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Selective and Efficient Synthesis of Cyclic Hexakis(thio-1,4-phenylene) through Oxidative Polymerization of Diphenyl Disulfide

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There has been a considerable interest in aromatic macrocyclic oligomers that can be utilized as reactive monomers in ring-opening polymerization reactions for the preparation of high molecular weight linear polyaromatics. Extensive efforts have been expended in this field for the last decade and several kinds of aromatic cyclic oligomers have been reported, e.g., cyclic carbonates,[1a] amides,[1b] ethers,[1c−e] and ether ether ketones.[1f] Recently, aromatic cyclic sulfides and disulfides have also been synthesized and used for the preparation of high molecular weight poly(thioarylene)s.[2] Most of the preparative methods described for these aromatic cyclics are based on a nucleophilic aromatic substitution reaction which is carried out at high temperatures (>150 °C) in an aprotic polar solvent such as DMF or DMAc. The reactions result in the formation of a mixture of cyclics with different numbers of repeating units. Until now, there has not been reported a highly selective preparation of a discrete macrocycle under mild conditions by a one-step reaction.

Oxidative polymerization has been recognized as an important preparative method both *in vivo* (lignin formation catalyzed by tyrosinase) and in industry (synthesis of poly(oxy-2,6-dimethyl-1,4-phenylene) catalyzed by a copper−amine complex) that proceeds efficiently under ambient conditions in the presence of oxygen. We have previously reported that linear poly(thiophenylene) can be prepared by the oxidative polymerization of diphenyl disulfide,[3a] 4-(methylsulfenyl)diphenyl sulfide,[3b] and diphenyl sulfide with sulfur monochloride,[3c] or by reaction of benzene with methanesulfinic acid in an electrophilic substitution reaction.[3d] These polymerization reactions result in the preferential formation of the thio-1,4-phenylene structure to give a very pure polymer without salt contamination at room temperature. These mild and selective reactions should be useful for the preparation of aromatic cyclic sulfides. In the present communication, we report preliminary results on the novel preparative method for the preparation of cyclic oligo(thio-1,4-phenylene) by the oxidative polymerization of diphenyl disulfide. Pseudo-high-dilution conditions result in the formation of the cyclic hexamer in high yield.

The oxidative polymerization of diphenyl disulfide was carried out in acidic dichloromethane solution with an equimolar amount of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as the oxidant.[4] Pseudo-high-dilution conditions were applied by slow addition of the monomer solution into a solution of DDQ with a period of 2 days. In order to obtain the cyclic oligo(thiophenylene) in a quantitative yield, the final concentration of the monomer should be less than 0.05 M.[5] After the reaction was stirred for another day and after it was poured into methanol, the oligomer as a white powder was obtained in 100% yield. The resulting oligomer was extracted with hot chloroform to obtain cyclic product in 48% yield, which was analyzed by the combination of IR, NMR, GPC, gradient HPLC, and MALDI−TOF−MS spectroscopies.

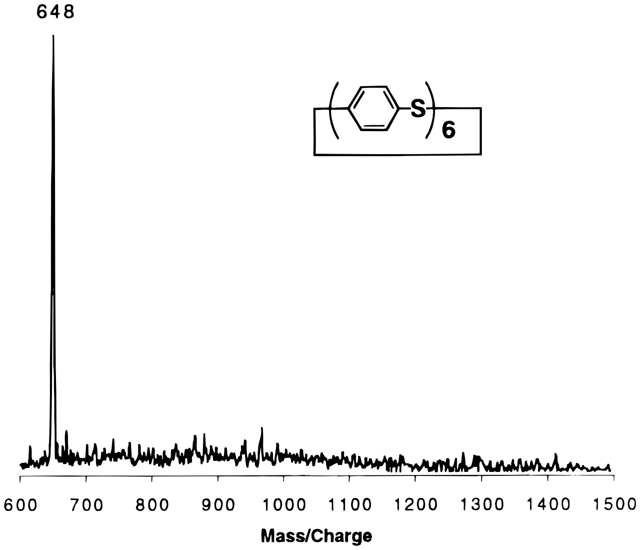

Figure 1. Positive ion MALDI−TOF mass spectrum of cyclic hexakis(thio-1,4-phenylene) obtained in the reflectron mode using dithranol as matrix and LiBr as cationization agent.

The chloroform-soluble part was confirmed to be a single product by gradient HPLC using THF and water as eluents.[6] The IR spectrum of the product is similar to that of linear oligo(thiophenylene), however, two distinct peaks at 1096 and 1074 cm^{-1} (δ_{ip}(CH)) were observed, which are characteristic for the cyclic(thiophenylene).[7] The absence of the peaks attributed to an end phenyl group around 690 - 740 cm^{-1} (δ_{oop}(CH)) also supports the cyclic structure of the product. In the ^{1}H NMR spectrum, only a singlet peak for the phenyl proton is observed at 7.25 ppm which is in agreement with that reported for cyclic hexakis(thiophenylene).[8] No peaks attributable to SH or end phenyl groups were observed. In the ^{13}C NMR spectrum, two aromatic carbon peaks are observed at 131.7 and 134.8 ppm, which further confirm the structure. These spectroscopic results confirm the formation of cyclic oligo(thio-1,4-phenylene) without any detectable structural defects.

Matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI−TOF−MS) analysis also indicates that the resulting oligomer is cyclic hexakis(thiophenylene). As shown in Figure 1, the correct molecular weight ion signal ($M^{+} = 648$) for cyclic hexakis(thiophenylene) was observed in the MALDI−TOF mass spectrum with a good signal to noise ratio using 1,8,9-anthracenetriol (dithranol) as matrix and lithium bromide as cationization agent. No signals attributed to the other cyclics or linear oligomers were observed. GPC analysis of the oligomer shows a single sharp peak, and M_w and M_n are determined to be 420 and 390 ($M_w/M_n = 1.1$) against polystyrene standards.

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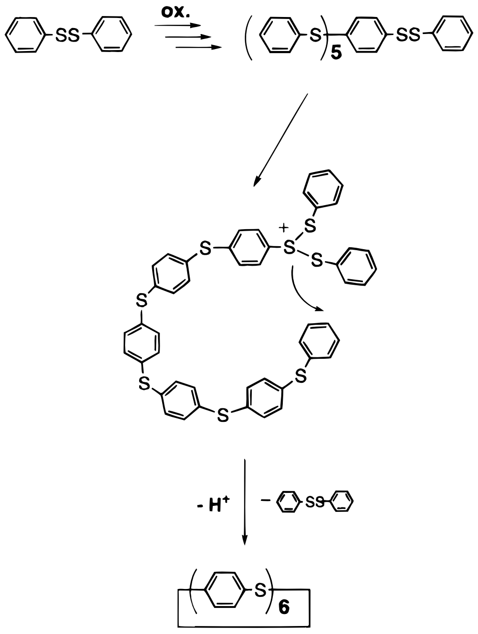
Scheme 1



(1)

The cyclic hexamer is highly crystalline and shows a single melting endotherm peak at 209 °C with an enthalpy change (heat of fusion, ΔH) of 46 J/g in DSC analysis. The melting peak is sharp as expected for a discrete cyclic hexamer compared to the mixture of cyclic thiophenylene oligomers ($n = 4-14$, $T_m = 172-263$ °C).[2a] The second DSC scan after quenching the sample from 280 °C to room temperature shows a T_g of 78 °C and a T_c of 142 °C.

As we have already reported,[2] cyclic aryl thioethers can be used as monomers for the preparation of linear poly(thioarylene) by free radical ring-opening polymerization. The cyclic hexamer was polymerized in the presence of 1.0 mol % 2,2′-dithiobis(benzothiazole) as an initiator under nitrogen at 300 °C for 30 min to obtain a linear poly(thiophenylene). DSC analysis showed that the resulting product is highly crystalline with a single melting endothermic peak at 277 °C. T_g of 85 °C and T_c of 131 °C were observed in the second scan after quenching from the melt. These values are comparable to those of high molecular weight poly(thiophenylene) prepared by the conventional polycondensation.

In order to evaluate the effect of dilution on the cyclization reaction, the oxidative polymerization of diphenyl disulfide was carried out at different feed concentrations. The cyclic hexamer was obtained in only 33% yield at 0.1 M monomer concentration, but more dilute conditions result in an increase in the yield of the hexamer. A maximum selectivity of more than 70% was achieved at 0.025 M concentration under our experimental conditions.

It has been previously proposed[3a] that the oxidative polymerization of diphenyl disulfide proceeds by the electrophilic substitution of the phenylbis(phenylthio)sulfonium cation as an active species to form an oligo(thio-1,4-phenylene) with a disulfide bond at the end of the chain (Scheme 1). At high monomer concentrations above 0.1 M, the formation of linear octamer is predominant.[9] In the pseudo-high-dilution reaction, the pentameric active species reacts preferentially with its tail (intramolecular head to tail reaction) giving rise to the formation of cyclic hexakis(thiophenylene). It would be reasonable to expect that the cyclics with lower numbers of repeating units would be difficult to form due to ring strain.

In conclusion, cyclic hexakis(thiophenylene) was prepared selectively by oxidative polymerization of diphenyl disulfide under pseudo-high-dilution conditions. The mild reaction conditions based on electrophilic aromatic substitution are found to be more effective for the preparation of a discrete aromatic cyclic sulfide than the conventional polycondensation method based on a nucleophilic substitution reaction. Ring-opening polymerization of the cyclic led to the formation of a linear poly(thiophenylene) with a T_m of 277 °C

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(4) A 20 mL dichloromethane solution of diphenyl disulfide (4 mmol) was added dropwise to 60 mL of dichloromethane containing 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (4 mmol), trifluoroacetic acid (0.08 mol), and trifluoroacetic anhydride (16 mmol) with a period of 2 days. The mixture was stirred for another day to ensure the completion of the reaction and then poured into 500 mL of 37% hydrochloric acid diluted 1:9 with methanol to precipitate the oligomer. The crude product was treated with three portions of 100 mL of aqueous 5% NaOH solution to remove 2,3-dichloro-5,6-dicyano-*p*-hydroquinone. The resulting white powder was washed with water and methanol and dried at 20 °C under vacuum for 20 h.

(5) The higher monomer concentration is possible by slowing the rate of addition over 2 days.

(6) Linear gradient HPLC was performed on a Milton Roy CM4000 multiple solvent delivery system with a C8 Prime Sphere 4.6 × 250 mm column, THF and water as eluent solvents, and a UV detector at 300 nm. The total running time for each injection was 30 min. The gradient condition was as follows: at 0 min, THF 70%; at 20 min, THF 90%; at 25 min, THF 100%; at 27 min, THF 70%; at 30 min (end), THF 70%.

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(9) Linear octakis(thio-1,4-phenylene) containing one disulfide at the end of the chain, which is insoluble in dichloromethane or chloroform. See ref 3a.

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