = -CF_3$; X = $-CO-$. Conditions: oxazole monomer **6**, 983.1 mg; 4,4′-dihydroxybenzophenone, 535.55 mg; reaction time, 6 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1650, 1601, 1594, 1480, 1441, 1232, 1124, 1018, 981, 952, 840. ^1H NMR ($CDCl_3$): δ (ppm) = 8.25 (m, H2′), 8.16 (m, H2″), 8.04 (m, H6″), 7.88 (m, H6′), 7.72 (m, H3‴), 7.35 (m, H2‴), 7.3 (m, H5″), 7.28 (s, H4), 7.1 (m, H5′). ^{13}C NMR ($CDCl_3$): δ (ppm) = 194.2 (*C*=O), 159.8 (C2), 154.4 (C4″), 152.5 (C4′), 150.3 (C5), 133.5 (C1‴), 129.9 (C4‴), 129.7 (C6″), 129.1/128.9 (C3‴), 129.0 (C6′), 127.4 (C2″), 126.0 (C2‴), 123.8 (C1″), 122.4 (C4), 122.1 (q, $^2J_{C-F}$ = 20 Hz, C3″), 121.9 (q, $^2J_{C-F}$ = 20 Hz, C3′), 120.9 (C1′), 120.5 (C2′), 119.8 (C5″), 119.1 (C5′); the signals of the trifluoromethyl groups R^1 and R^2 could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.5 (R^1 and R^2). Anal. Calcd for $(C_{30}H_{15}F_6NO_4)_n$, (567.45 g·mol^{-1})$_n$: C, 63.50; H, 2.66. Found: C, 62.5; H, 2.8.

Polymer 10e: $R^1 = R^2 = -CF_3$; X = $-SO_2-$. Conditions: oxazole monomer **6**, 983.1 mg; 4,4′-dihydroxydiphenyl sulfone, 625.7 mg; reaction time, 6 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1614, 1580, 1483, 1455, 1234, 1108, 1020, 988, 957, 831. ^1H NMR ($CDCl_3$): δ (ppm) = 8.25 (m, H2′), 8.16 (m, H2″), 8.04 (m, H6″), 7.88 (m, H6′), 7.42 (m, H5″), 7.34 (s, H4), 7.1 (m, H5′), 6.9 (m, H2‴ and H3‴). ^{13}C NMR ($CDCl_3$): δ (ppm) = 162.2 (C1‴), 160.7 (C2), 156.4 (C4″), 153.8 (C4′), 150.5 (C5), 131.2 (C4‴), 130.0 (C6″), 129.9/128.9 (C3‴), 129.7 (C6′), 123.4 (C2″), 123.1 (C1″), 122.9 (C4), 122.8 (q, $^2J_{C-F}$ = 22 Hz, C3″), 121.9 (C2′), 121.7 (q, $^2J_{C-F}$ = 23 Hz, C3′), 120.9 (C1′), 119.9 (C5′), 118.5 (C5″), 116.0 (C2‴); the signals of the trifluoromethyl groups R^1 and R^2 could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.5 (R^1 and R^2). Anal. Calcd for $(C_{29}H_{15}F_6NO_sS)_n$, (603.50 g·mol^{-1})$_n$: C, 57.72; H, 2.51. Found: C, 57.5; H, 2.5.

Polymer 10f: $R^1 = R^2 = -CF_3$; X = —. Conditions: oxazole monomer **6**, 983.1 mg; 4,4′-dihydroxybiphenyl, 465.5 mg; reaction time, 6 h.

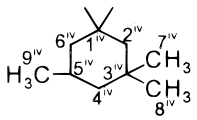
IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1614, 1587, 1490, 1420, 1240, 1150, 1012, 968, 950, 834. ^1H NMR ($CDCl_3$): δ (ppm) = 8.2 (m, H2′), 8.0 (m, H6′), 7.8 (m, H2″), 7.6 (m, H6″), 7.5 (m, H2‴), 7.1 (m, H5′ and H5″), 7.0 (m, H3‴), 6.8 (s, H4). ^{13}C NMR ($CDCl_3$): δ (ppm) = 160.0 (C2), 157.4 (C4′), 156.8 (C1‴), 155.9 (C4″), 150.5 (C5), 136.3 (C4‴), 128.9 (C6″), 128.7 (C6′), 127.6 (C3‴), 125.6 (q, $^3J_{C-F}$ = 4 Hz, C2″), 124.9 (q, $^3J_{C-F}$ = 4 Hz, C2′), 123.4 (C1″), 123.3 (C4), 122.2 (C1′), 121.8 (q, $^2J_{C-F}$ = 20 Hz, C3″), 121.4 (q, $^2J_{C-F}$ = 21 Hz, C3′), 119.6 (C2‴), 119.5 (C5′), 118.9 (C5″); the signals of the trifluoromethyl groups R^1 and R^2 could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.0 (R^1 and R^2). Anal. Calcd for $(C_{29}H_{15}F_6NO_3)_n$, (539.44 g·mol^{-1})$_n$: C, 64.57; H, 2.80. Found: C, 64.4; H, 2.9.

