

## **Syntheses and properties of soluble poly(arylene thioether imide)s and the corresponding poly(arylene sulfone imide)s**

**Frank P. Glatz and Rolf Mülhaupt\***

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany

### **Summary**

A series of soluble 6F polyimides were prepared from monodisperse diamine-terminated oligo(phenylene thioether)s varying the number of phenylene thioether units between one and six. In a formic acid/hydrogen peroxide slurry the 6F poly(arylene thioether imide)s were converted into the corresponding poly(arylene sulfone imide)s containing controlled oligo(phenylene sulfone) segments. The oxidation process and the influence of oligo(phenylene thioether) and oligo(phenylene sulfone) segments on polymer phase transitions and thermal degradation were investigated.

### **Introduction**

Sulfur-containing polymers play an important role in the development of high performance engineering thermoplastics (1). For instance, poly(arylene thioether), well-known as PPS, is semicrystalline and exhibits high strength, stiffness, dimensional and environmental stability combined with high toughness. Amorphous poly(arylene ether sulfone)s are components of advanced structural materials. More recently, sulfides and difunctional thiols have been applied extensively in aromatic nucleophilic displacement reactions of activated aromatic dihalides, to produce aromatic polythioethers, e.g., poly(arylene thioether ketone)s (2,3). Various difunctional oligo(phenylene thioether)s were first described by Daccord and Sillion (4-7). Diamine-terminated oligo(phenylene thioether)s, prepared by endcapping dihalide-terminated oligo(phenylene thioether)s with *p*-amino-thiophenol (7-10), have been used as monomers for the synthesis of amorphous and semicrystalline polyamides (7), poly(thioether imide)s (8-10), and poly(amide imide)s (11). Chieng and Cheng (12) describe the synthesis of poly(arylene sulfone imide)s containing three phenylene sulfone units in the repeat unit. In their synthetic scheme, diamine-terminated oligo(phenylene thioether) monomers are oxidized to yield the corresponding diamine-terminated oligo(phenylene sulfone)s. Since also aromatic amines are readily oxidized, the thioether oxidation requires protecting and deprotecting of the amine functionality. This three-step monomer synthesis is limited to diamines containing  $n \leq 3$  phenylene sulfone units because at higher segment length the diamine monomers exhibit low solubilities in dipolar aprotic solvents used in polyimide synthesis.

\*Corresponding author

In our research polyimides containing well-defined aromatic thioether and sulfone moieties have proven to be attractive candidates for gas separation membrane materials (13). For the investigation of the basic structure/property relationships governing gas permeabilities and mechanical properties, higher segment lengths are highly desirable. Therefore we have developed a process in which the thioether groups in the polymer backbone are oxidized to yield the corresponding poly(sulfone imide)s. Here we report the synthesis and properties of soluble 6F polyimides containing well-defined oligo(phenylene thioether) and oligo(phenylene sulfone) segments. Emphasis is being placed on the investigation of the oxidation of poly(thioether imide)s and the influence of the segment lengths on the polymer phase transitions and the thermal polymer degradation.

## **Experimental**

### **Materials**

Hexafluoroisopropylidene(4-bisphthalic anhydride) ("6F-dianhydride") was supplied by Hoechst AG and used without further purification. N-Methyl-2-pyrrolidone (NMP) was distilled from  $P_4O_{10}$  under reduced pressure. The diamine-terminated oligo(phenylene thioether)s were prepared as reported in a previous communication (13). All reactions were performed under dry nitrogen.

### **Polymer syntheses**

Poly(arylene thioether imide)s were prepared as shown in Scheme 1. Typically, 6F-dianhydride (4.442 g, 10 mmol) dissolved in 10 ml NMP was added slowly to a solution of bis(4-aminophenyl)thioether (2.161 g, 10 mmol) in 25 ml NMP at room temperature and stirred for 12 hours. Then acetic anhydride (4.2 g, 40 mmol) and triethylamine (3.5 g, 35 mmol) were added to the poly(amic acid) solution, and the reaction mixture was heated to 90°C and held for 6 hours. The poly(thioether imide) was precipitated in water using a blender, washed with boiling water, extracted with acetone and dried to give a quantitative yield of the poly(thioether imide) PI 1 (n=1). The inherent viscosity of 0.5 g/dl PI 1 solution in NMP was 0.70 dl/g at 30°C.  $T_g$  (DMA) 292°C, FTIR (film): 1784  $cm^{-1}$ (C=O), 1724  $cm^{-1}$ (C=O), 1495  $cm^{-1}$ , 1255  $cm^{-1}$  (C-F), 815  $cm^{-1}$ , 730  $cm^{-1}$ . The other polymers were prepared accordingly. Their elemental analyses are summarized in Table 1.

