

Novel Synthesis of Macrocyclic Disulfides from Poly(phenylene sulfide) by Depolymerization Reaction

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Received 13 January 2006; accepted 8 July 2008

DOI 10.1002/app.29010

Published online 23 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new effective method is presented for the easier preparation of macrocyclics from poly(phenyl sulfide) by two steps: (1) depolymerization reaction of poly(phenyl sulfide) with Na₂S in the presence of weak base,

and (2) oxidation reaction of depolymerization products. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 4049–4054, 2008

Key words: macrocyclics; high performance polymers

INTRODUCTION

Recently, thiol and dithiol compounds attract much attention as intermediates in many organic syntheses. For example, they can be used as intermediates in medical, pesticide, and dyestuff production, and can also be used as monomers to synthesize high performance polymers.^{1–3} It has been documented that aliphatic thiols and dithiols are very easily synthesized by halocarbon/dihalocarbon reacting with thiourea in aprotic solvent or Na₂S in the presence of phase transfer catalyst. However, aromatic dithiols are rather difficult to synthesize because of the characteristic of easily being oxidized. Three different methodologies have been reported for the preparation of aromatic dithiols from various aromatic compounds, including (1) reduction reaction of aryldisulfonyl chlorides, (2) Newman-Kwart rearrangement reaction of bis(*N,N*-dimethylthiocarbamate), and (3) nucleophilic substitution reaction of dichloride compounds with NaHS.^{4–9} The main disadvantages of above methods are: (1) low yield of (<30%) for the first method, and severely corrosive reagent of aryldisulfonyl chlorides used; (2) high

cost of synthesis for the other two methods due to too many synthetic steps involved.

On the other hand, poly(phenyl sulfide) (PPS) is a commercial available high performance polymer because of its inherent nonflammability, long term thermal stability, excellent affinity for variety of fillers, and its ability to be crosslinked at elevated temperatures.^{10,11} Many applications of PPS have been developed in electrical/electronic areas and mechanical areas.^{12–14} Yu et al. obtained PPS oligomers via depolymerization of high-molecular-weight PPS with sodium sulfide in HMPA at 220°C without catalyst.¹⁵

Herein, we reported a new method to synthesize aromatic dithiols from PPS by depolymerization reaction with Na₂S in the presence of K₂CO₃ weak base as catalyst in 1-methyl-pyrrolidone (NMP). The main merit of this methodology is a direct synthesis way to obtain aromatic dithiol. It avoids the synthesis of aromatic dithiols intermediate, which are rather difficult to synthesize due to the characteristic of easily being oxidized. Moreover, this method is more effective and favorable in economy because of the very short synthetic road. These aromatic dithiols can then undergo cyclization reaction by well-documented methods to produce the *in situ* self-polymerizable macrocyclic oligomers, which we have extensively reported.^{15–17} The realized procedure is described as follows (Scheme 1).

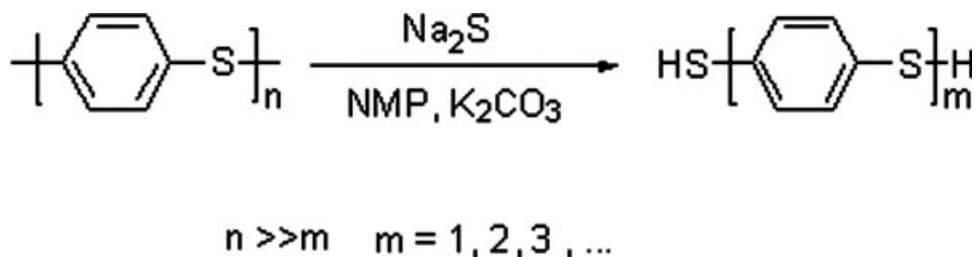
The used PPS was obtained from commercial sources and used as received. Aromatic dithiol oligomers were synthesized according to the route given in scheme 1. To a 250-mL flask equipped with a Dean-Stark trap and condenser, a nitrogen inlet was charged with 200 mL of NMP, 5 mL of toluene,

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Contract grant sponsor: China High-Tech Development 863 Program; contract grant number: 2007AA03Z217.

