

## Synthesis of rigid rod polymers

### I. Diphenylthiazolothiazole pendant group

Raimond Liepins and Brian C. Benicewicz

Materials Science and Technology Division, Mail Stop E549, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

#### Summary

Rigid rod polymers containing long rigid side chains have been prepared. The initial approach to this class of materials involved the synthesis of a poly(p-phenyleneterephthalamide) (PPT) backbone with diphenylthiazolothiazole pendant groups. The synthesis and preliminary characterization of the monomer and polymer are reported.

#### Introduction

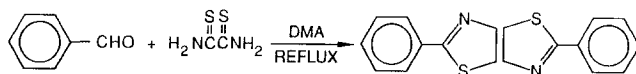
One of the goals of the liquid crystalline polymers effort at Los Alamos National Laboratory is to investigate new polymers which may lead to improvements in the compressive and tensile properties of polymers.<sup>1,2</sup> One general class of materials currently under investigation is composed of rigid or extended rodlike polymers containing rigid rod-like side chains. A number of other studies have focused on shorter or more flexible side chain modifications.<sup>3-5</sup>

In this paper, we describe our initial detailed synthetic chemistry to prepare PPT backbone polymers containing diphenylthiazolothiazole side groups attached through a sulfide linkage. Detailed accounts of other structurally similar polymers will be described in future contributions.

#### Experimental

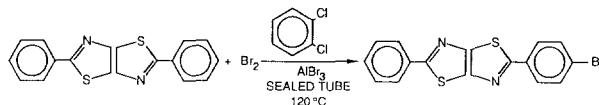
##### Monomer Synthesis:

##### 2,5-Diphenylthiazolo[5,4-d]thiazole, 1



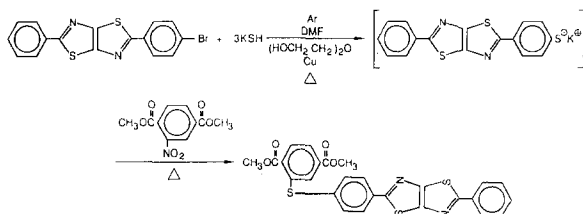
The compound was synthesized according to the reported procedure.<sup>6</sup> Typical yield 70-80%; mp 214°C (lit. 210°C).

##### 2-Phenyl-5-(4'-bromophenyl)thiazolo[5,4-d]thiazole, 2



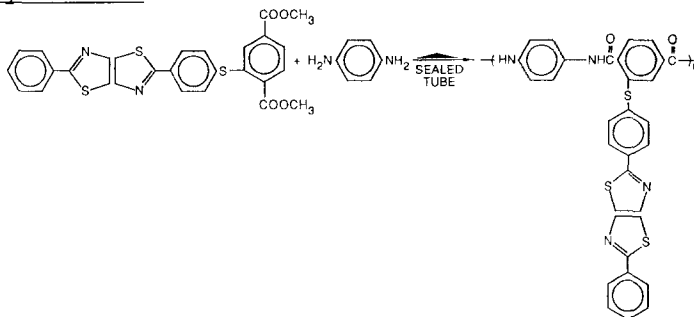
To a solution of 5g (0.017 mol) **1** in 30 mL o-dichlorobenzene in a thick walled glass tube was added 2.72g (0.017 mol) bromine and 0.1g aluminum bromide. The mixture was degassed to  $5 \times 10^{-4}$  torr three times before it was sealed at approximately  $10^{-4}$  torr. The tube was placed in an oven at  $120^\circ\text{C}$  for 72 h with periodic shaking. The reaction mixture was cooled to room temperature and combined with 250 mL 30/70 anisole/o-dichlorobenzene. It was heated to  $80^\circ\text{C}$  and filtered to remove the dibromo co-product. Refrigeration for 16 h allowed isolation of **2** (4.5g, 70%), mp  $261^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_9\text{N}_2\text{S}_2\text{Br}$ : C, 51.34; H, 2.67; N, 7.49; S, 17.11; Br, 21.39. Found: C, 51.18; H, 2.59; N, 7.47; S, 17.25; Br, 21.10.

Dimethyl-2-[4-thio-(2,5-diphenylthiazolo[5,4-d]thiazole)] terephthalate, **3**



Compound **2**, 1.0g (0.0027 mol), was dissolved into a solution of 30 mL DMF and 10 mL 2-hydroxyethylether at  $120^\circ\text{C}$ . Potassium hydrogen sulfide (0.54g, 0.0075 mol) and 0.16g copper powder were added. The mixture was stirred and refluxed for 3 h under argon, cooled to  $120^\circ\text{C}$  and 0.894g (0.0037 mol) dimethyl-2-nitroterephthalate added. This mixture was heated at  $130^\circ\text{C}$  for 2 h, hot filtered and poured into 100 mL water with good stirring. The mixture was then chilled for 16 h. The gelatinous precipitate was collected and purified by reprecipitating from DMF/ $\text{H}_2\text{O}$  to yield **3** (0.46g, 40%), mp  $189\text{--}191^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{18}\text{N}_2\text{S}_3\text{O}_4$ : C, 60.20; H, 3.47; S, 18.58. Found: C, 59.25; H, 3.36; S, 18.36.

