

Catalytic regioselective chlorination of phenols in the presence of polysulfide polymer containing 1, 3, 4-thiadiazole unit

الكلورة الانتقائية للفينولات باستخدام عوامل مساعدة من بوليمرات السلفايد التي تحتوي على وحدة 1، 3، 4-ثايودايزول.

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Abstract

Polymeric sulfides containing 1, 3, 4-thiadiazole unit with different spacer group length have been synthesized and established to be useful catalysts for the chlorination of phenol, *o*-cresol, *m*-cresol and *m*-xylenol using freshly distilled sulfonyl chloride in the presence of Lewis acid as a co-catalyst at room temperature. The yields of *para*-isomers and *para/ortho* ratios were higher compared to cases where no catalyst was used with most catalysts for most phenols even when a very low concentration of poly sulfide was used.

Keywords: Regioselective chlorination, polymeric sulfide, catalysts, phenol, Lewis acid

الخلاصة

تم تحضير بوليمرات السلفايد التي تحتوي على مجموعة 1، 3، 4-ثايا دايازول وكذلك مجاميع الكايل مختلفة. تم استخدام البوليمرات المحضرة كمعامل مساعدة في عملية كلورة الفينول و *o*-كريسول و *m*-كريسول وكذلك ميتا-زايلينول باستخدام كلوريد سلفوريل وبوجود حامض لويس كعامل مساعد. ان حصيلة الكلورة في موقع بارا وكذلك نسبة الاورثو الى البارا كانت عالية مقارنة بنتائج الكلورة في حالة عدم وجود العامل المساعد (البوليمر) لجميع انواع الفينولات المستخدمة حتى عند استخدام تراكيز ضئيلة من بوليمرات البولي سلفايد.

الكلمات المفتاحية: الكلورة الانتقائية، بوليمرات السلفايد، العوامل المساعدة، الفينولات، حامض لويس.

1. Introduction

Chlorinated phenols are important materials as intermediates for industrial and pharmaceutical chemical applications.^{1,2} They are the starting materials in a series of household and industrial disinfectants. In the past, crude mixtures of chlorophenols were sometimes considered acceptable for such applications, but concerns have increased about the toxic nature and environmental accumulation of some chlorinated phenolic compounds and their potential by-products.³⁻⁵ Excessive amount of waste can be produced from the chlorination process of phenols due to low selectivity.⁶⁻⁹ Therefore, it is important to expand chlorination catalysts capable of reducing unwanted waste products.

Work have been done by Watson, reported a process for the chlorination of phenols using a mixture of particular divalent sulfur compounds and metal halides.^{10,11} For example, chlorination of *o*-cresol with sulfonyl chloride in the presence of diphenyl sulfide and aluminum chloride (AlCl₃) gave predominantly *p*-chloro-*o*-cresol (*para/ortho* ratio was *ca.* 20). A similar process was reported for the chlorination of phenols in which the sulfonyl chloride is added in portions in order to avoid solidification of the reaction mixture.¹²

Sulfides have been used for the catalytic chlorination reaction of phenols using sulfonyl chloride.^{13,14} Unfortunately, volatile examples of such materials are undesirable on an industrial scale because of their odours. The problem of the volatility of certain sulfides was overcome by the use of substituted Merrifield resins and polythiaalkanes.^{15,16}

In addition, compounds of the type $(R_3N-Cl)^+Cl^-$ and R_2N-Cl are successful in producing very highly regioselective chlorination of activated aromatics in acidic solutions.¹⁷ In particular, *N*-chloropiperidine and *N*-chlorotriethylammonium chloride are both highly regioselective chlorinating reagents for phenols, and both gave monochlorophenol *para:ortho* ratios of 32, in yields of 100 and 98%, respectively, on reaction with phenol. The reactions are acid dependent and are carried out in trifluoroacetic acid or in sulfuric acid. In sulfuric acid the selectivity increases with increasing acidity.

The high regioselectivity in these reactions has been attributed to the bulk of the chlorinating species, which inevitably leads to the more accessible reactive species being favoured, and in this case the *para*-position is therefore favoured over the *ortho*-position.