Poly(arylene sulfone imide)s were obtained from the poly(arylene thioether imide)s by oxidation in formic acid/hydrogen peroxide slurry (Scheme 2). Typically, 30 % aqueous hydrogen peroxide (8 g, 100 mmol) was added dropwise to a stirred suspension of the poly(thioether imide) PI 2 (0.9 g, 1 mmol) in 20 ml 90% formic acid at 50°C. After stirring for 1 hour at 50°C, the reaction mixture was poured into methanol, filtered off, washed with methanol and dried to give the poly(sulfone imide) PSI 2 in 90% yield,  $\eta_{inh} = 0.57$  dl/g,  $T_g$  (DMA) 331°C, FTIR (film) : 1790  $cm^{-1}$  (C=O), 1734  $cm^{-1}$ (C=O), 1499  $cm^{-1}$ , 1330  $cm^{-1}$  (Ar-SO<sub>2</sub>), 1259  $cm^{-1}$ (C-F), 1165  $cm^{-1}$  (Ar-SO<sub>2</sub>), 830  $cm^{-1}$ , 740  $cm^{-1}$ . The other PSEK were prepared applying the same procedure. Elemental analyses are reported in Table 1.

### **Polymer Characterization**

Elemental analyses were conducted using a Perkin-Elmer Model 240 analyzer. The inherent viscosities of 0.5 g/dl polymer solutions in NMP were measured using an

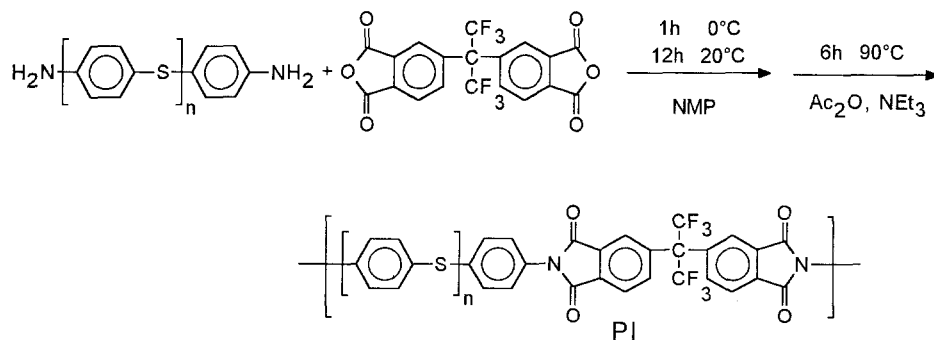
Ubbelohde viscosimeter at 30°C. FTIR spectra were recorded on a Bruker IFS 88 infrared spectrometer. The glass transition temperatures were analyzed using a Rheometrics Solid Analyzer RSA II at 1 Hz and 10 K/min heating rate. The 6F polyimides were investigated as films of 50  $\mu\text{m}$  thickness. The films were casted from 20 wt % solutions in DMF at 100°C and dried for 24 hours at 100°C. Powders were analyzed using a Perkin Elmer DSC 7 and 10 K/min heating rate. Weight losses at 500°C under nitrogen were measured on a Netzsch Thermal Analysis System at 10 K/min heating rate.

