Synthesis and Characterization of Poly[(benzo[1,2-d:5,4-d']bisthiazole-2,6-diyl)-1,4-phenylene]

Chunxiao Zhang, Satoshi Tanigawa, Tetsuya Uchida and Kaoru Shimamura

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Poly[(benzo[1,2-d:5,4-d']bisthiazole-2,6-diyl)-1,4-phenylene](cis-PBZT) with a relatively high molecular weight was prepared by a new synthesis route. Properties of the synthesized polymer, such as thermostability, liquid crystallinity etc. were investigated and compared with those of trans-PBZT. cis-PBZT was crystallized from dilute solution and the electron microscopy showed that the precipitate was a rod-like crystal similar to that of trans form. In spite of rigid nature of the back bone, cis-PBZT showed poor crystallinity.

INTRODUCTION

Poly[(benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl)-1,4-phenylene](trans-PBZT) and poly[benzo(1,2-d:5,4-d') bisoxazole-2,6-diyl]-1,4-phenylene(cis-PBZO) were firstly prepared by Wolfe[1,2] and are well known for their excellent mechanical properties and thermal and oxidative resistances. Their isomers, poly[(benzo[1,2-d:5,4-d']bisthiazole-2,6-diyl)-1,4-phenylene](cis-PBZT) and poly[benzo(1,2-d:4,5-d') bisoxazole-2,6-diyl]-1,4-phenylene(trans-PBZO)(Scheme 1), also have a rigid rod nature and therefore good properties will be expected. Wolfe tried to synthesize cis-PBZT but failed. It was suggested that the monomer: 4,6-diamino-1,3-benzenedithiol dihydrochloride(DABDD) has an inherent instability toward oxidation and was difficult to be purified[1]. Okada[3] had reported the synthesis of the monomer and incorporated it into thiazine-containing polymers, but the molecular weight was very low. In our study, the monomer DABDD was synthesized by a new route(Scheme 2). By polycondensation of this monomer with terephthalic acid (TPA) in poly(phosphoric acid)(PPA), cis-PBZT's were successfully prepared with relatively high molecular weight. Properties of cis-PBZT, such as thermo-

Department of Applied Chemistry
stability, liquid crystallinity etc. were investigated and compared with those of trans-PBZT.

EXPERIMENT

![Chemical Structures]

**Scheme 2**

**Synthesis of 2,6-Diaminobenzo[1,2-d:5,4-d']bisthiazole(5)**

12g of 4,6-diamino-1,3-dithiocyanobenzene(2)[3] in 120mL acetic acid was stirred at reflux for 15 min. From the resulting solution, white needle crystals precipitated upon cooling. The crystals were collected and then recrystallized from acetic acid once again. Resultant white needle crystals were washed with pure acetic acid and dried at 80 °C under reduced pressure to give 10.2g (67%) of 2,6-diaminobenzo[1,2-d:5,4-d']bisthiazole di-acetic acid(4). \(^1\)H-NMR(DMSO-d6): \(\delta\) 7.40(1H); 7.50 (6H); 7.99(1H) and 2.03(6H)ppm. \(^13\)C-NMR(DMSO-d6): 173.1, 166.9, 152.5, 125.5, 113.3, 108.1 and 22.0 ppm.

10.2g of 4 was dissolved in water and neutralized with ammonia solution when pale-white crystals appeared. The crystals were filtered and dried to yield 6.2g(77.1%) of 5. \(^1\)H-NMR(DMSO-d6): \(\delta\) 7.85(1H); 7.37(4H); 7.27(1H)ppm. \(^13\)C-NMR(DMSO-d6): 166.1, 151.7, 124.3,112.5 and 107.0 ppm.

IR(KBr): 3400, 3280cm\(^{-1}\) (NH \(z\)), 1640cm\(^{-1}\) (C=\(N\)), 857cm\(^{-1}\) (1,2,4,5-C \(z\) H \(z\)).

