

## Syntheses and thermal properties of aromatic and semi-aromatic polythioetheramides containing oligo(thio-1,4-phenylene) segments

Frank P. Glatz and Rolf Mülhaupt\*

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

### Summary

A family of aromatic and semi-aromatic polythioetheramides was prepared from well-defined diamine-terminated oligo(thio-1,4-phenylene)s (PPS-DA) containing  $n=1,2,3,4,5,6$  thio-1,4-phenylene units. Polycondensation reactions with adipic, sebacic, terephthalic and isophthalic acid chlorides were carried out in N-methyl-2-pyrrolidone solution at room temperature to yield amorphous and semi-crystalline polythioetheramides. The influence of the oligo(thio-1,4-phenylene) segment lengths on phase transitions and thermal degradation of the polythioetheramides was investigated. As a function of the PPS segment lengths, glass transition temperatures vary between 120°C and 300°C, and melting temperatures between 290°C and 500°C. The thermal stabilities determined by thermogravimetric analysis under nitrogen increase with increasing PPS segment lengths. In the case of the higher molecular weight PPS segments, the resulting semi-aromatic polyamides exhibit two crystalline phase transitions.

### Introduction

Poly(p-phenylene sulfide) is widely applied as engineering resin which combines high thermal, environmental and dimensional stabilities with toughness and excellent electrical properties. In the first generation of commercial processes, polycondensation of 1,4-dichlorobenzene and sodium sulfide yielded oligomers which required post-curing during processing to form infusible and insoluble polymers (1). More recently, the aromatic nucleophilic displacement reaction has been refined to produce melt processable linear and branched high molecular weight poly(p-phenylene sulfide)s (2). The new generation of thermoplastic poly(p-phenylene sulfide)s offers attractive potential for manufacturing novel blends with various other thermoplastics. Since the semi-crystalline high molecular weight poly(p-phenylene sulfide) is incompatible with most other polymers, segmented copolymers containing well-defined oligo(thio-1,4-phenylene) (PPS) units are of interest as blend compatibilizers. Such compatibilized single or multiphase blends are likely to exhibit unusual property synergisms (3). Moreover, the incorporation of PPS segments into polyamides is expected to improve the flame retardance and reduce smoke emission of the corresponding semi-aromatic and aromatic polythioetheramides. In our research we have examined the influence of well-defined PPS segments on phase transitions and thermal degradation of polyamides prepared from PPS diamines.

### Experimental

#### Materials

Terephthalic and isophthalic acid chloride were purchased from Fluka and sublimed prior to use. Adipic and sebacic acid chloride (Fluka) were purified by distillation. N-Methyl-2-pyrrolidone was distilled from  $P_4O_{10}$  under reduced pressure. THF was refluxed over sodium and distilled. Lithium chloride (Fluka) was vacuum oven dried at 90°C for 24 h prior to use. All reactions were carried out under dry nitrogen. The 4-aminothiophenol was prepared from 4-chloronitrobenzene and sodium sulfide as reported by Gilman (4) followed by reduction with tin in aqueous hydrogen chloride. Typically, a mixture of sodium sulfide nonahydrate (480 g, 2.00 mol) and p-chloronitrobenzene (128 g, 0.81 mol) in 2 l water was refluxed for 12 h. The solution was saturated with sodium chloride, and acetic acid (240 g, 4.00 mol) was added. The precipitate was filtered off and suspended in 250 ml

\*Corresponding author

conc. aqueous hydrogen chloride and 250 ml water. Tin (50 g, 0.42 mol) was added slowly to the boiling suspension and stirred for 1 h, then the resulting solution was filtered and cooled down to room temperature. Sodium sulfide was added, and tin was precipitated as black tin sulfide, then the product was extracted with 2 l diethyl ether. Subsequent to drying with sodium sulfate, distillative removal of the ether, and vacuum distillation, 66 g (65%) of product distilling at 85°C/0.1 Torr was obtained, m.p. 45°C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS): δ (ppm) = 3.5 (s, 3H), 6.5 (d, 2H), 7.1 (d, 2H), amine conc.: calc. (found): 7.98 mol/kg (7.95 mol/kg), mercapto titration: 97% purity.