Contract grant sponsor: Guangdong Province Sci and Tech Bureau; contract grant numbers: Key Strategic Project Grant No. 2006B12401006, 06300332.

Contract grant sponsor: Guangzhou Sci and Tech Bureau; contract grant number: 2005U13D2031.



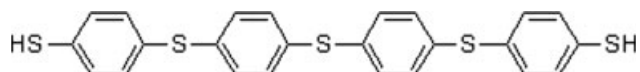
Scheme 1 Depolymerization of PPS into aromatic dithiol oligomers.

and 6.67 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. The mixture was kept refluxing at 150–155°C under N_2 for 2 h to remove water entirely and then 1.0 g K_2CO_3 and 2.80 g PPS were introduced. Upon finishing the addition, the reaction mixture was heated to 170–175°C and kept refluxing for further 48 h. The resulting mixture was cooled down and filtered to remove K_2CO_3 . The filtrate was then poured into 500 mL 5% HCl solution to precipitate out. After vigorously stirred for 20 min, the precipitates were collected by filtration and washed consecutively with water thoroughly. The result powder was extracted with methylene chloride for 24 h. The extracted mixture was evaporated and dried in a vacuum oven at 40°C for 24 h yielded 1.73 g of ashen powder (Sample A).

The as-prepared Sample A is soluble in most organic solvents indicating the conversion of PPS into small molecules because of the insoluble nature of PPS. Moreover, Sample A showed a clear melting point when subjected to differential scanning calorimeter (DSC) measurement. This also demonstrated the formation of small molecules because PPS is a semi-crystalline polymer with a glass transition temperature of about 85°C and a melting point of about 285°C. Some properties of the Sample A are listed in Table I.

Identification and quantification of sample A were carried out using liquid chromatography-mass spectrometry (LC-MS) trace, shown in Figure 1. It can be seen from this figure that the cleavage of the protons of $-\text{SH}$ groups was detected during the ionization of the sample. The molecular weights of four aromatic dithiol oligomers detected are 356.2, 464.2, 572.0, and 680.0, in the turn. These peaks corresponds the trimer, tetramer, pentamer, and hexamer of the resulted oligomers since the difference of their molecular weight is exactly 108 Da ($\text{C}_6\text{H}_4\text{S}$ or $-\text{C}_6\text{H}_4-\text{S}-$). Other two corresponding R.T = 1.31 and R.T. = 2.48, respectively, were not detectable because of small molecular weight. The predominant composition was tetramer (R.T: 4.06 min) with a total content higher than 50%. The reason for the tetramer being the main product is governed by two factors. One is the concentration of the reaction mixture, and the second is the size of the cyclic

repeating unit. The above two factors favor the formation of tetramer for the studied system. We have explained this in the revised manuscript. The resulting products were isolated and purified by chromatography method using methylene chloride and methanol as eluent through silica gel, affording Sample B (R.T. = 4.06 min).



Elemental analysis was performed on Vario EL, Elementar Analysensysteme GmbH. Elemental Analysis Calcd. for sample B: C, 61.71%; H, 3.92%; S, 34.37%. Found: C, 61.76%; H, 3.89%; S, 34.37%. According to the elemental analysis and LC-MS, the sample B should be $\text{C}_{24}\text{H}_{18}\text{S}_5$.

NMR spectra were recorded at 400 MHz on a Bruker DRX-400 NMR instrument. ^1H -NMR and ^{13}C -NMR spectra of sample B are shown in Figures 2 and 3, respectively. From Figure 2, there are five protons with different environments in the spectra. A threefold peak ranging from 3.40 to 3.50 ppm for $-\text{HS}$ protons was observed due to the coupling effect between the adjacent protons and the proton of aromatic dithiol. From Figure 3, it can be clearly seen that eight different kinds of protons related to the structure of sample B as shown below.

