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Novel Synthesis of Poly(arylene thioether)s via One-pot Polymerization of Bis(N,N'-dimethyl-S-carbamate)s with Activated Dihalo Aromatic Compounds

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Abstract: A novel and convenient method to prepare poly(arylene thioether)s by a one-pot polymerization of N,N'-dimethyl-S-carbamate masked bisthiols was developed. The polymerization reactions were carried out in diphenyl sulfone in the presence of a cesium carbonate and calcium carbonate mixture at 200 - 240 °C. N,N'-Dimethyl-S-carbamate masked bisthiols can be conveniently prepared from the corresponding dihydroxy compounds by the Newman-Kwart rearrangement reaction. A series of novel poly(arylene thioether)s were prepared from 9,9'-bis(4-hydroxyphenyl)fluorene and 2,2'-bis(hydroxyphenyl)hexafluoropropane, respectively. High molecular weight polymers were obtained in 3 - 4 hours. © 1997 Published by Elsevier Science Ltd.

INTRODUCTION

Poly(phenylene sulfide) (PPS) and poly(ether sulfone)s are very important commercial high performance polymers. The incorporation of thioether linkages into the polymers provides the excellent properties associated with PPS into the polymers, such as excellent nonflammability, low moisture absorption, high dimensional stability, and good compatibility with inorganic fillers. However, research on the synthesis and study of poly(arylene thioether)s is very limited, compared with their counterparts the poly(arylene ether)s. One of the most commonly used methods to prepare poly(arylene ether)s is the reaction of dihydroxy aromatic compounds with activated dihalo compounds in the presence of potassium carbonate as a base in a polar solvent, such as N,N-dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP).[1] Several dihydroxy compounds are readily available commercially, however, the availability of arylene dithiols is very limited because of their instability and unpleasant odor.

Several reports have appeared in the literature for the preparation of poly(arylene thioether)s. From a few arylene dithiols, a series of poly(arylene thioether ketone)s[2] and poly(arylene thioether sulfone)s[3] were synthesized in N,N-dimethylformamide (DMF) in the presence of anhydrous K_2CO_3. Poly(thioether ketone)s and poly(thioether)s were also prepared from activated aromatic fluoro compounds and anhydrous sodium sulfide in N-cyclohexyl-2-pyrrolidinone (CHP)[4] or with sodium hydrosulfide.[5] By using phosphorous pentoxide/methanesulfonic acid (PPMA) as condensing agent and solvent, Ueda *et al* synthesized a series of poly(thioether ketone)s.[6] Silylated dithiols[7] and S-(N-propyl carbamate) masked dithiols[8] have been prepared and used to prepare poly(arylene thioether)s. However, they are either moisture sensitve and unreactive or have to be prepared from existing dithiol compounds, which limits their availability. We have also prepared many poly(thioether)s from cyclic (arylene disulfide) oligomers and iodo or bromo compounds[9,10] as well as from the polymerization of arylenedithiols with dibromo compounds in the presence of a free radical initiator.[11,12]