#### Synthesis of the diamine-terminated oligo(thio-1,4-phenylene)s

**4,4'-Diamino-diphenylthioether (PPS-DA, n=1):** The reaction of 4-chloronitrobenzene and sodium sulfide yielded 4,4'-dinitro-diphenylthioether (5) which was reduced with tin in aqueous hydrogen chloride as described by Price (6). The PPS-DA (n=1) was obtained in 82% yield, m.p. 107°C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS): δ (ppm) = 3.8 (s, 4H), 6.7 (d, 4H), 7.2 (d, 4H), <sup>13</sup>C-NMR: δ (ppm) = 117.1(C2), 127.3(C4), 135.1(C3), 149.4(C1), IR (KBr): 3380 cm<sup>-1</sup> (N-H), 3310 cm<sup>-1</sup> (N-H), 1620 cm<sup>-1</sup> (N-H), 1600 cm<sup>-1</sup>, 820 cm<sup>-1</sup>, elemental analysis for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>S (216.1): calc. (found): C: 66.7%(66.7%), H: 5.5% (5.6%), N: 12.9% (12.9%), S: 14.8% (14.6%), amine conc.: calc. (found): 9.25 mol/kg (9.19 mol/kg).

PPS-DA with n=2,3,4,5,6 were prepared from dibromo-terminated oligo(thio-1,4-phenylene)s which were end-capped with 4-aminothiophenol via aromatic nucleophilic displacement similar to procedures reported by Takekoshi (7,8) and Sillion (9,10). A typical synthesis is described for the preparation of PPS-DA with n=2. PPS-DA with n=3,4,5,6 were prepared according to the same procedure. The dibromo-terminated oligo(thio-1,4-phenylene)s (PPS-DB, n=1,2,3,4) were synthesized by endcapping the dibromo-terminated PPS with benzenethiolate followed by selective bromination in the presence of ferric chloride. This basic reaction scheme was proposed by Takekoshi (7,8) and Heitz (11,12). The preparation of dibromo-terminated PPS with n=4 is described below as an illustration of a typical procedure.

**1,4-Bis[4-(4-phenylthio)phenylthio]benzene (PPS, n=4):** 1,4-Bis(4-bromophenylthio)benzene (n=2) (13.6g, 30 mmol), thiophenol (7.9 g, 72 mmol) and sodium hydroxide (2.9 g, 72 mmol) in NMP were reacted at 50°C for 1 h, at 150°C for 2 h and at 210°C for 1 h. The reaction mixture was precipitated from water, filtered off and recrystallized from toluene. Yield 90%, m.p. 145°C, IR (KBr): 1565 cm<sup>-1</sup>, 810 cm<sup>-1</sup>, 730 cm<sup>-1</sup>, 680 cm<sup>-1</sup>, elemental analysis: C<sub>30</sub>H<sub>22</sub>S<sub>4</sub> (510.6): calc (found): C: 70.6% (70.8%), H: 4.3% (4.4%), S: 25.1% (24.8%).

**1,4-Bis[4-(4-bromophenylthio)phenylthio]benzene (PPS-DB, n=4):** Bromine (8.6 g, 54 mmol) in 50 ml CCl<sub>4</sub> was added slowly to PPS (n=4) (13.8 g, 27 mmol) and ferric chloride (0.2 g) in 200 ml CCl<sub>4</sub> at 60°C. The reaction mixture was stirred for 24 h then cooled to room temperature. The precipitate was filtered off, washed with sodium bicarbonate, extracted with CCl<sub>4</sub> and dried. Yield 55%, m.p. 198°C, <sup>13</sup>C-NMR: δ (ppm) = 120.2(C1), 129.6(C2', C3'), 131.3(C3), 131.9(C2), 132.9(C1', C4', C4), IR (KBr): 1460 cm<sup>-1</sup>, 1000 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, elemental analysis: C<sub>30</sub>H<sub>20</sub>S<sub>4</sub>Br<sub>2</sub> (668.5): calc (found): C: 53.9% (54.2%), H: 3.0% (2.8%), S: 19.2% (18.8%), Br: 23.9% (23.6%).

**1,4-Bis(4-aminophenylthio)benzene (PPS-DA, n=2):** 1,4-Dibromobenzene (58.9 g, 0.25 mol), 4-aminothiophenol (68.8 g, 0.55 mol) and potassium carbonate (91.2 g, 0.66 mol) were dissolved in NMP. The reaction mixture was heated and held at 50°C for 1 h, at 150°C for 2 h and at 210°C for 1 h. After distillative removal of NMP, the product was precipitated from water, collected by filtration and recrystallized from ethanol. Yield 88%, m.p. 166°C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) = 4.9 (s, 4H), 7.0 (m, 12H), <sup>13</sup>C-NMR: δ (ppm) = 117.2(C2), 127.5(C4), 130.2(C3, C2), 135.2(C1'), 148.4(C1), IR (KBr): 3410 cm<sup>-1</sup> (N-H), 3340 cm<sup>-1</sup> (N-H), 1610 cm<sup>-1</sup> (N-H), 1595 cm<sup>-1</sup>, 820 cm<sup>-1</sup>, elemental analysis: C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub> (324.3): calc (found): C: 66.7% (66.6%), H: 4.9% (4.9%), N: 8.6% (8.5%), S: 19.7% (19.4%), amine conc.: calc. (found): 6.17 mol/kg (6.11 mol/kg).