It was also found that the yield and composition of resulting aromatic dithiol oligomers were affected by the amount of Na_2S because Na_2S acted as an initiator for the depolymerization of PPS, which can

TABLE I
Properties of the Aromatic Dithiol Oligomers Derived from the Depolymerization of PPS

	Yield, %	Melting point ^a (°C)	T_g^a (°C)
Sample A	62	108.8 144.8	
Sample B	34	108.5	
Sample C	52	125.5	
The resultant polymer	–	–	61.0

^a Measured under N_2 protection at a heating rate of 20°C/min.

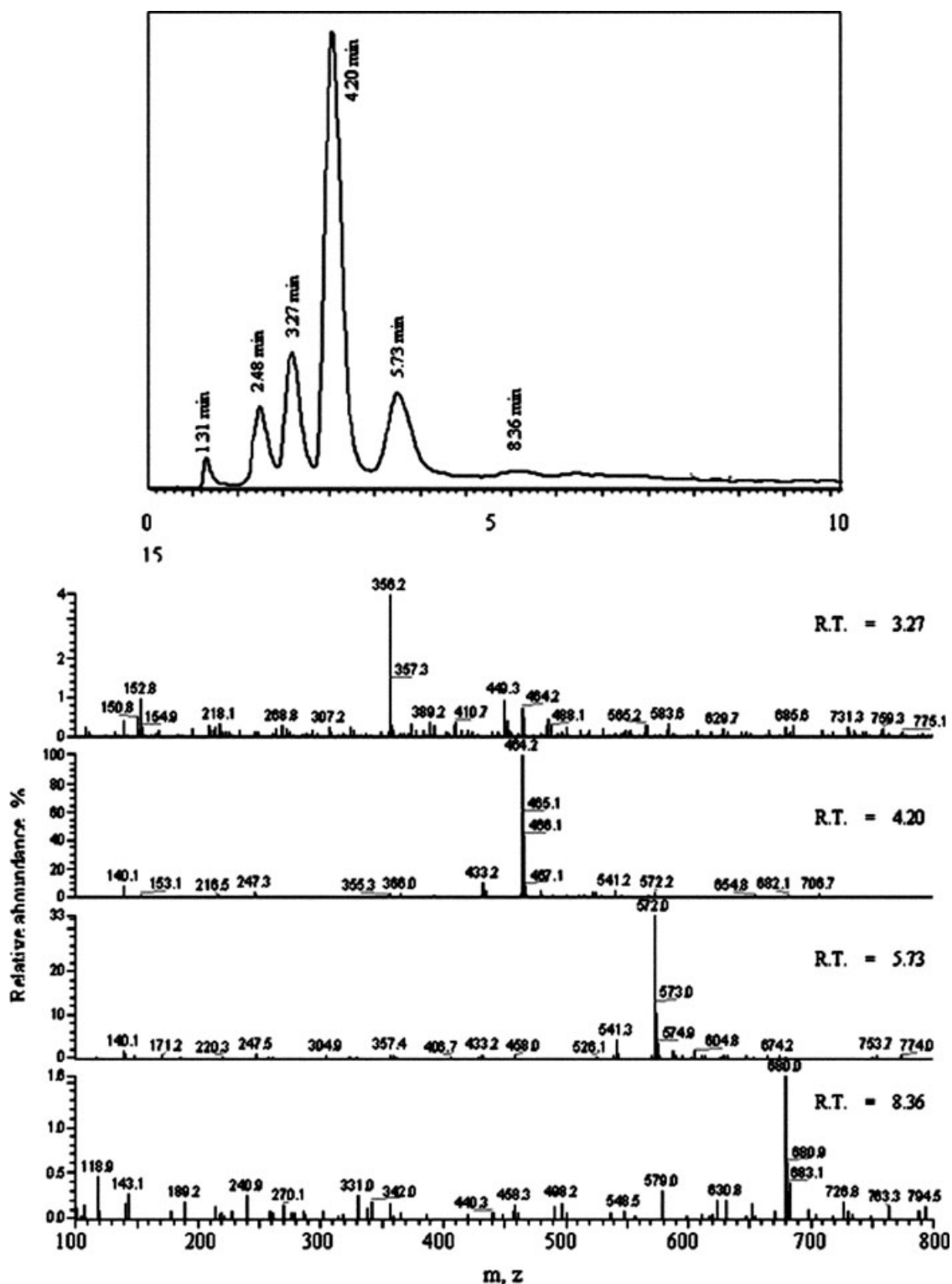


Figure 1 LC-MS trace of sample A (mixture of aromatic dithiol oligomers).

lead to the cleavage of C–S bonds. Furthermore, K_2CO_3 was found to accelerate the depolymerization of PPS greatly. Certainly, temperature is another critical factor to affect the depolymerization reaction of PPS, for example, the reaction cannot be performed below $150^\circ C$. The completion of the depolymeriza-

tion of PPS can be easily indicated by the dissolution of PPS into the reaction solution, because PPS is insoluble whereas depolymerized products are very soluble in organic solvents. The feasibility of the synthesis of aromatic dithiol oligomers by depolymerization method resulted from two factors: the