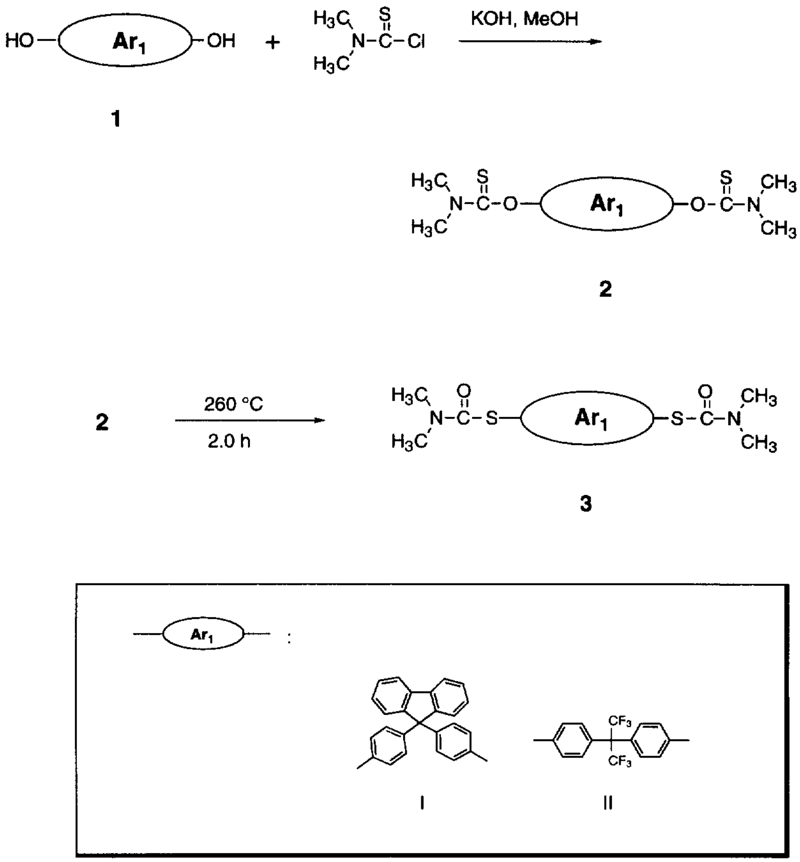
An elegent synthesis of arylthiols is the Newman-Kwart rearrangement reaction.[13] By using this reaction, many N,N'-dimethyl-S-carbamate masked arylene dithiols can be conveniently prepared from the readily available dihydroxy aromatic compounds. If the one-pot polymerization of N,N'-dimethyl-S-carbamate masked arylene dithiols and activated dihalo aromatic compounds is successful, a wide variety of poly(arylene thioether)s would be readily available from easily available dihydroxy compounds and the isolation and purification of the thiols would be avoided. Since thioethers can also be readily oxidized to form sulfones, many poly(arylene sulfone)s would also become readily available. Herein, we report our success in the preparation of poly(arylene thioether)s by a one-pot polymerization of N,N'-dimethyl-S-carbamate masked dithiols and activated dihalo aromatic compounds. A series of novel poly(arylene thioether)s was prepared and characterized.

RESULTS AND DISCUSSION

Monomer synthesis

Our objective was to establish a convenient and general method for the preparation of a series of novel poly(arylene thioether) polymers. Two commonly used dihydroxy compounds, 9,9'-bis(4-hydroxyphenyl)fluorene and 2,2'-bis(4-hydroxyphenyl)hexafluoropropane, were used to demonstrate the synthetic method. Fluorene containing polymers have high glass transition temperatures, high thermal stabilities, and good solubilities.[14] The incorporation of the hexafluoroisopropylidene group into polymers increases the solubility, thermal stability, flame resistance, oxidation resistance, adhension and optical transparency while decreasing the crystallinity, dielectric constant and water absorption of polymers.[15]

The synthesis of the N,N'-dimethyl-S-carbamate masked dithiols is very straight forward and is illustrated in Scheme 1. The N,N'-dimethyl-O-thiocarbamates were prepared from the respective dihydroxy compounds in chilled methanolic KOH solution. The rearrangement reactions were readily carried out at 260 °C. Diphenyl ether was used as solvent for the rearrangement of the fluorene containing thiocarbamate. However, no solvent was necessary for the rearrangement of the hexafluoroisopropylidene containing thiocarbamate. The rearrangement reactions have been confirmed by HPLC and ^{1}H-NMR. The retention times were longer for **3I-II** than those of **2I-II** in HPLC using methanol as the eluent. The comparison of ^{1}H-NMR spectra of **2I-II** and **3I-II** are shown in Figure 1. The two sets of well separated doublets from the benzene rings substituted by N,N'-dimethyl-O-thiocarbamate moved closer and down field after rearrangement to the N,N'-dimethyl-S-carbamates for both **I** and **II**. The proton signals of the dimethyl groups in N,N'-dimethyl-O-thiocarbamate groups are at lower fields and sharper than those of the N,N'-dimethyl-S-carbamates.