**4,4'-Bis(4-aminophenylthio)diphenylthioether (PPS-DA, n=3)** was prepared from 4,4'-dibromodiphenylthioether and 4-aminothiophenol as described above. The yield after recrystallization from isopropanol was 78%, m.p. 141°C, <sup>13</sup>C-NMR: δ(ppm) = 119.4(C2), 124.3(C4), 130.4(C2'), 132.1(C3), 135.4(C1), 145.9(C1), IR (KBr): 3430 cm<sup>-1</sup>, 3340 cm<sup>-1</sup> (N-H), 1605 cm<sup>-1</sup> (N-H), 1590 cm<sup>-1</sup>, 820 cm<sup>-1</sup>, elemental analysis: C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>S<sub>3</sub> (432.4): calc. (found): C: 66.7% (66.6%), H: 4.6% (4.5%), N: 6.6% (6.5%), S: 22.2% (22.3%), amine conc.: calc. (found): 4.62 mol/kg (4.60 mol/kg).

*1,4-Bis-[4-(4-aminophenylthio)phenylthio]-benzene (PPS-DA, n=4)* was recrystallized from toluene. Yield 79%, m.p. 171°C,  $^{13}\text{C-NMR}$ :  $\delta$  (ppm) = 118.4(C2), 125.4(C4), 131.0(C2', C3), 134.8(C1'), 145.2(C1), IR (KBr): 3420  $\text{cm}^{-1}$  (N-H), 3320  $\text{cm}^{-1}$  (N-H), 1605  $\text{cm}^{-1}$  (N-H), 1580  $\text{cm}^{-1}$ , 820  $\text{cm}^{-1}$ , elemental analysis:  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{S}_4$  (540.5): calc (found): C: 66.7% (66.8%), H: 4.4% (4.2%), N: 5.2% (4.8%), S: 23.7% (23.5%), amine conc.: calc. (found): 3.70 mol/kg (3.63 mol/kg).

*4,4'-Bis-[4-(4-aminophenylthio)phenylthio]-diphenylthioether (PPS-DA, n=5)* was recrystallized from toluene. Yield 77%, m.p. 171°C,  $^{13}\text{C-NMR}$ :  $\delta$  (ppm) = 117.3(C2), 132.8(C2', C3), 134.4(C1'), 144.9(C1), IR (KBr): 3410  $\text{cm}^{-1}$  (N-H), 3310  $\text{cm}^{-1}$  (N-H), 1610  $\text{cm}^{-1}$  (N-H), 1570  $\text{cm}^{-1}$ , 820  $\text{cm}^{-1}$ , elemental analysis:  $\text{C}_{36}\text{H}_{28}\text{N}_2\text{S}_5$  (648.7): calc (found): C: 66.7% (66.5%), H: 4.3% (4.5%), N: 4.3% (4.4%), S: 24.7% (24.3%), amine conc.: calc. (found): 3.08 mol/kg (3.02 mol/kg).

*1,4-Bis-[4-(4-(4-aminophenylthio)phenylthio)phenylethio]benzene (PPS-DA, n=6)* was recrystallized from toluene. Yield 75%, m.p. 207°C,  $^{13}\text{C-NMR}$ :  $\delta$  (ppm) = 117.3(C2), 132.4(C2', C3), 134.7(C1'), 145.6(C1), IR (KBr): 3410  $\text{cm}^{-1}$  (N-H), 3340  $\text{cm}^{-1}$  (N-H), 1605  $\text{cm}^{-1}$  (N-H), 1590  $\text{cm}^{-1}$ , 820  $\text{cm}^{-1}$ , elemental analysis:  $\text{C}_{42}\text{H}_{32}\text{N}_2\text{S}_6$  (756.9): calc (found): C: 66.7% (66.5%), H: 4.2% (4.3%), N: 3.7% (3.9%), S: 25.4% (24.9%), amine conc.: calc. (found): 2.64 mol/kg (2.54 mol/kg).