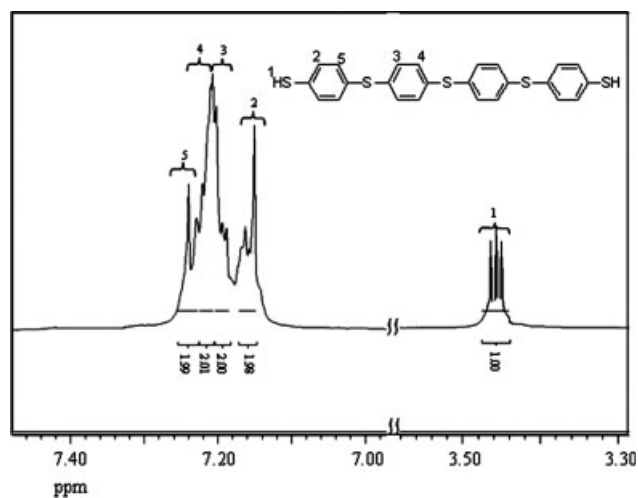


Figure 2 ^1H -NMR of the sample B (tetramer of aromatic dithiol oligomers).

solubility difference of the dithiols and their polymeric counterpart, and the catalytic cleavage of thioether bonds in PPS chain. In other word, dithiols are preferably formed in case that original polymer is insoluble but the resulting dithiols. The reaction mechanism can be depicted in Scheme 2.

Conventional synthesis of cyclic aromatic disulfide oligomer was conducted by oxidative coupling of the as-prepared dithiol oligomers with oxygen catalyzed by CuCl and N,N,N',N' -tetramethylethylenediamine (TMEDA), as illustrated in previous studies (Scheme 3).^{16–18} A 150-mL one-neck cylinder (height/diameter = 2.5 : 1) with an oxygen inlet at the bottom equipped with a highspeed vibromix stirrer was charged with 0.15 g of CuCl , 0.3 g of TMEDA, and >100 mL DMAc. Then, ~ 30 mL extracted mixture was introduced dropwise into the reaction mixture over 2 ± 3 h. The resulting mixture was stirred for another hour to ensure the comple-