**Table 1** Elemental analyses of poly(thioether imide)s and poly(sulfone imide)s

Sample	Formula	$M_n$	% C		% H		% N		% S	
			calc.	exp.	calc	exp	calc	exp	calc	exp
PI 1	$\text{C}_{31}\text{H}_{14}\text{N}_2\text{F}_6\text{O}_4\text{S}$	624.4	59.6	59.4	2.2	2.1	4.5	4.5	5.1	5.0
PI 2	$\text{C}_{37}\text{H}_{18}\text{N}_2\text{F}_6\text{O}_4\text{S}_2$	732.4	60.6	60.2	2.4	2.3	3.8	3.9	8.8	8.5
PI 3	$\text{C}_{43}\text{H}_{22}\text{N}_2\text{F}_6\text{O}_4\text{S}_3$	840.5	61.4	61.1	2.6	2.6	3.3	3.4	11.4	11.3
PI 4	$\text{C}_{49}\text{H}_{26}\text{N}_2\text{F}_6\text{O}_4\text{S}_4$	948.5	62.0	61.6	2.7	2.7	3.0	3.0	13.5	13.6
PI 5	$\text{C}_{55}\text{H}_{30}\text{N}_2\text{F}_6\text{O}_4\text{S}_5$	1056.6	62.5		2.8		2.7		15.2	
PI 6	$\text{C}_{61}\text{H}_{34}\text{N}_2\text{F}_6\text{O}_4\text{S}_6$	1164.6	62.9		2.9		2.4		16.5	
PSI 1	$\text{C}_{31}\text{H}_{14}\text{N}_2\text{F}_6\text{O}_6\text{S}$	656.4	56.7	56.4	2.1	2.1	4.3	4.2	4.9	5.0
PSI 2	$\text{C}_{37}\text{H}_{18}\text{N}_2\text{F}_6\text{O}_8\text{S}_2$	796.5	55.8	55.5	2.3	2.2	3.5	3.7	8.0	7.8
PSI 3	$\text{C}_{43}\text{H}_{22}\text{N}_2\text{F}_6\text{O}_{10}\text{S}_3$	936.5	55.1	54.8	2.3	2.4	3.0	2.9	10.3	10.1
PSI 4	$\text{C}_{49}\text{H}_{26}\text{N}_2\text{F}_6\text{O}_{12}\text{S}_4$	1076.6	54.7	54.3	2.4	2.3	2.6	2.4	11.9	12.2
PSI 5	$\text{C}_{55}\text{H}_{30}\text{N}_2\text{F}_6\text{O}_{14}\text{S}_5$	1216.6	54.3		2.5		2.3		13.2	
PSI 6	$\text{C}_{61}\text{H}_{34}\text{N}_2\text{F}_6\text{O}_{16}\text{S}_6$	1356.7	54.0		2.5		2.1		14.2	

## Results and discussion

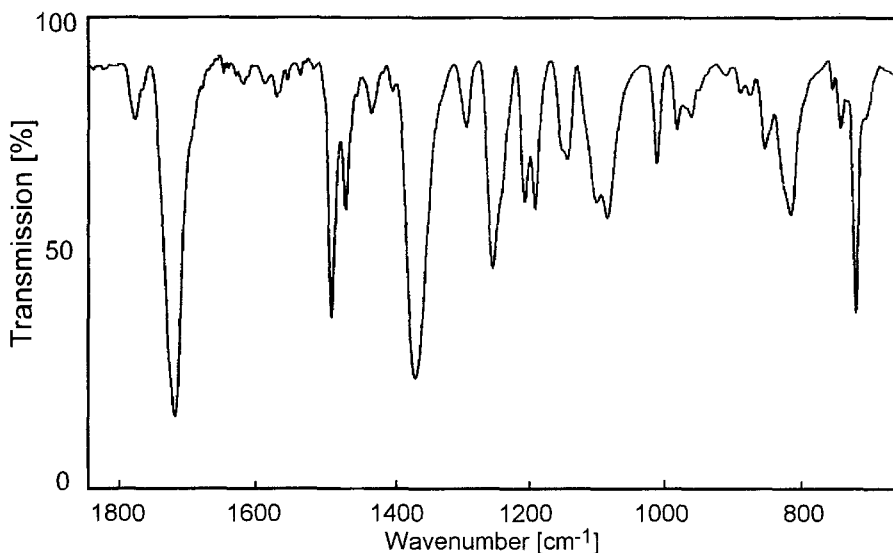
Monodisperse diamine-terminated oligo(phenylene thioether)s with  $n=1$  to  $n=6$  phenylene thioether units (cf. Scheme 1) were obtained by endcapping of the corresponding monodisperse dibromo-terminated oligo(phenylene thioether)s similar to procedures reported by Sillion (7) and Takekoshi (8).