Scheme 1. Syntheses of N,N'-dimethyl-S-carbamate masked arylene dithiols

Polymer synthesis

The one-pot polymerization of N,N'-dimethyl-S-carbamate masked dithiols and acivated dihalo aromatic compounds is shown in Scheme 2. It has been shown that N,N'-dimethyl carbamates can not be cleaved by K_2CO_3 in NMP at reflux temperature over a 24 hour period, although the same system has been successfully used to prepare polymers from N-propyl carbamate masked phenols or thiophenols.[16,17] This is due to the active N-H bond in the N-propyl carbamate which facilities the cleavage.[18] We have now found that N,N'-dimethyl-S-carbamate masked arylene dithiols can be efficiently cleaved with the formation of N,N-dimethylamine and CO_2 at 200 - 240 °C in diphenyl sulfone in the presence of a cesium carbonate and calcium carbonate mixture. High molecular weight polymers can be readily prepared within 3 - 4 hours in a one-pot reaction between bis(N,N'-dimethyl-S-carbamate)s and activated dihalo aromatic compounds. Generally, after 2 hours of reaction, the reaction mixture became very viscous and additional diphenyl sulfone had to be added to dilute the mixture. DMAc and NMP, which are commonly used for polymerization reactions which proceed *via*

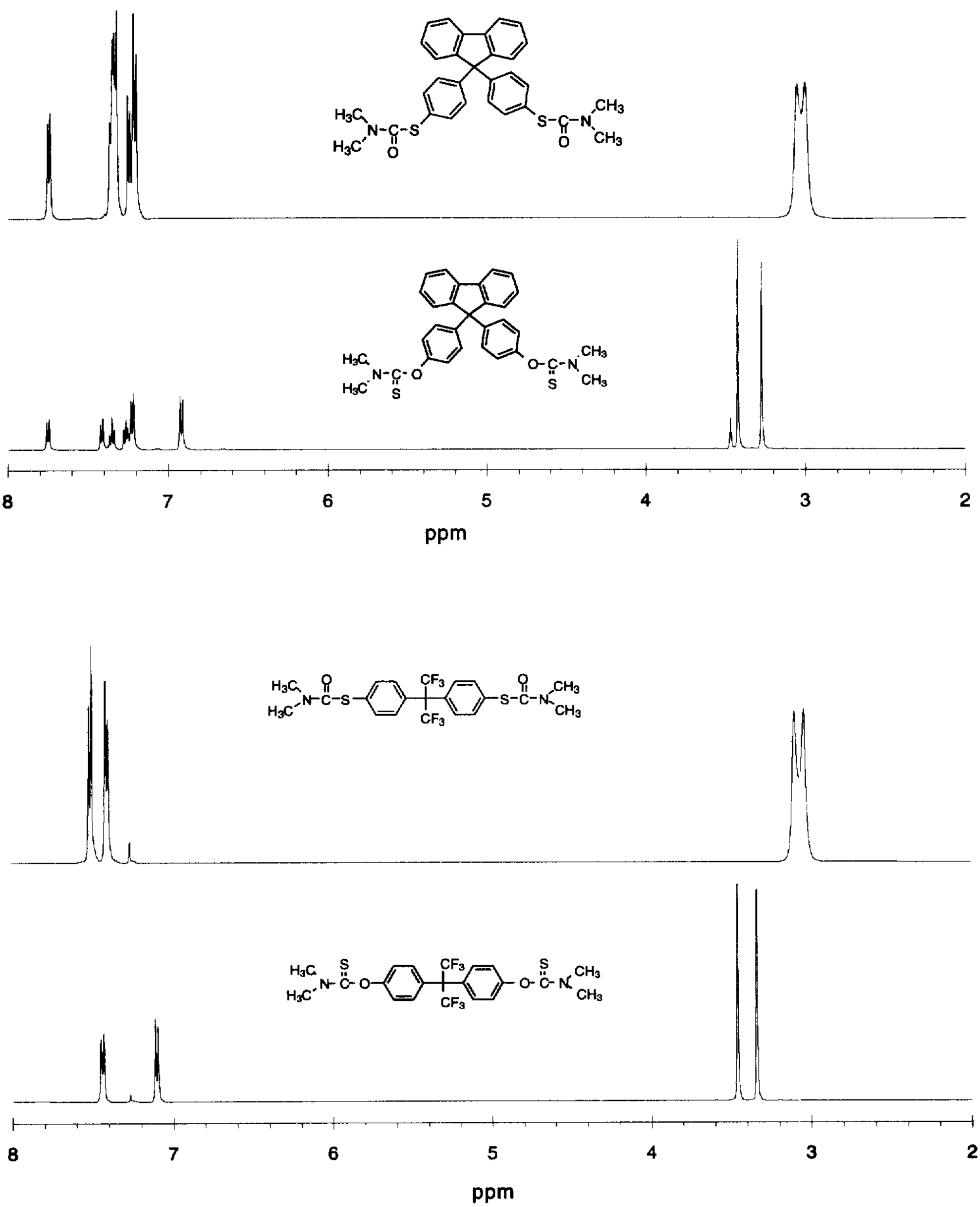
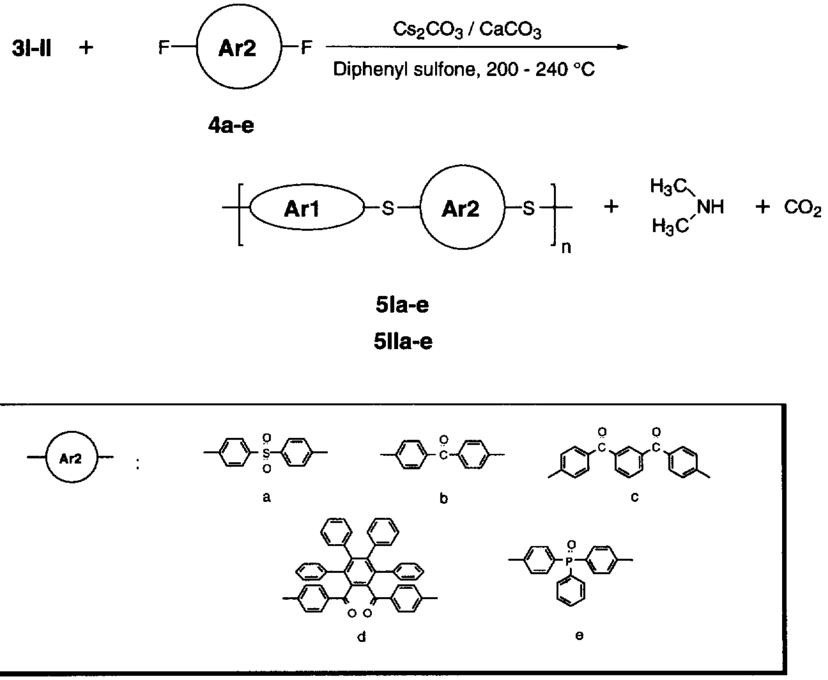


Figure 1. ¹H-NMR spectra of O-(N,N'-dimethyl thiocarbamate)s and S-(N,N'-dimethyl carbamate)s ($CDCl_3$)

a nucleophilic substitution reaction, are not suitable for the present polymerization reaction. The active methyl or methylene groups interfere with the polymerization reactions and high molecular weight polymers could not be obtained. To obtain high molecular weight polymers, it is also necessary to carry out the polymerization at relatively lower temperatures at the beginning, and then gradually increase the temperature. When the polymerization reactions were started at higher temperatures (> 250 °C), only low molecular weight oligomers were obtained. Fukawa and Tanabe have observed that 4,4'-difluorobenzophenone reacts with potassium carbonate and forms oligomeric ether ketones at 300 °C in diphenyl sulfone.[19] A similar reaction is believed to happen here at temperatures higher than 250 °C, which results in an imbalance of stoichiometry and the formation of low molecular weight oligomers. Generally, we started the polymerization at 200 °C, and then raised the temperature to 240 °C.