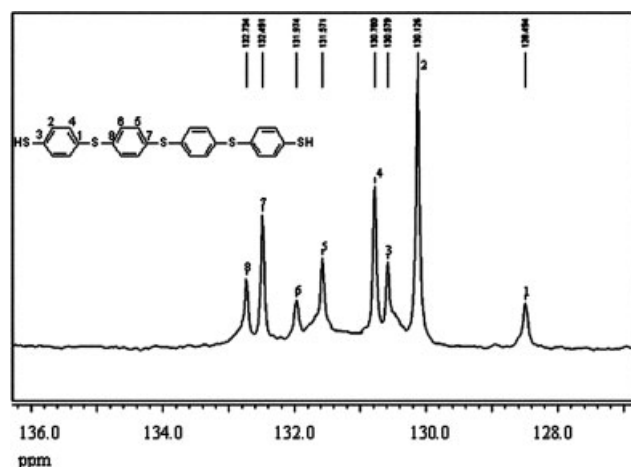
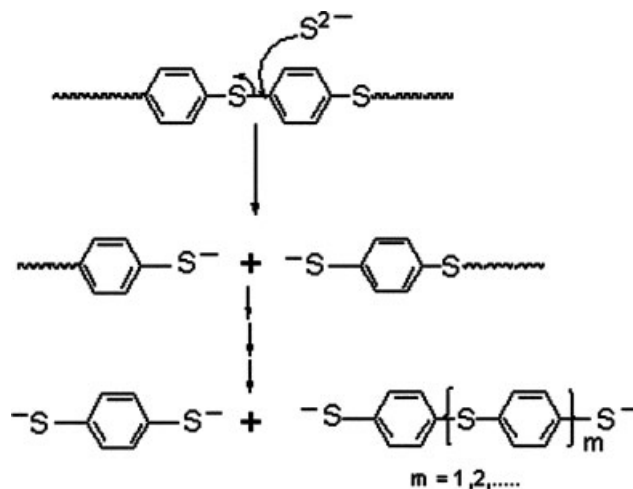


Figure 3 ^{13}C -NMR of the sample B (tetramer of aromatic dithiol oligomers).

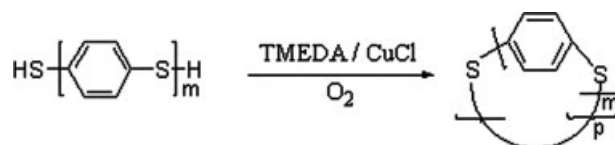


Scheme 2 Mechanism of the depolymerization of PPS.

tion of the oxidation and then was filtered through a layer of alumina. The filtrate was treated with 100 mL of 5% HCl solution and the precipitate was collected by filtration, washed with methanol twice, and dried at room temperature under vacuum for 24 h, sample C. Some properties of the sample C are list in Table I.

^1H -NMR spectra of sample A and C are shown in Figure 4. From Figure 4, a peak for $-\text{HS}$ protons was observed ranging from 3.40 to 3.50 ppm in NMR spectra of Sample A but no $-\text{SH}$ group in that of Sample C, demonstrating the completion of cyclic enclosure. Elemental analysis was also performed for sample C. Found: C, 60.44%; H, 3.04%; S, 36.52%. The matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) technique has been used recently to analyze linear polymers and has been particularly successful for macrocyclic oligomer mixtures.^{17,18} In MALDI-TOF-MS spectra of the novel disulfide macrocyclic oligomers (Fig. 5, data analysis was shown in Table II), macrocyclics were detected which corresponds to cyclics $((\text{C}_6\text{H}_4\text{S})_m)_p$ with $m = 1, 2, 3, 4, 5, \dots$ and $p = 2, 3, 4, 5, \dots$

Melt ring-opening polymerizations of the macrocyclic oligomers prepared by CDP and oxidative coupling were performed at $(200 \pm 5)^\circ\text{C}$ for 5 min in a N_2 protective atmosphere (Scheme 4). Both of the resulting polymers were insoluble in both DMAc and THF and behave as an elastic material when



Scheme 3 Catalytic oxidation cyclization of aromatic dithiol oligomers.