**Scheme 1**

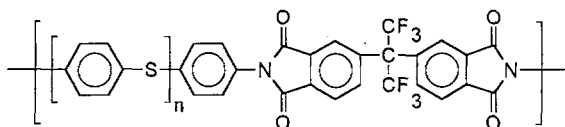
A range of soluble 6F polyimides were prepared from the telechelic diamines and 6F-dianhydride in NMP solution using the chemical imidization with acetic anhydride/triethylamine to convert the polyamic acid intermediates into the polyimides. The resulting 6F polyimides are amorphous and give tough optically transparent films when casted from DMF solution.

The FTIR spectroscopic analysis of poly(thioether imide) films, depicted for sample PI 3 in Figure 1, shows characteristic absorptions of hexafluoroisopropylidene-bisphthalimide group at  $1784\text{ cm}^{-1}$  (C=O),  $1724\text{ cm}^{-1}$  (C=O),  $1255\text{ cm}^{-1}$  (C-F) and  $730\text{ cm}^{-1}$ . Other characteristic absorption bands at  $1495\text{ cm}^{-1}$  and  $815\text{ cm}^{-1}$  are associated with aromatic groups.



**Figure 1** FTIR spectrum of poly(thioether imide) PI 3

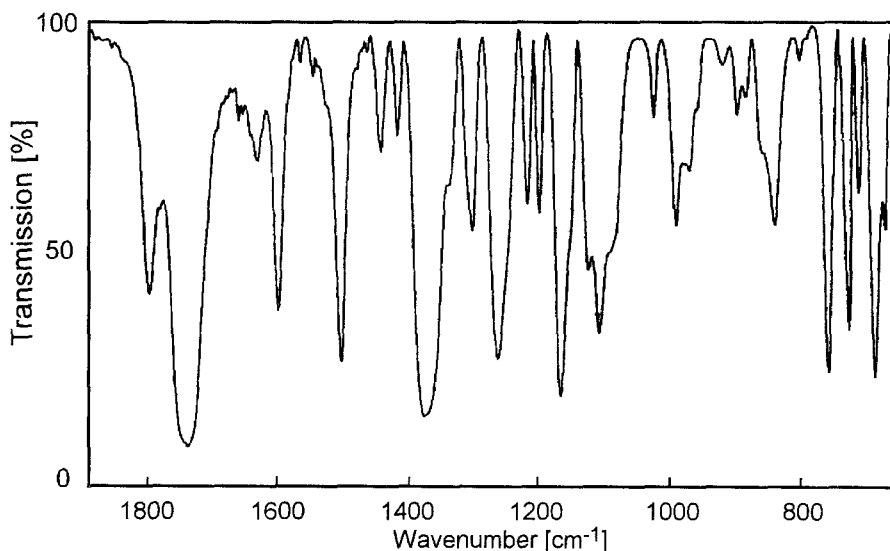
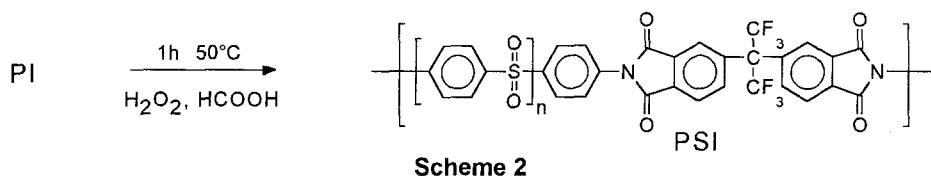
**Table 2** Poly(arylene thioether imide)s (PI)



Sample	n	$\eta_{inh}$ (dl/g)	T <sub>g</sub> (°C)	% Weight loss at 500°C
PI 1	1	0.70	292	1.9
PI 2	2	0.68	257	2.1
PI 3	3	0.65	233	2.5
PI 4	4	0.99	216	3.3
PI 5	5	0.54	203	4.0
PI 6	6	0.32	190	5.2

Poly(thioether imide) properties are summarized in Table 2. The glass temperatures decrease from 292°C to 190°C, when  $n$  is increased from 1 to 6. The lower glass temperatures result from the chain flexibility introduced by incorporating the more flexible phenylene thioether units into the polyimide backbone. Concerning thermostabilities, the weight loss measured at 500°C under nitrogen increases slowly with increasing length of the oligo(phenylene thioether) segments. Since thermal stability corresponds to weak bonds in the polymer backbone, the cleavage of the C-S bonds may account for the slightly higher weight loss observed under nitrogen. In fact, at higher segment length the weight loss is about equivalent to that of the high molecular weight poly(phenylene sulfide).