### Syntheses of polythioetheramides

A typical example of a polycondensation was conducted as follows. Polyamide PSA 1: sebacic acid chloride (4.780 g, 20 mmol) dissolved in 9 ml THF was added quickly at 0°C to a solution of PPS-DA (n=1) (4.322 g, 20 mmol) in 90 ml NMP containing 3.0 g lithium chloride. After 1 h the temperature was raised to room temperature and stirred for 12 h. The polyamide was precipitated in water using a blender, washed with boiling water, extracted with acetone and dried. The yield was quantitative. The inherent viscosity of a 0.5 g/dl polymer solution in NMP 3 wt % LiCl was 0.88 dL/g at 30°C. Elemental analysis:  $(\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2\text{S})_n$  (382.2) $_n$ : calc (found): C: 69.1% (68.1%), H: 6.8% (6.6%), N: 7.3% (7.2%), S: 8.3% (7.9%).

### Polymer characterization

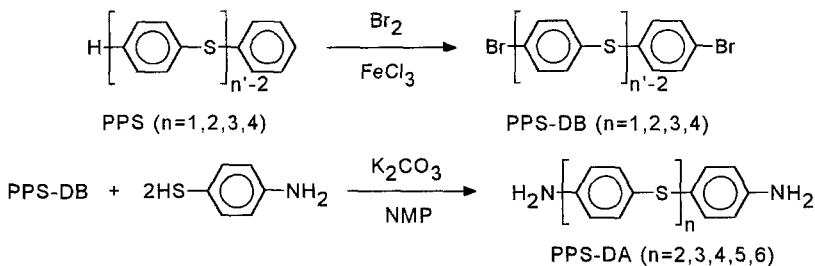
Elemental analyses were conducted using a Perkin-Elmer Model 240 analyzer. The 300 MHz  $^1\text{H-NMR}$  spectra were recorded by use of a Bruker WM 300 spectrometer from a  $\text{CDCl}_3$  solution at room temperature using TMS as an internal standard. The MAS  $^{13}\text{C-NMR}$  spectra were obtained on a Bruker CX 300 spectrometer with a frequency of 59.6 MHz. Samples were packed in aluminium oxide rotors and were spun at the magic angle (MAS) at speeds of 2-3.5 MHz. Infrared spectra were obtained using a Perkin Elmer 1330 Infrared spectrometer. The inherent viscosities of 0.5 g/dl polymer solutions in NMP 3 wt % LiCl were measured using an Ubbelohde viscosimeter at 30°C. The glass transition temperatures were determined by dynamic mechanical analysis using a Rheometrics Solid Analyzer RSA II at a frequency of 1 Hz. The differential scanning calorimetry and thermogravimetric analyses were obtained on a Netzsch Thermal Analysis System with a heating rate of 10°C/min under nitrogen.

## Results and discussion

### Polythioetheramide syntheses

Takekoshi (7,8), Daccord and Sillion (9,10), Heitz (11,12) and Wimmer (13) have reported the synthesis of difunctional telechelic polythioethers, including the diamine-terminated oligo(thio-1,4-phenylene)s (PPS-DA), which are useful monomers for the preparation of polythioetheramides, polythioetherimides, and polythioetheramideimides. In the preferred synthetic scheme for the preparation of PPS-DA, dibromo-terminated oligo(thio-1,4-phenylene)s (PPS-DB) are used as versatile intermediates. When reacted with 4-aminothiophenol in NMP in the presence of anhydrous potassium carbonate, the PPS-DB are converted into the corresponding PPS-DA. The same PPS-DB can also be used as intermediate in the synthesis of PPS-DA with a well defined number  $n$  of thio-1,4-phenylene units. For example, the PPS-DB are end-capped with thiophenolate to form PPS oligomers which are selectively brominated in para-position in the presence of ferric chloride to yield the higher PPS-DB and the corresponding PPS-DA. Both endcapping reactions with thiophenolate and 4-aminothiophenolate were conducted in NMP in the presence of anhydrous potassium

carbonate, raising the reactor temperature stepwise from 50°C to 150°C and to 210°C. For PPS-DA with even numbers  $n=2,4,6$  of thio-1,4-phenylene units, 1,4-dibromo-benzene is used as starting material to initiate the reaction sequence involving endcapping with thiophenolate followed by bromination or endcapping with 4-aminothiophenolate respectively. Accordingly, the 4,4'-diphenylthioether represents the appropriate starting material for the preparation of PPS-DA with odd numbers  $n=3,5$ . With this reaction sequence, as illustrated in Scheme 1, PPS-DA with  $n=2,3,4,5,6$  were prepared. The melting temperatures of PPS-DA increase with increasing  $n$  and show typical odd/even effects with slightly higher melting temperatures for even numbers of the thio-1,4-phenylene units. At oligomerization degree  $n>6$ , the melting temperatures of PPS-DA reach a plateau value approaching the range in which the melting temperature of poly(*p*-phenylene sulfide) is to be found. Such high molecular weight PPS-DA crystallize readily and are insoluble in common dipolar aprotic solvents used in low temperature solution polycondensation.