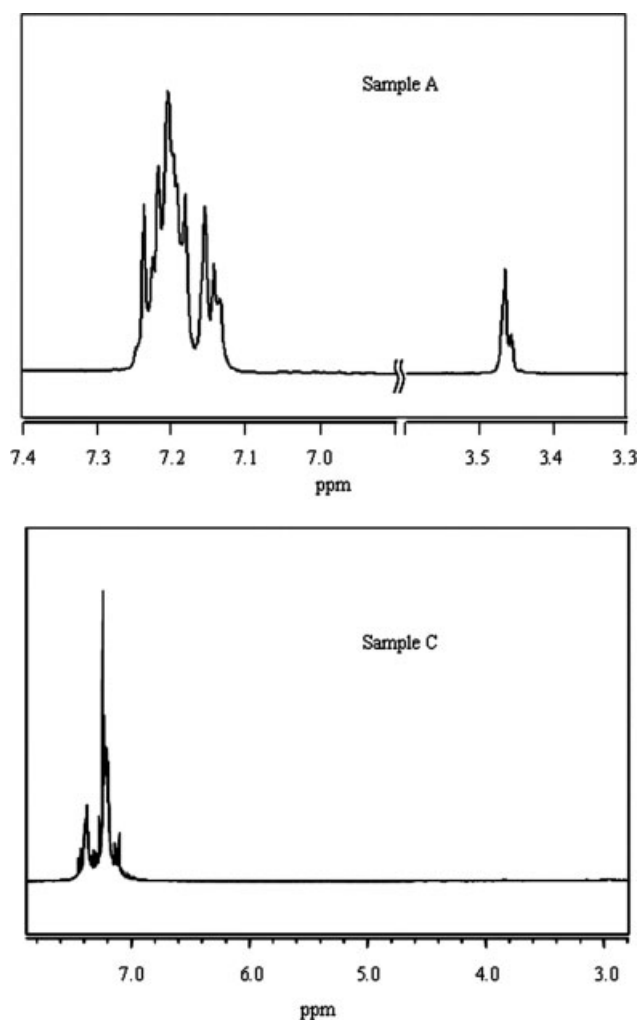


Figure 4 $^1\text{H-NMR}$ of the sample A and C.

heated to their glass transition temperatures. The molecular weights of the polymers were not determined owing to their insolubility.

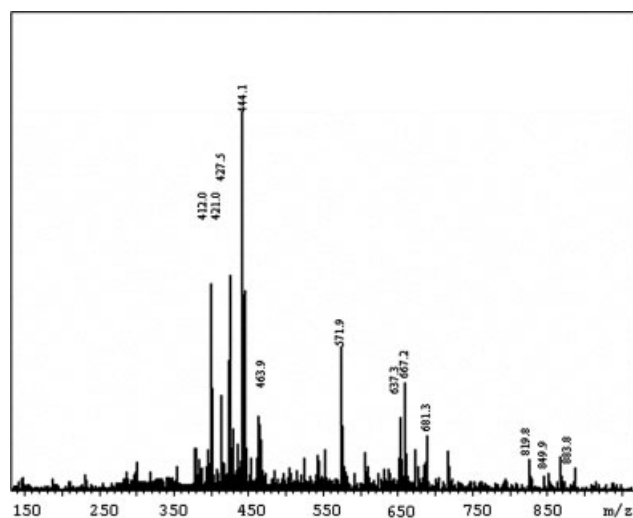
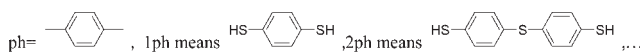


Figure 5 MALDI-TOF-MS spectrum of sample C.