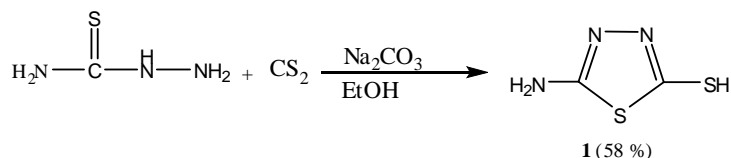
The use of strong acids in excess on an industrial scale is undesirable in terms of green chemistry, but the selectivity achieved is very good, so a replacement for the excess acid solution was investigated by means of using an acidic silica as a solid support.¹⁸ Surprisingly under these conditions the *ortho*-product was the major product; the exact reason for that finding is unclear, but by investigating other *N*-chlorodialkylamines, an *ortho:para* selectivity as high as 16 was achieved using *N*-chlorobis(2-chloroethyl)amine as the chlorinating reagent; monochlorinated products are also favoured using this reagent. Solid catalysts, have been used successfully to enhance the *para*-selectivity in aromatic electrophilic substitution reactions¹⁹⁻²¹

Recently we have investigated two cyclic and two polymeric disulfides as catalysts for the chlorination of *m*-xylenol, *o*-cresol, *m*-cresol and phenol.²²

Therefore, we decided to investigate chlorination of various phenols using Polymeric sulfides containing 1, 3, 4-thiadiazole units with different spacer group length as catalysts with the aim to enhance the *para*-selectivity and the yields of *para*-isomers. Such a study would reveal whether the 1, 3, 4-thiadiazole units and length of repeating unit of a polymeric sulfide would have an effect on the catalytic properties of such catalysts.

Results and Discussion

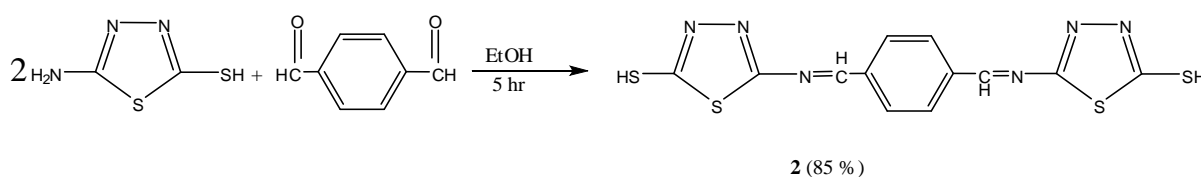
The first task was to synthesize Polymeric sulfides containing 1, 3, 4-thiadiazole units with different spacer group length between the disulfide units. A mixture of thiosemicarbazide, absolute ethanol, anhydrous sodium carbonate and carbon disulfide was warmed with continuous stirring at 60 °C for 1 hr. Then refluxed for 4 hrs, the mixture cooled down to room temperature. It was then filtered and the solvent was removed under reduced pressure. The residue was dissolved in distilled water, and acidified with conc. HCl to give a yellow precipitate. The crude product was filtered and recrystallized from water as yellow needles (2-amino-5-mercapto-1, 3, 4-thiadiazole) (**1**; Scheme 1) in 58 % yield²³.



Scheme 1 Synthesis of 2-amino-5-mercapto-1,3,4-thiadiazole (**1**).

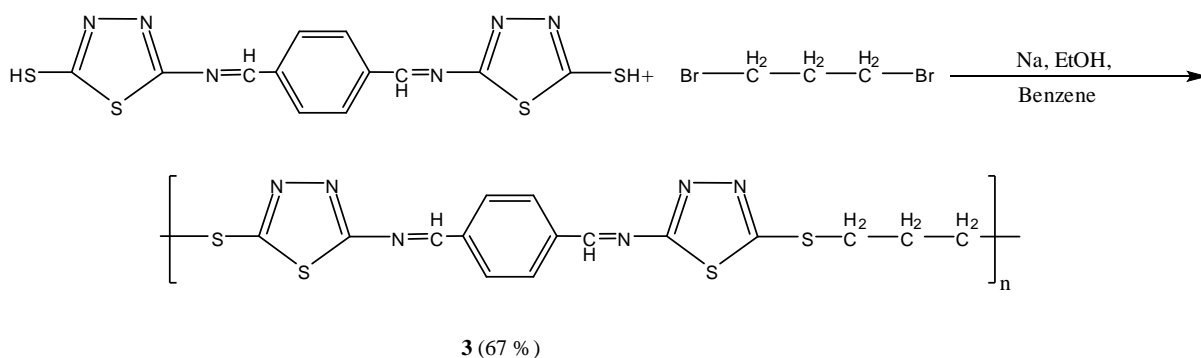
¹H NMR spectrum a NH can be observed, representative of a thioamide (9.85 ppm) instead of a thiol (SH) group (2.0-4.0 ppm). It can therefore be concluded that compound **1** exists in its thione form in dimethyl sulfoxide solution.

A mixture of 2-amino-5-mercapto-1, 3, 4-thiadiazole and Terephthalaldehyde in absolute ethanol was refluxed for 5 hrs. After cooling to room temperature the precipitate was filtered and recrystallized from ethanol in 85 % yield (2; Scheme 2).



Scheme 2 Synthesis of *N,N'*-Terephthalalylidene di-[2-amino-5-mercapto-1,3,4-thiadiazole] (2).