Scheme 1

The solid state  $^{13}\text{C}$ -NMR spectroscopic analysis of PPS-DA with  $n=1,3,5$  depicted in Figure 1 shows the signals at 117 ppm (C4) and 145 ppm (C1) which are assigned to the carbon atoms attached or in para position to the amine group. At a higher degree of oligomerization, the intensities of those signals are reduced with respect to the signals at 132 ppm (C2') and 135 ppm (C3'), which correspond to the oligo(thio-1,4-phenylene) unit. Poly(*p*-phenylene sulfide) only shows the signals at 132 ppm (C2') and 135 ppm (C1') (14).

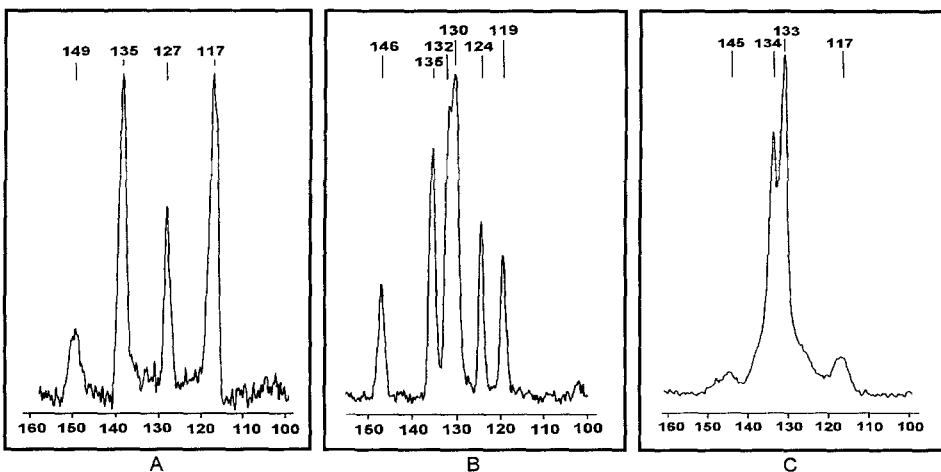
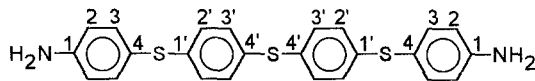
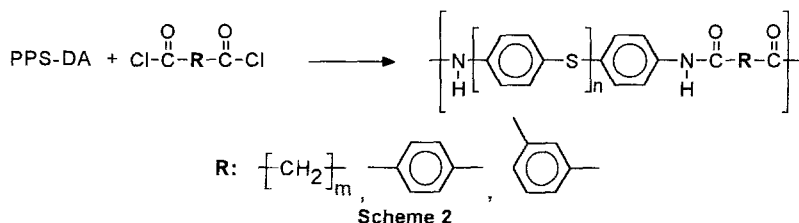


Figure 1. 59.6 MHz MAS  $^{13}\text{C}$ -NMR spectrum of PPS-DA  $n=1$  (A),  $n=3$  (B),  $n=5$  (C)

Typically, semi-aromatic and aromatic polythioetheramides were prepared from PPS-DA monomers and the stoichiometric amounts of dicarboxylic acid chlorides in a low temperature solution polycondensation process. Preferably, the solution polycondensation was performed in NMP containing 3 wt % LiCl, stirring the reaction mixture 1 hour at 0°C and 12 hours at room temperature.



### Segmented semi-aromatic polythioetheramides

Table 1 summarizes the properties of the semi-aromatic polyamides derived from PPS-DA and adipic acid (PAA samples) or sebacic acid (PSA samples). In both polythioetheramide series glass transition temperatures as well as melting temperatures decrease with increasing segment length of the oligo(thio-1,4-phenylene). While PAA melting temperatures vary between 320°C and 360°C in the range of the polymer decomposition, the PSA samples melt around 310°C and are melt processable. From Figure 2 which displays the DSC traces of PSA samples as a function of the number of thio-1,4-phenylene units and from Table 1, it is apparent that two distinct phase transitions corresponding to the crystalline phase exist in the case of  $n=4,5,6$ . Even in the case of  $n=2$ , there is an indication of crystallization when the temperature reaches 250°C. The second melting temperature of PAA as well as PSA decreases with increasing  $n$  and approaches 282°C which is typical for the melting of higher oligo(thio-1,4-phenylene)s. Therefore, PPS segments with  $n=4,5,6$  are large enough to induce the formation of a separate crystalline phase.