In order to increase the glass transition temperature of soluble 6F poly(arylene thioether imide)s, sulfone moieties were introduced. Instead of oxidizing the thioether monomer, the poly(arylene thioether imide)s are used as intermediates to oxidize the thioether groups located in the polyimide backbone. In the preferred process, the 6F polyimide powders are suspended in formic acid, and hydrogen peroxide is added at 50°C to form sulfone groups in high yields.



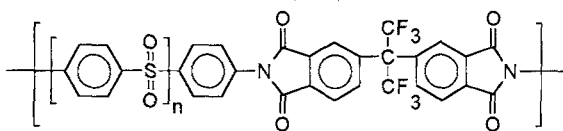
**Figure 2** FTIR spectrum of poly(sulfone imide) PSI 3

The FTIR spectra of poly(sulfone imide) films, e.g. PSI 3 in Figure 2, shows additional absorption bands associated with aromatic sulfone groups at 1330  $\text{cm}^{-1}$

and 1165  $\text{cm}^{-1}$ . The characterization by FTIR spectroscopy as well as by elemental analysis (Table 1) confirms the high conversions of the poly(thioether imide)s.

When the inherent viscosities of poly(thioether imide)s in Table 2 are compared with those of the corresponding poly(sulfone imide)s in Table 3, it is evident that polymer degradation remains in the acceptable range. All oxidized 6F polyimides are soluble in NMP, form tough films and exhibit glass transition temperatures well above 300°C.

**Table 3** Poly(arylene sulfone imide)s (PSI)



Sample	n	$\eta_{\text{inh}}$ (dl/g)	T <sub>g</sub> (°C)	% Weight loss at 500°C
PSI 1	1	0.47	337	3.2
PSI 2	2	0.57	331	3.4
PSI 3	3	0.52	327	4.1
PSI 4	4	0.83	323	5.1
PSI 5	5	0.43	321	6.0
PSI 6	6	0.22	-	7.7

The segment length of the oligo(phenylene sulfone) units only marginally affects the high glass transition temperatures. When compared to the oligo(phenylene thioether) segments, the oligo(phenylene sulfone) segments account for slightly higher weight losses which also increase with increasing sulfur content. Again, this indicates that the thermal decomposition of the bonds between phenylene groups and thioether or sulfone groups respectively may contribute to the polymer degradation reaction.

In conclusion, the incorporation of sulfone moieties into polyimide by oxidation of the poly(arylene thioether imide)s represents a convenient route to poly(arylene sulfone imide)s with substantially higher glass transition temperatures. Such sulfone-containing polymers are of interest as blend components and membrane materials.

### **Acknowledgement**

The authors would like to thank the "Deutsche Forschungsgemeinschaft" for financial support of this research project. We also thank Hoechst AG for providing us with free samples of the 6F-dianhydride.

### **References**

- (1) Seymour RB, Kirshenbaum GS (eds.), "High Performance Polymers: Their Origin and Development", Elsevier Sci. Publ. Co., New York (1986)

- (2) Cleary JW, Phillips Petroleum Co., US Pat. 4,795,799 (1987)
- (3) Gaughan RG, Phillips Petroleum Co., EP 258 866 (1987)
- (4) Daccord G, Sillion B, Polym. Bull. (Berlin) 4, 459 (1981)
- (5) Daccord G, Sillion B, Polym. Bull. (Berlin) 6, 477 (1982)
- (6) Daccord G, Sillion B, Makromol. Chem. 184, 1861 (1983)
- (7) Daccord G, Sillion B, Thibert C, Makromol. Chem. 184, 1869 (1983)
- (8) Takekoshi T, Anderson PP, Matson J.L, Pacific Polymer Prepr. 1, 93 (1989)
- (9) Takekoshi T, Anderson PP, General Electric Co., US Pat. 4,716,216 (1986)
- (10) Takekoshi T, Anderson PP, General Electric Co., US 4,769,424 (1987)
- (11) Wimmer W, Lenzinger Berichte, 66, 10, 1989
- (12) Chien JC, Cheng ZS, J. Polym. Sci. Part A: Polym. Chem. 27, 915 (1989)
- (13) Mülhaupt R, Glatz FP, Schultze JD, Springer J, Am. Chem. Soc., Polym. Chem. Div., Polym. Prepr. 33(1), 203 (1992)

Accepted May 21, 1993      C