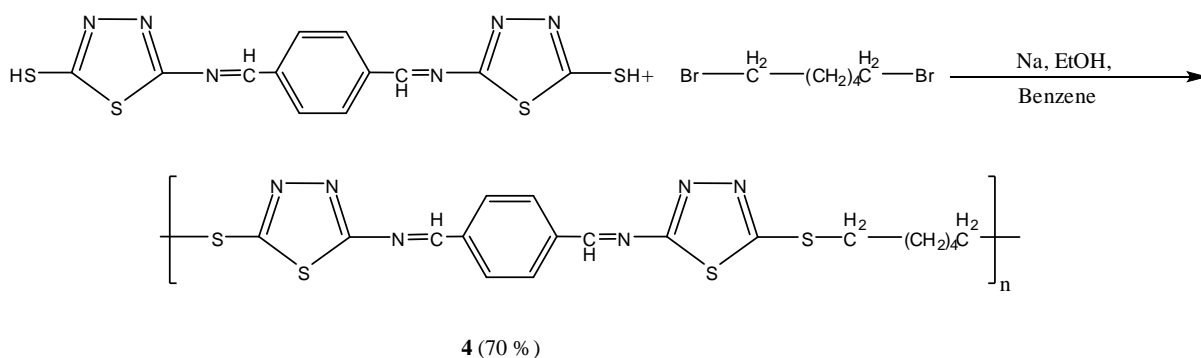
Poly sulfide polymers 3 was synthesized by dissolving Na in 25 ml of absolute ethanol followed by the simultaneous addition of compound 2, and the solution was heated. To the resulting boiling solutions benzene were added (45 ml) and 1, 3-dibromopropane. After the vigorous and spontaneous reaction subsided, 45 ml of benzene was added and the mixture was refluxed overnight. After mixture was cooled, it was filtered. The solution was evaporated under reduced pressure to give the corresponding polymeric sulfide 3 in 67% yield²⁴.



Scheme 3 Synthesis of poly sulfide 3.

The number average molecular weight (M_n) of the polymer 3, measured by gel permeation chromatography (GPC), was found to be 6519, suggesting an average number of repeating units in the region of 16. The use of a polystyrene standard for the GPC may exaggerate M_n for a polymer with a totally different kind of repeating unit.

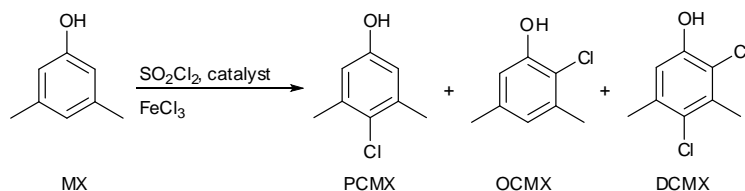
Poly sulfide polymer (4; 70% yield) was synthesized by a similar procedure except using 1, 6-dibromohexane instead of 1,3-dibromopropane (Scheme 4). The number average molecular weight M_n determined by GPC (6321) suggested that the average number of repeating units in the region of 14.



Scheme 4 Synthesis of poly sulfide 4.

Chlorination reactions of *m*-xyleneol, *o*-cresol, *m*-cresol and phenol (50 mmol) were carried out under standard conditions in the presence of the synthesized polysulfides 3 and 4 (or without catalyst) using sulfonyl chloride (57.7 mmol) in the presence of a Lewis acid as a co-catalyst. The chlorination of *m*-xyleneol (MX) in the presence of FeCl₃ as Lewis acid (Scheme 5) was studied first.

The chlorination of *m*-xyleneol (50 mmol) using SO₂Cl₂ (57.7 mmol) in the presence of a polymeric sulfide (30 and 50 mg) and ferric chloride (FeCl₃; 25 mg) in DCM (25 ml) gave the results shown in Table 1.



Scheme 5 The chlorination of *m*-xyleneol.

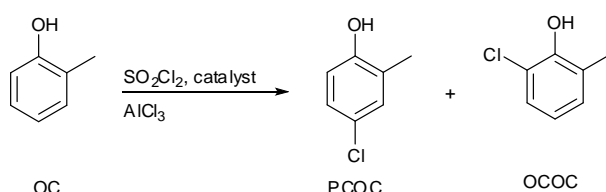
Table 1 Chlorination of *m*-xyleneol in the presence of polymers 3 and 4 and FeCl₃

Catalyst (mg)	Yield (%) ^b				p/o ratio	Mass balance (%) ^c
	MX	OCMX	PCMX	DCMX		
—	3.0 (4.5)	10.0 (11.3)	84.6 (82.0)	0.2 (1.0)	8.4 (7.2)	97.8 (98.8)
3 (30)	0.0	7.4	91.2	1.1	12.3	99.7
3 (50)	0.0	7.0	91.0	2.3	13.0	100.3
4 (30)	0.0	9.0	87.0	3.8	9.6	99.8
4 (50)	0.0	9.2	86.0	4.5	9.3	99.7

^b Yield percentage was calculated using quantitative GC. Figures in parentheses are for the reaction carried out in the absence of FeCl₃. ^c Mass balances are calculated by adding together the yields of identified compounds; any deficiency from 100% represents unidentified components or experimental measurement errors.