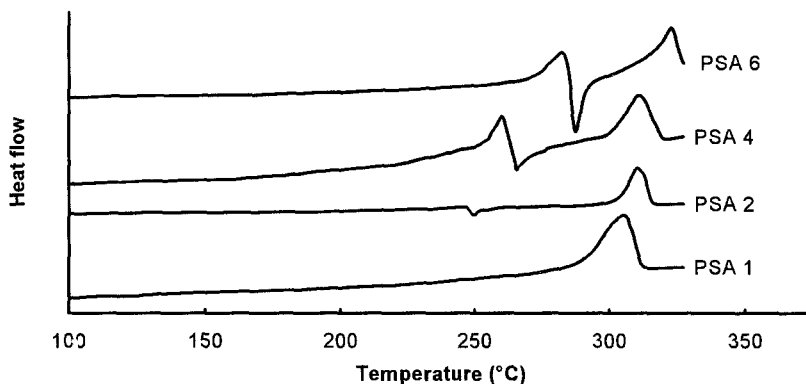
**Table 1** Properties of semi-aromatic polythioetheramides

$$\left[ \text{N} \left( \text{H} \right) \left[ \text{C}_6\text{H}_4 \right]_m \text{S} \left[ \text{C}_6\text{H}_4 \right]_n \text{N} \left( \text{H} \right) \overset{\text{O}}{\parallel}{\text{C}}-\left[ \text{CH}_2 \right]_m-\overset{\text{O}}{\parallel}{\text{C}} \right]$$

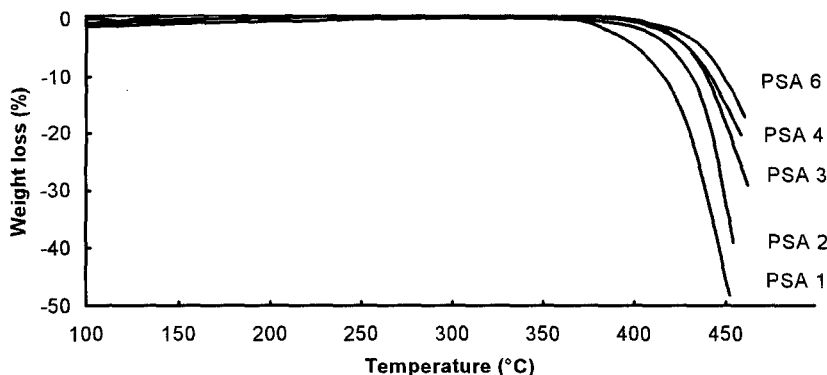
Sample	m	n	$\eta_{\text{inh}}$ (dl/g)	$T_g$ (DMA) (°C)	$T_m$ (DSC) (°C)	Weight loss at 400°C (%)
PAA 1	4	1	1.08	198	363	37.1
PAA 2	4	2	0.71	178	354	28.0
PAA 3	4	3	0.34	169	347	16.9
PAA 4	4	4	0.73	161	280/341	16.2
PAA 5	4	5	0.31	149	275/315	13.8
PAA 6	4	6	0.35	144	281/323	5.8
PSA 1	8	1	0.88	149	308	5.6
PSA 2	8	2	0.53	143	310	2.7
PSA 3	8	3	0.69	138	316	2.4
PSA 4	8	4	0.87	131	261/311	1.2
PSA 5	8	5	0.43	124	274/320	2.6
PSA 6	8	6	0.36	119	282/322	2.5

The thermogravimetric analysis of the segmented semi-aromatic polyamides under nitrogen, reported in Table 1 and shown for PSA in Figure 3, clearly reveals that thermal degradation is affected by the PPS segment lengths as well as the type of aliphatic dicarboxylic acid. Since weight losses encountered at elevated temperatures result from thermal cleavage of chemical bonds in the polymer backbone, the thermal stabilities are improved when the aliphatic hydrocarbon segments of the dicarboxylic acids are replaced by more stable aromatic thioethers. As a consequence, PSA and

PAA give much higher resistance to thermal degradation when the PPS segment length and PPS content are increased. For example, in the case of polythioetheramides derived from adipic acid, the incorporation of six thio-1,4-phenylene units reduces weight loss at 400°C from 37.1% to 5.8%. The improvement of PSA thermal stabilities with the number  $n$  of thio-1,4-phenylene units ( $n=1,2,3,4,6$ ) is shown in Fig. 3.