Scheme 2. One-pot polymerization of N,N'-dimethyl-S-carbamate masked arylene dithiols with acitivated dihalo aromatic compounds

Polymer Characterization

A series of poly(arylene thioether)s containing fluorene and hexafluoroisopropylidene groups has been prepared by a one-pot polymerization reaction and characterized. As expected, they are all amorphous polymers with high glass transition temperatures (Tgs) and high thermal stabilities. They are readily soluble in $CHCl_3$, DMF, DMAc, and NMP.

The apparent molecular weights of these polymers were obtained by gel permeation chromatography (GPC) using polystyrene standards and they are listed in Table 1. The molecular weights of phenyl phosphine oxide containing polymers **5Ie** and **5IIe** are not obtainable by GPC although they are very soluble in chloroform. In all cases, high molecular weight polymers were obtained and the SEC traces showed the presence of only very small amounts of cyclic oligomers. Transparent and flexible films can be cast from chloroform solutions. The inherent viscosities (η_{inh}) of these polymers range from 0.30 to 0.63 dL/g in $CHCl_3$ solutions at 25 °C.

Table 1. Properties of Poly(arylene thioether)s

Polymer	M_w[a]	M_n[a]	η_{inh}[b] (dL/g)	T_g (°C)[c]	TGA (°C)[d]
5Ia	38,000	20,000	0.32	272	473
5Ib	41,000	23,000	0.32	239	516
5Ic	83,000	31,000	0.39	220	480
5Id	170,000	42,000	0.37	288	514
5Ie	ND[e]	ND[e]	0.39	268	509
5IIa	39,000	24,000	0.30	181	489
5IIb	59,000	32,000	0.33	157	514
5IIc	90,000	47,000	0.63	161	503
5IId	80,000	40,000	0.44	244	516
5IIe	ND[e]	ND[e]	0.56	191	524

a. Apparent molecular weights from GPC using polystyrene standards. The eluent was and the flow rate was 1 mL/min.

b. 5 g/dL in $CHCl_3$ at 25.0 °C.

c. Obtained by DSC under nitrogen atmosphere with heating rate of 20 °C.

d. 5 % weight loss temperature.

e. Not obtained.

The thermal properties of these polymers were determined in differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) instruments and the results are listed in Table 1. These polymers have high Tgs and very high thermal stabilities. The T_g of fluorene containing poly(thioether)s range from 220 - 288 °C. Polymer **5Id** has the highest T_g and polymer **5Ic** has the lowest T_g among this series of polymers. The T_g of hexafluoroisopropylidene group containing polymers range from 157 - 244 °C. Polymer **5IId** has the highest T_g and polymer **5IIb** has the lowest T_g among this series of polymers. The glass transition temperatures of the poly(thioether)s are several degrees lower than their polyether analogs. For example, polymers **5Ia**, **5Ib**, and **5Ic** have T_gs of 272 °C, 239 °C, and 220 °C, respectively, while their polyether analogs have T_gs of 280 °C, 252 °C, and 223 °C, respectively.[14]

The 5 % weight loss temperatures in nitrogen atmosphere of these poly(thioether)s are greater than 473 °C. (Table 1). Generally, the hexafluoroisopropylidene group containing polymers have higher thermal stabilities than the fluorene containing polymers. For example, the 5 % weight loss temperature of polymer **5Ic** is 480 °C, while that of polymer **5IIc** is 503 °C.

CONCLUSIONS

A novel and convenient method to prepare poly(arylene thioether)s has been developed. High molecular weight poly(thioether)s were obtained from one-pot polymerization of bis(N,N'-dimethyl-S-carbamate)s with activated dihaloaromatic compounds in diphenyl sulfone in the presence of a cesium carbonate and calcium carbonate mixture at 200 - 240 °C. Several advantages are associated with this novel polymerization reaction. Many monomers can be conveniently prepared from readily available dihydroxy aromatic compounds and the monomers are stable and easy to purify. Furthermore, the handling of oxidatively unstable and unpleasant smelling arylene dithiols is avoided. By using the present polymerization reaction, a wide variety of poly(arylene thioether)s can be readily synthesized. A series of poly(arylene thioether)s containing fluorene and hexafluoroisopropylidene moieties have been prepared which were characterized by GPC, DSC, TGA and inherent viscosity. These polymers are amorphous and have high glass transition temperatures and high thermal stabilities. The T_gs of the polymers are above 157 °C and 5% weight loss temperatures are above 473 °C. The inherent viscosities of these polymers are in the range of 0.30 - 0.63 dL/g.