Anal. Calcd for C \(z\) H \(z\) N \(z\) S \(z\) : C,43.13; H,2.71.

Found: C,42.8; H,3.0.

**4,6-Diamino-1,3-benzenedithiol dihydrochloride(7)**

To a stirred suspension of 8.09g(0.0364 mol) of 5 in 28.8ml of deaerated water was added 32.6g (0.582 mol) of 85.5% potassium hydroxide while the flask was swept with a stream of argon. The mixture was heated at 160 °C for 6h under an argon blanket and then the resulting yellow solution was allowed to cool with stirring overnight. Upon cooling to 5 °C for 0.5 h, the potassium salt (6) of yellow color crystallized from the reaction mixture. The resultant slurry was then transferred via a closed system to an argon filled glove-box. Then the yellow crystals were collected by filtration, and pressed as dry as possible. This extremely air-sensitive potassium salt was dissolved in 12ml of deaerated water, and added dropwise to a solution of 50ml of dilute hydrochloric acid(\(H \_2 O\HCl= 1:1\)). Then to this solution, concentrated HCl(about 30ml) was added slowly to give white needles
of 7. After dried in argon atmosphere at room temperature for 48h under reduced pressure, 2.8g of 7 was obtained.

2,6-Diphenylbenzo[1,2-d:5,4-d']bisthiazole(E in Scheme 1)

The synthesis method was the same reported by Wolfe. E was obtained with a yield of 91.6%. IR (KBr): 1482,1308 cm⁻¹ (hetero-ring stretch), 960cm⁻¹ (hetero ring "breathing"), 860cm⁻¹ (1,2,4,5-C = H). ¹ H-NMR(CISO s H-D z SO + ): δ 9.12(1H); 8.76(1H); 8.19(4H); 8.05(2H); 7.87(4H)ppm.

¹¹ C-NMR(CISO s H-D z SO + ): 177.0; 137.8; 135.6; 129.1; 128.3; 126.8; 126.3; 121.0; 117.8ppm.


Found: C,69.3; H,3.7; N,8.0.

Poly[(benzo[1,2-d:5,4-d']bisthiazole-2,6-diy1)-1,4-phenylene](cis-PBZT)

A mixture of 7 (1.363g, 5.56mmol) and pre-deaerated PPA(45g) was heated at 40 °C for 4h, 70 °C for 24h under a slow stream of argon and then reduced pressure was applied until the solution became clear without bubbles(24h). Terephthalic acid(TPA)(0.923g, 5.56mmol) was then added to the solution which was stirred at 40 °C for 5h. Then the mixture was heated as follows: 70 °C / 72h, 90 °C / 72h, 120 °C / 72h, 165 °C / 72h, 180 °C / 72h, 195 °C / 24h, 205 °C / 5h. The final sticky brown solution was put into a large volume of water in order to remove PPA to yield a copper-colored polymer. The product was washed repeatly with water until it was acid free and then dried. 1.67g of cis-PBZT was obtained with an intrinsic viscosity of 3.8 dL/g(MSA). IR(film): 1482,1407,1310 cm⁻¹ (hetero-ring stretch), 959cm⁻¹ (hetero-ring "breathing"), 868cm⁻¹ (1,2,4,5-C = H).

Anal. Calcd for C : H : N : S : C, 63.13; H,2.27; N,10.51; S,24.08.

Found: C,59.1; H,2.8; N,9.8; S,21.9.

The polymers prepared by the above method are summarized in table 1.

Viscosity Determination

Intrinsic viscosity of the polymer was determined by extrapolation of ( η * = 1) / C and ln η * = 1 / C to zero concentration, using freshly distilled methanesulfonic acid(MSA).