**Figure 2** DSC traces of semi-aromatic PSA polythioetheramides derived from sebacic acid and PPS-DA



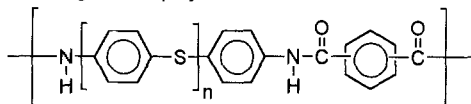
**Figure 3** Thermogravimetric analysis of semi-aromatic PSA polythioetheramides as a function of the PPS-segment length

Similar to the thermal degradation of aliphatic polyamides, the degradation of polythioetheramides is greatly dependent upon the polymer structures and the monomeric units. In spite of the higher content of hydrocarbon segments in polythioetheramides derived from sebacic acid, the semi-aromatic polythioetheramides are much more stable when adipic acid is replaced by sebacic acid. While PAA polythioetheramides decompose readily at temperatures slightly above 300°C, the corresponding PSA polythioetheramides resist temperatures of 400°C for prolonged periods of time. In the case of aliphatic polyamides the thermal degradation of many polyamides in the absence of air is thought to be related to the cleavage of the C-N bonds. In fact, polyamide-6,6 is much less thermally stable in comparison to polyamide-6,10. A characteristic feature of the pyrolysis of adipic acid-based polyamides is the formation of large amounts of cyclopentanone resulting from thermal decomposition of the adipoyl units (15). This cyclization reaction is thermodynamically much less favored in the case of sebacic acid derivatives. As a consequence, the thermal stability of the PSA polythioetheramides is markedly higher when compared to PAA.

### Segmented Polythioetheraramides

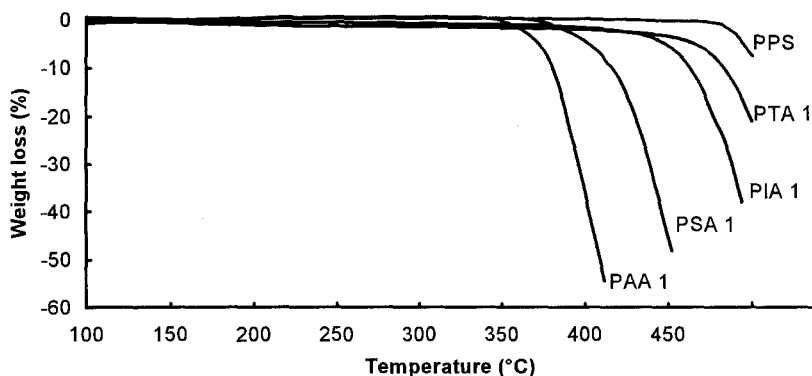
Polyaramides, especially poly(p-phenylene terephthalamide), are known as heat resistant polymers of exceptionally high specific modulus and tensile strength. While rigid-rod polyaramides are insoluble in most common solvents, the corresponding poly(m-phenylene isophthalamide)s can be processed from solutions of conventional dipolar aprotic solvents. A range of polythioetheraramides was prepared in low temperature solution polycondensation reactions of PPS-DA ( $n=1,2,3,4,5,6$ ) with aromatic dicarboxylic acid chlorides from terephthalic and isophthalic acid as well as (50/50) blends of terephthalic and isophthalic acid (PIA). From the results summarized in Table 2, it is apparent that the solution polycondensation in NMP/LiCl yields soluble segmented polythioetheraramides of high molecular weights. The PTA polythioetheraramides derived from terephthalic acid and PPS-DA are semi-crystalline materials with high glass transition and melting temperatures. Both phase transition temperatures are adversely affected when PPS segment length is increased. While PTA1 melts above decomposition, the incorporation of six thio-1,4-phenylene units reduces the melting temperature to 358°C and the glass transition temperature by 100°C to 194°C. Such polythioetheraramides represent interesting candidates for melt processable polyaramides. In contrast to the semi-aromatic polythioetheraramides and the corresponding PIA polythioetheraramides derived from isophthalic acid, the PTA thermal degradation is not influenced by the PPS segment length, and PPS-type crystallization is not observed. In the case of PIA polythioetheraramides, for  $n=1$  and  $n=4,5,6$ , the polymers are semi-crystalline, while PIA with  $n=2,3$  are amorphous. In the case of PIA with  $n=4,5,6$ , similar to the corresponding semi-aromatic polythioetheraramides PAA and PSA, the melting temperatures fall in the range of 286°C to 291°C typical for the crystallization of the PPS segments. When isophthalic and terephthalic acid (50/50) are blended together, the resulting copolymers are amorphous with glass transition temperatures decreasing with increasing PPS segment length. The copolymer glass transition temperatures measured by dynamic mechanical analysis are in good agreement with the values calculated from PTA and PIA on the basis of the 50/50 blend ratio.