Polymer Synthesis:



0.380g (0.00073 mol) **3** and 0.0792g (0.00073 mol) purified p-phenylene diamine (recrystallized three times from hot xylene) were placed in a 1 x 20 cm glass pressure tube, degassed to  $10^{-3}$  torr and sealed. The tube was then treated according to the following schedule: 1) 228°C, 5 h 2) cooled to room temperature, opened under nitrogen 3) 280°C, 1 h, under nitrogen 4) cooled under nitrogen 5) 280°C, 0.5 h, dynamic vacuum ( $-10^{-2}$  torr). The black solid product, 0.19g (46%) showed Tg 212°C, melting endotherm 393°C. Anal. Calcd for  $C_{30}H_{18}N_4S_3O_2$ : C, 64.02; H, 3.20; N, 9.96. Found: C, 67.50; H, 3.26; N, 10.11.

### Results and Discussion

The thiazolo[5,4-d]thiazole moiety exhibits broad absorption in the UV region, has a simple IR spectrum, possesses strong electrophilic character, is resistant to attack by strong nitric or sulfuric acids, and cannot be easily brominated.<sup>7</sup> Monobromination of diphenylthiazolothiazole presented equally great difficulties. Bromination in an open flask in the presence of UV or thallium acetate or metering in of an excess of bromine over long periods of time (several days) yielded little or no product. A high temperature, sealed tube technique was developed and optimized to give a good yield of **2** plus a small amount of the dibromo compound [(2,5-bis-(4-bromophenyl)thiazolo[5,4-d]thiazole]. Most of the dibromo compound was separated out by fractional recrystallization from 30/70 (v/v) anisole/o-dichlorobenzene mixture.

A number of typical reactions for sulfide synthesis were explored for the preparation of the monomer, **3**. These included: 1) condensation of the alkali salt of a thiol with a bromide, 2) reaction of sodium sulfide with bromides, 3) reaction of sodium ethyl xanthate with bromides, and 4) cuprous oxide catalyzed reaction between a thiol anion and a bromide. A difficulty in these reactions is the poor solubility of **2** and other reaction components in most solvents. In our laboratory, the cuprous oxide catalyzed reaction gave the best results.

For our initial polymerization studies, the reaction of the dimethylester **3** with p-phenylene diamine was investigated. The dimethyl ester monomer was used for the polymerization reaction because it required fewer synthetic steps than the diacid or diacid chloride and only small amounts of material were available at this time. Table I shows that low inherent viscosities were measured for the polymers prepared under these conditions. It appeared that the higher temperatures used to advance the molecular weight also led to degradation of the polymer or undesirable side reactions. Subsequent work on other condensation reactions will be described in future contributions.

Table 1. Polymerization Results

Sample	Solubility			Inherent Viscosity*	Color
	CHCl <sub>3</sub>	HMPA	conc. H <sub>2</sub> SO <sub>4</sub>		
Polymer I	no	yes	yes	0.07	light brown
Polymer II	no	yes	yes	0.11	brown
Polymer III	no	no	yes	0.20	dark brown
Polymer IV	no	no	partially	>0.20	black

\*Dilute solution viscosities in conc. H<sub>2</sub>SO<sub>4</sub> at 0.125% concentration.

Polymer III had a glass transition temperature of 212°C and displayed a melting endotherm at 393°C. For comparison, commercial PPT fiber showed a glass transition of 345°C and no endotherms up to 500°C. The IR spectrum of Polymer III contained all of the absorptions of PPT plus 13 other absorptions attributed to the pendant diphenylthiazolothiazole group. Thermal gravimetric analysis of Polymer III in air showed initial material loss of about 25 wt. % at 319°C. Further heating showed a second decomposition point at approximately 578°C, which is the same as that for the commercial PPT fiber. A yellow crystalline solid, identified as 2,5-diphenyl thiazolo[5,4-d]thiazole, was collected as a byproduct of the degradation process. Polymer III gave a char yield of 15-20 wt % of a shiny black residue at a temperature of 900°C. PPT left no residue at 690°C. The IR spectrum of the 900°C residue contained only the following absorptions: 1623 (w), 1100 (m), and 600 (w) cm<sup>-1</sup>. The 1623 cm<sup>-1</sup> absorption is indicative of aromatic C=C and/or C=N and the absorption at 1100 cm<sup>-1</sup> is present in graphite.

#### Acknowledgements

We would like to thank Sandra Cisneros-Flores for synthesizing the 2,5-diphenylthiazolo[5,4-d]thiazole and the DSC and TGA work; Robb Hermes for the GC/MS work on the bromination products of the diphenylthiazolothiazole, and to Dave Duchane for stimulating discussions. This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy.

#### References

1. F. Dowell, J. Chem. Phys. 91 (2), 1316 (1989).
2. F. Dowell, J. Chem. Phys. 91 (2), 1326 (1989).
3. D. M. Sutherland and J. K. Stille, *Macromolecules* 18, 2669 (1985).
4. M. Ballauff and G. F. Schmidt, *Makromol. Chem. Rapid Comm.* 8, 93 (1987).
5. J. Y. Jadhav, W. R. Krigbaum, and J. Preston, *Macromolecules*, 21, 538 (1988).

6. J. R. Johnson and R. Ketcham, *J. Am. Chem. Soc.* 82, 2719 (1980).
7. J. R. Johnson, D. H. Rotenberg, and R. Ketcham, *J. Am. Chem. Soc.* 90, 4046 (1970).

Accepted February 27, 1990      K