Crystallization from Dilute Solution

A mixture of the synthesized polymer IV and sulfuric acid(92wt%) was sealed in a glass tube and dissolved at 110 °C for 10h. The polymer concentration was 0.1wt%. Upon slow cooling, the polymer deposited from the solution as yellow crystals which were observed by using of a transmission electron microscope(TEM). The cloudy and the dissolving temperatures were measured by naked eyes. For comparison, trans-PBZT with an intrinsic viscosity of 3.4dL/g was crystallized under the same condition as the cis-polymer.

RESULT AND DISCUSSION

Monomer Synthesis

The synthesis of intermediate compound 2 was carried out following Okada[3]. The rude product was fractionated by the column chromatography. Fig.1 shows three ¹ H-NMR spectra of the rude product and the two fractions, which were assigned to a mixture of 2 and 3, pure 2 and pure 3 respectively. thus the rude product 2 contained roughly equal amount of vice product 3. This method
actually purified compound 2, but unfortunately it heavily sacrificed the final yield. So we applied another method. The rude product 2 was reacted twice with glacial acetic acid. During this process, the product 4 was subject also to recrystallization, so simultaneously the vice-product was expelled and pure compound 4 was obtained.

The method to synthesize 7 from 5 was similar to the synthesis of the monomer of trans-PBZT that reported by Wolfe. It was found that the solubility of monomer 7 in water was close to that of potassium chloride (KCl) which was generated when the potassium salt 6 was neutralized by hydrochloric acid. Thus when monomer 7 precipitated as needle crystals, fair amount of potassium chloride also precipitated as an impurity, which was indentified by using Na[B(C₆H₅)₄].

KCl affects the molecular weight of the synthesized polymer in two ways. It will induce the incorrect stoichiometric value of the monomer in polycondensation. On the other hand, it will also yield hydrochloride in PPA during polymerization, which correspond to incomplete dehydrochlorination of monomer 7.

Remove of KCl from 7 was very difficult because the extreme instability of 7. To decrease the content of KCl, it is preferable to use as small amount of concentrated hydrochloric acid as possible in the process of 7.

In order to know the purity of 7, following titration method was applied. As shown below, 7 was neutralized by sodium hydroxide and precipitated. In an argon filled glove box, the mixture of 7 and KCl was dissolved in deaerated water and then titrated with 0.1N sodium hydroxide solution. pH was continuously changed during the titration. After equivalence point (pH ~ 7) was achieved, the content of pure 7 can be calculated as follows:

\[
\text{monomer wt\%} = \frac{0.1 \times V_{\text{NaOH}}}{W \times 2000} \times \frac{M}{100}
\]

- \( V_{\text{NaOH}} \): volume of sodium hydroxide solution used (ml);
- \( W \): weight of 7 mixed with KCl (g);
- \( M \): molecular weight of 7 (245.2 g/mol).

The content of KCl was also calculated (KCl wt\% = 100\% - monomer wt\%) as shown in Table 1.

Because monomer 7 was extremely sensitive to oxidation, it could not be characterized correctly by using the common analytical methods. So we synthesized the model compound to determine the soundness of the monomer. The reaction of monomer 7 with benzoic acid in poly(phosphoric acid) (PPA) afforded the model compound 2,6-diphenylbenzo[1,2-d:5,4-d']bisthiazole in 91.6\% yield. IR,
elemental analysis, $^{13}$C and $^1$H-NMR spectrum are consistent with the assigned structure.

**Polymerization**

The polycondensation of monomer 7 with terephthalic acid (TPA) was carried out in deaerated PPA because 7 was extremely sensitive to oxygen. Complete dehydrochlorination of 7 is essential to get it in a reactive form before the other monomer (TPA) was added. The polymerization must be carried on with stepwise heating since immediate exposure of the reaction mixture to relatively high temperature may cause decomposition of 7. After stirring at 120 °C for several hours, the solution became transparent indicating the complete dissolving of terephthalic acid. Because the sublimation of TPA occurs easily at high temperature, reduced pressure was suspended above 140 °C. The reacting solution continued to increase in viscosity but remained stirrable throughout the polymerization. Intrinsic viscosities of the synthesized polymers were measured and summarized in Table 1.