**Table 2** Properties of segmented polythioetheraramides



Sample	Substitution	n	$\eta_{inh}$ (dl/g)	$T_g$ (DMA) (°C)	$T_m$ (DSC) (°C)	Weight loss in %	
						450°C	500°C
PIA 1	m	1	0.47	263	385	10.4	32.1
PIA 2	m	2	0.52	238	-	4.8	29.4
PIA 3	m	3	0.56	218	-	3.6	28.1
PIA 4	m	4	0.97	194	291	2.7	25.0
PIA 5	m	5	0.68	180	286	2.5	24.5
PIA 6	m	6	0.31	171	291	2.6	22.8
PTA 1	p	1	1.74	-	499	2.6	16.1
PTA 2	p	2	1.05	298	456	2.2	24.0
PTA 3	p	3	0.99	274	431	1.8	23.2
PTA 4	p	4	1.25	238	394	2.6	23.0
PTA 5	p	5	1.21	213	370	2.5	22.8
PTA 6	p	6	0.38	194	358	3.0	21.5
PITA 1	m. p	1	0.89	292	-	5.6	30.6
PITA 2	m. p	2	0.64	263	-	4.9	28.9
PITA 3	m. p	3	0.63	233	-	2.3	26.4
PITA 4	m. p	4	0.53	213	-	2.4	23.6
PITA 5	m. p	5	0.68	189	-	2.8	23.0
PITA 6	m. p	6	0.33	182	-	3.0	22.5

When the thermal stabilities as measured by thermogravimetric analysis under nitrogen are compared, as depicted in Figure 4, the higher melting polythioetheraramides PTA give the highest thermal resistance. However, with the isophthalic acid-based polythioetheraramides PIA and PITA similar performance is achieved when the PPS segment lengths are increased.



**Figure 4** Thermogravimetric analysis of the polythioetheraramides in comparison to poly(thio-1,4-phenylene) and the corresponding semi-aromatic polythioetheraramides.

### Conclusion

The incorporation of well-defined oligo(thio-1,4-phenylene) units into semi-aromatic polythioetheraramides and polythioetheraramides yields a range of sulfur-containing polymers with improved processability in melt and solution. While the glass transition and melting temperatures are reduced with increasing oligo(thio-1,4-phenylene) segment length, the resistance of polyamides against thermal degradation improves. This class of polymers offers interesting potential for blend formation with poly(p-phenylene sulfide) and other polyamides.

### Acknowledgement

We would like to thank the Deutsche Forschungsgemeinschaft for their financial support of this research.

### References

- Hill HW, Jr., "High Performance Polymers: Their Origin and Development", Seymour RB, Kirshenbaum GS (eds.), Elsevier Science Publ., New York (1986)
- Idel K, "Houben Weyl", Georg Thieme Verlag, Stuttgart (1987), vol. E 20 II, p. 1461
- Utracki LA (ed.), "Polymer Alloys and Blends", Hanser Publishers, Munich (1989), p.125.
- Gilman H, Gainer G, J. Am. Chem. Soc. 71, 1749 (1949)
- R. Fuson and M. Melamed, J. Org. Chem. 13, 690 (1948)
- Price P, Leonard D, Stacy W., Am. Soc. 69, 85 (1959)
- Takekoshi T, Anderson PP, Matson JL, Pacific Polymer Prepr. 1, 93 (1989)
- U.S. Pat. 4,716,216 & 4,769,424 (1988), invs.: Takekoshi T, Anderson PP
- Daccord G, Sillion B, Polymer Bull. 4, 459 (1981)
- Daccord G, Sillion B, Polymer Bull. 6, 477 (1982)
- Koch W, Heitz W, Makromol. Chem. 184, 779 (1983)
- Freund L, Heitz W, Makromol. Chem. 191, 815 (1990)
- Wimmer W, Lenzinger Ber. 66, 10 (1989)
- Gomez MA, Tonelli AE, Am. Chem. Soc., Polym. Chem. Div., Polym. Prepr., 30, 155 (1990)
- Zimmerman J, Encycl. Polym. Sci. Technol. (Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI, eds.), Wiley Interscience Publ., New York (1988), vol. 11, p. 355.