TABLE II
Positive Ion MALDI-TOF-MS Data for SAMPLE C Using 2,5-Dihydroxy Benzoic Acid as the Matrix

Structure	Calculated (m/z)	Signal (m/z)	Deviation (Da)
1 ph + 2 ph + Na^+	411.5	412.0	0.5
3×1 ph	420.7	421.0	0.3
1 ph + 2 ph + K^+	427.5	426.9	0.6
3×1 ph + K^+	443.6	444.1	0.5
4 ph self condensation	464.0	463.9	-0.1
5 ph self condensation	572.0	571.9	-0.1
1 ph + 2×2 ph	637.0	637.3	0.3
3×1 ph + 2 ph	667.9	667.2	-0.7
6 ph self condensation	681.0	681.3	0.3
3 ph + 4 ph 或 6 ph + 1 ph	820.0	819.8	-0.2
1 ph + 2 ph + 4 ph	852.0	849.9	-1.1
3×1 ph + 4 ph	884.0	883.8	-0.2

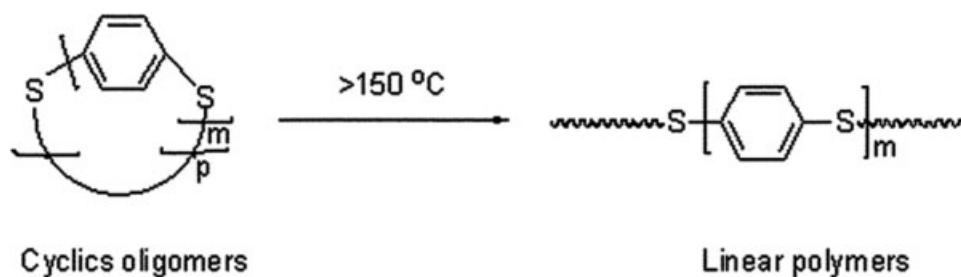


Deviation = (experimental value) - (calculated value)

In conclusion, we have demonstrated that the depolymerization of PPS in the presence of Na_2S and weak base is an efficient and easier way to synthesize aromatic dithiol oligomers. The aromatic dithiol oligomers can be used to prepare macrocyclic disulfide oligomers by oxidative coupling with oxygen catalyzed by CuCl and TMEDA which undergo ROP to form high-molecular weight polydisulfides. The experiment results demonstrated that the synthesized polydisulfides had exactly same properties as that synthesized from conventional methods. The novelty and merits of this work arises from the convenient technology both to prepare aromatic dithiols and to recycle PPS. To our knowledge, this new methodology has not been reported so far.

EXPERIMENTAL

Liquid Chromatography-mass Spectrometry (LC-MS) was performed on a LCQ DECA XP multiple solvent delivery system consisted of a Spectra System P 4000 pump, a Spectra System AS 3000 autosampler with the volume injection set to 10 μL and a Surveyor MSQ quadrupole mass spectrometer equipped with an electrospray ionization LC-MS interface (ESI). Chromatographic separation was performed with a C18 Prime Sphere 4.6 mm \times 200 mm column with methanol and water as eluent solvent, and a UV detector operated at 254 nm. The chromatographic parameters (composition and flow rate of mobile phase) and the operating parameters of ESI (cone voltage, temperature of the ionization source and capillary potential) were optimized. The optimum working conditions were as follows: isocratic elution with a mobile phase consisted of methanol-water (95 : 5, v/v) at a flow rate of 1.0 mL/min. ESI was



Scheme 4 ROP of cyclic oligomers.

applied in the negative ionization mode and the capillary was held at a potential of 3.5 kV.

NMR spectra were recorded at 400 MHz on a Bruker DRX-400 NMR instrument and the chemical shifts were listed in parts per million downfield from tetra-methylsilane.

MALDI-TOF-MS were recorded on a Bruker MALDI-III TOF instrument with a maximum laser output of 6 mW at a wavelength of 337 nm (N_2 laser light, 3 nm pulse width, 100 mm diameter spot). The MALDI-TOF instrument was operated in a positive reflection mode. The ions produced from each laser shot were accelerated to 25 keV into a 1-m drift region. The matrix used for all experiments was 2,5-dihydroxy benzoic acid (Aldrich).

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