The intrinsic viscosity of polymer I was very low because the content of KCl that mixed in 7 was left unmeasured and so the polycondensation was carried on with nonstoichiometric ratio of the two monomers. For polymers II and III, although the amount of monomer 7 was analyzed and commensurate with TPA, the molecular weight were also not high because that the high content of the potassium chloride strongly refrained the wholly dehydrochlorination of 7. For polymer IV, however, there was little KCl in the monomer and therefore, the polymer was obtained with relatively high molecular weight.

It was found in FTIR spectra that most bands of cis-PBZT appeared in the same frequencies as those of trans-PBZT except those between 600 cm$^{-1}$ and 750 cm$^{-1}$ where cis bands shifted to higher absorption frequencies, indicating the lower molecular symmetry of the the cis form.

**Thermal Evaluation**

The thermostability of the synthesized polymer was evaluated by thermogravimetric analysis (Fig. 2). It was found that cis-PBZT is of high thermostability which is comparable with that of trans-PBZT.

**Liquid Crystallinity**

To investigate the liquid crystallinity of cis-PBZT (polymer IV), polymer solution in MSA with different concentrations of 3%, 5%, 8% and 10% (wt%) were prepared and observed under a polarizing microscope. It was

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<table>
<thead>
<tr>
<th>Polymer polymerization solvent</th>
<th>reaction temp, °C</th>
<th>KCl contents in monomer</th>
<th>$\eta$</th>
<th>$d \delta /g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I PPA</td>
<td>70-205</td>
<td>-</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>II PPA</td>
<td>70-205</td>
<td>54 %</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>III PPA</td>
<td>70-205</td>
<td>20 %</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>IV PPA</td>
<td>70-205</td>
<td>6 %</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. cis-PBZT Polymers: Dependence of $\eta$ on KCl Content

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Fig.2 Thermogravimetric analysis of cis-PBZT.
found that even at such a high concentration of 10%, the solution exhibited no obvious birefringence except when strong shearing force was added. Fig. 3 shows the nematic texture of the polymer IV solution after shearing.

For trans-PBZT (with an intrinsic viscosity of 3.4 dL/g), however, liquid crystalline phase was presented when the polymer concentration was just higher than 5 wt%. It is not clear why the cis-PBZT has such a poor liquid crystallinity even though it is also rigid-rod like.

Meanwhile, a spherulitic texture was observed in the solution after it was allowed to coagulate in air for about one hour (Fig. 4). The same phenomenon was reported with trans-PBZT/MSA solution by Cohen et al. [4,5]. They proposed that the solid spherulites were a kind of crystal-solvates: co-crystals of protonated trans-PBZT and the acid anion.

**Crystallization from Dilute Solution**

Figure 5 shows an electron micrograph of cis-PBZT crystals precipitated from dilute solutions by slow cooling. For cis-PBZT, the crystal morphology is essentially rod-like, similar to the isothermally crystallized trans-PBZT crystals [6,7].

As shown in Table 2, the solution of trans-PBZT has both higher clouding temperature and dissolving temperature than that of cis-PBZT even they have similar intrinsic viscosities. This indicates that cis-PBZT has higher solubility than trans one. The higher solubility may be resulted
from the fact that the repeating units have two sulfur atoms at the same side. Therefore, they have higher polarity than that of trans-PBZT and hence the protonation would be much promoted.

CONCLUSION

New route to synthesize cis-PBZT with high molecular weight was developed. cis-PBZT has high thermostability that is comparable to that of trans-PBZT. Though its chemical structure seems to be rigid like trans-PBZT, it showed only poor liquid crystallinity. Crystallization from dilute solution gave rod-like crystals. Corresponding to lower symmetry of chemical structure, the solubility of cis-PBZT was higher than that of trans form. To get cis-PBZT with higher molecular weight, KCl must be removed from the monomer DABDD.

REFERENCES