EXPERIMENTAL

Measurements

Differential scanning calorimetry scans were conducted on a Seiko 220 DSC instrument at a heating rate of 20 °C/min in N_2 atmosphere (160 mL/min). The 5 % weight loss data were obtained from a Seiko 220 TG/DTA at a heating rate of 20 °C/min in N_2. Gel permeation chromatography (GPC) analyses were performed on a Waters 510 HPLC equipped with 4 phenogel columns (1 x linear, 3 x 500 Å). $CHCl_3$ was used as the eluent and the UV detector was set at 254 nm. Inherent viscosities were measured in $CHCl_3$ at 25.0 ± 0.1 °C using a Ubbelohde viscometer. HPLCs were performed on a Milton Roy CM4000 system equipped with a Lichrosphere 5 RP18e reverse phase column and methanol was used as the eluent. NMR spectra were recorded on a Varian Unity 500 instrument in $CDCl_3$ solution. TMS was used as reference for ^{1}H-NMR and the solvent, $CDCl_3$, was used for ^{13}C-NMR. Melting points were taken on a Fisher-Johns melting point apparatus and the thermometer was uncorrected.

Materials

Diphenyl sulfone was purchased from Aldrich Chemical Inc. and recrystallized from ethanol prior to use. 9,9'-Bis(4-hydroxyphenyl)fluorene, 2,2'-bis(hydroxyphenyl)hexafluoropropane, and N,N'-dimethyl thiocarbamoyl chloride were obtained from commercial sources and used as received. Bis(4-fluorophenyl)sulfone, 4,4'-difluorobenzophenone, cesium carbonate and fine grade calcium carbonate were used without purification. Monomers **4c**,[20] **4d**,[21] **4e**[22] were prepared according to previously reported methods.

Preparation of 2I.

Bisphenol **1I** (20.0 g, 0.057 mol) was added to 100 mL of an ice cold KOH methanolic (7.3 g, 0.13 mol) solution and stirred at 0 °C for 0.5 h. N,N'-Dimethylthiocarbamoyl chloride (15.5 g, 0.125 mol) was then added in one portion and the mixture was stirred for another 2 h. The precipitated white solid was collected by filtration and washed with ice-cold methanol : water (1 : 1) (150 mL). A white solid **2I** (25.4 g, yield 85 %) was obtained after recrystallization from $CHCl_3$/methanol. M.p. 239 - 241 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.75 (d, 2H, J = 7.6 Hz), 7.41 (d, 2H, J = 7.6 Hz), 7.34 (t, 2H, J = 7.6 Hz), 7.25 (t, 2H, J = 7.6 Hz), 7.22 (d, 4H, J = 8.6 Hz), 6.92 (d, 4H, J = 8.6 Hz), 3.42 (s, 6H), 3.28 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 187.4, 152.7, 150.9, 143.1, 140.0, 128.9, 127.8, 127.6, 126.2, 122.3, 120.1, 64.6, 43.2, 38.6. MS: *m/z* 524 (M^+, 38), 437(15), 88(100), 72(80). HRMS: found, 524.1595; calcd for $C_{31}H_{28}N_2O_2S_2$, 524.1592.

Preparation of 2II.