Polymer 10g: $R^1 = R^2 = -CF_3$; X =

Conditions: oxazole monomer **6**, 983.1 mg; 1,1-bis(4′-hydroxyphenyl)cyclohexane, 670.9 mg; reaction time, 9 h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2950, 1595, 1480, 1451, 1236, 1220, 1160, 1001, 952, 942, 825. ^1H NMR ($CDCl_3$): δ (ppm) = 8.12 (m, H2′), 8.02 (m, H2″), 7.95 (m, H6″), 7.7 (m, H6′), 7.3 (s, H4), 7.22 (m, H5″, H3′ and H3″), 7.05 (m, H5′ and H3‴), 6.95 (m, H2‴), 2.6−08 (H2^{iv}, H3^{iv} and H4^{iv}). ^{13}C NMR ($CDCl_3$): δ (ppm) = 159.8 (C2), 152.6 (C4″), 152.2 (C4′), 157.9/156.5 (C1‴), 150.3 (C5), 143.2/138.6 (C4‴), 130.2 (C6″), 130.0 (C6′), 129.2/124.0 (C3‴), 128.6 (C2′), 123.4 (C4), 123.0 (C2″), 121.9 (q, $^2J_{C-F}$ = 25 Hz, C3″), 120.6 (q, $^2J_{C-F}$ = 25 Hz, C3′), 116.5/116.1 (C2‴), 50.9 (C1^{iv}), 32.1 (C2^{iv}), 26.8 (C3^{iv}), 25.2 (C4^{iv}); the signals of the trifluoromethyl groups R^1 and R^2 as well as C5′ and C5″ could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.7 (R^1 and R^2). Anal. Calcd for $(C_{35}H_{25}F_6NO_3)_n$, (621.58 g·mol^{-1})$_n$: C, 67.5; H, 3.8. Found: C, 67.63; H, 4.05.

Polymer 10h: $R^1 = R^2 = -CF_3$; X =



Conditions: oxazole monomer **6**, 983.1 mg; 1,1-bis(4′-hydroxyphenyl)-3,3,5-trimethylcyclohexane, 766.0 mg; reaction time, 9h.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3002, 1605, 1491, 1441, 1258, 1238, 1161, 1015, 964, 932, 833. ^1H NMR ($CDCl_3$): δ (ppm) = 8.12 (m, H2′), 8.02 (m, H2″), 7.95 (m, H6″), 7.7 (m, H6′), 7.3 (s, H4), 7.22 (m, H5″, H3′ and H3″), 7.05 (m, H5′ and H3‴), 6.95 (m, H2‴), 2.6/2.4 (H2^{iv}), 1.85 (m, H6^{iv}), 1.23 (m, H5^{iv}), 1.1/0.9 (H4^{iv}), 0.95 (s, H7^{iv} and H8^{iv}), 0.4 (H9^{iv}). ^{13}C NMR ($CDCl_3$): δ (ppm) = 160.1 (C2), 154.6 (C4″), 152.8 (C4′), 156.5/155.0 (C1‴), 151.5 (C5), 145.6/139.3 (C4‴), 129.8 (C6″), 129.6 (C6′), 129.3/127.5 (C3‴), 128.9 (C2′), 123.6 (C4), 123.2 (C2″), 122.5 (q, $^2J_{C-F}$ = 28 Hz, C3″), 121.6 (q, $^2J_{C-F}$ = 27 Hz, C3′), 115.8/115.3 (C2‴), 67.9 (C1^{iv}), 49.2 (C2^{iv}), 48.35 (C6^{iv}), 46.6 (C4^{iv}), 34.8 (C5^{iv}), 26.5/25.8 (C7^{iv} and C8^{iv}), 25.75 (C3^{iv}), 22.35 (C9^{iv}); the signals of the trifluoromethyl groups R^1 and R^2 as well as C5′ and C5″ could not be identified due to the large number of strong signals in the relevant area. ^{19}F NMR ($CHCl_3$): δ (ppm) = −63.4 (R^1 and R^2). Anal. Calcd for $(C_{38}H_{31}F_6NO_3)_n$, (663.67 g·mol^{-1})$_n$: C, 68.77; H, 4.71. Found: C, 68.0; H, 4.3.

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