Bisphenol **1II** (20.0 g, 0.06 mol) was added to 100 mL of ice cold methanolic KOH (7.3 g, 0.13 mol) solution and stirred at 0 °C for 0.5 h. N,N'-Dimethylthiocarbamoyl chloride (16.3 g, 0.13 mol) was then added and the mixture was stirred for another 2 h. The precipitated white solid was collected by filtration and washed with ice-cold methanol : water (1 : 1) (150 mL). A white solid **2II** (26.8 g, yield 88 %) was obtained after recrystallization from $CHCl_3$/methanol. M.p. 213 - 215 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.44 (d, 4H, J = 8.3 Hz), 7.10 (d, J = 8.3 Hz), 3.46 (s, 6H), 3.34 (s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 186.8, 154.2, 131.1, 130.4, 122.6, 43.2, 38.7. MS: *m/z* 510(M^+, 28), 423(7), 88(100), 72(97). HRMS: found, 510.0873; calcd for $C_{21}H_{20}F_6N_2O_2S_2$, 510.0870.

Preparation of 3I.

The mixture of **2I** (20.0 g) and diphenyl ether (15.0 g) was heated at 260 °C under N_2 atmosphere for 2 h. The cooled mixture was washed with 150 mL of methanol to obtain the crude product. After recrystallization from a $CHCl_3$/ methanol mixture, a white solid **3I** (14.8 g, yield 74 %) was obtained. M.p. 279 - 280 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.74 (d, 2H, J = 7.3 Hz), 7.3 (m, 14H), 3.0 (d, 12H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 166.8, 150.3, 146.6, 140.1, 135.5, 128.7, 127.9, 127.7, 127.0, 126.2, 120.2, 65.1, 36.9. MS: *m/z* 524(M^+, 33), 453(8), 72(100). HRMS: found, 524.1596; calcd for $C_{31}H_{28}N_2O_2S_2$, 524.1592.

Preparation of 3II.

2I (15.0 g) was placed in a 100 mL of round bottom flask and heated at 260 °C under N_2 atmosphere for 2 h. After recrystallization from methanol/water, a white solid **3II** (13.2 g, yield 88 %) was obtained. M.p. 138 - 139 °C. ^{1}H-NMR ($CDCl_3$): δ (ppm) 7.51 (d, 4H, J = 8.5 Hz), 7.41 (d, J = 8.5 Hz), 3.10 (s, 6H), 3.04

(s, 6H). ^{13}C-NMR ($CDCl_3$): δ (ppm) 166.0, 135.1, 133.8, 130.5, 130.5, 36.9. MS: *m/z* 510(M^+, 56), 72(100). HRMS: found, 510.0874; calclcd for $C_{21}H_{20}F_6N_2O_2S_2$, 510.0870.

General procedure for polymerization of 3I with activated dihalocompounds.

A typical example is given as follows. To a 25 mL three neck flask equipped with magnetic stirrer and a N_2 inlet, **3** (1.0494 g, 2.0 mmol), bis(4-fluorophenyl) sulfone (0.5085 g, 2.0 mmol), cesium carbonate (0.32 g, 1.0 mmol), calcium carbonate (0.60 g, 6.0 mmol) and 5.0 g of diphenyl sulfone were charged. The mixture was brought up to 200 °C and kept at that temperature for 2 h. Then, an additional 2.0 g of diphenyl sulfone was added to dilute the solution and the reaction temperature was brought up to 240 °C and kept at that temperature for another 2 h. The mixture was cooled down and dissolved in 15 mL of $CHCl_3$. The $CHCl_3$ solution was poured into 150 mL of acetone to precipitate out the polymer which was collected by filtration. The polymer was redissolved in $CHCl_3$ and filtered through a thin layer of celite and reprecipitated out by pouring into methanol. The polymer was collected and dried at 100 °C in vaccuo for 24 h.

General procedure for polymerization of 3II with activated dihalocompounds.

The polymerization was carried out as above. The mixture was then diluted with 15 mL of $CHCl_3$ and poured into 150 mL of hot methanol to precipitate out the polymer. The crude polymer was dissolved in 20 mL of $CHCl_3$ and filtered through a thin layer of celite. The $CHCl_3$ solution was poured into 150 mL of methanol to precipitate out fibrous polymer. The polymer was dissolved in $CHCl_3$ and poured into methanol once more to remove any remaining diphenyl sulfone. The polymer was collected and dried at 100 °C in vacuo for 24 h.

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