As Table 1 shows, chlorination of *m*-xyleneol with any disulfide present was more selective than when no catalyst was used and with any specific polymeric sulfide the result was virtually identical with either 30 mg or 50 mg of the material. The materials with a trimethylene spacer encouraged greater para-selectivity than their counterparts with a hexamethylene spacer for chlorination of phenol, giving *para-chloro-meta-xyleneol* (PCMX) in 91% yield with p/o ratio of 13 even when only 50 mg of catalyst was used.

Our attention was next turned to chlorination of *o*-cresol (OC) using the disulfide catalysts (Scheme 6). In this case it was not necessary to use a solvent for the reactions since the substrate could be melted and would then remain liquid at 20 °C in the presence of other materials. First we attempted use of various quantities of poly sulfide (3; 1–100 mg for 50 mmol of *o*-cresol) as catalyst. The results are shown in Table 2 along with the baseline results for the chlorination of *o*-cresol in the absence of any polymeric catalyst.



Scheme 6 Chlorination of *o*-cresol.

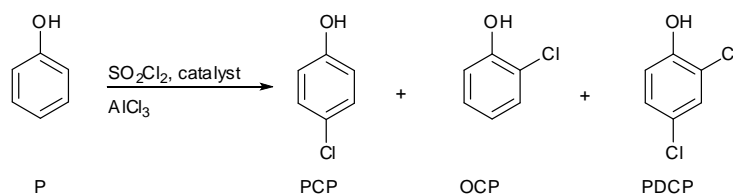
Table 4 Chlorination of *m*-cresol in the presence of polymeric sulfide (3) or (4) and AlCl₃^a

catalyst (mg)	Yield (%) ^{b,c}			p/o ratio	Mass balance (%) ^d
	MC	OCMC	PCMC		
(—)	2.5 (3.2)	9.5 (10.0)	87.2 (86.0)	9.1 (8.6)	99.2 (99.2)
3 (50)	1.0	7.0	91.5	13.0	99.5
3 (1)	1.0	8.5	90.0	10.5	99.5
4 (50)	1.3	7.0	91.5	13.0	99.8
4 (1)	0.2	8.1	91.6	11.3	99.9

^b See footnote b to Table 3. ^c The two ortho-chlorinated products have been grouped under the banner OCMC because the two isomers were not separated by the GC system used. ^d See footnote c to Table 1.

From Table 4 it is noticeable that both polymeric sulfide (3) and (4) acts as selective catalysts for the chlorination of *m*-cresol compared to the situation where no catalyst is used. Both catalysts show comparable results and it is noteworthy that a considerable decrease in the quantity of either catalyst had only a modest effect on the selectivity. The yield of *para*-chloro-*meta*-cresol (PCMC) was in the range of 90–91% with both catalysts, irrespective of the quantity of catalyst.

Finally, we attempted use of the polymeric disulfides as potential selective catalysts in the chlorination of phenol (P, Scheme 8) in a solvent free system (following initial melting of the phenol, which then remained liquid in the presence of the other materials used in the reaction) under otherwise standard conditions. The results are recorded in Table 5.



Scheme 8 Chlorination of phenol.

Table 5 Chlorination of phenol in the presence of cyclic and polymeric disulfides 3 and 4 and AlCl₃^a

Catalyst (mg)	Yield (%) ^b				p/o ratio	Mass balance (%) ^c
	P	OCP	PCP	PDCP		
—	6.0 (6.5)	19.0 (20.2)	73.0 (71.0)	2.0 (1.5)	3.8 (3.5)	100 (99.2)
3 (50)	0.0	3.9	93.0	2.0	23.8	98.9
3 (1)	0.0	4.5	92.5	2.0	20.5	99.0
4 (50)	0.5	6.0	92.0	1.0	15.3	99.5
4 (1)	1.5	6.0	89.9	2.5	14.9	99.9

^b See footnote b to Table 2. ^c See footnote c to Table 1.

Both polymers 3 and 4 acted as selective catalysts, but poly sulfide 3 resulted in greater para-selectivity than poly sulfide 4. However, a significant decrease in the amount of sulfide polymer 4 from 50 mg to only 1 mg had almost no deleterious effect on the selectivity, while a similar decrease in the amount of the poly sulfide 3 from 50 to only 1 mg had a deleterious effect on the selectivity. Interestingly, within each chlorination series the catalyst having a trimethylene spacer demonstrated greater selectivity than that with a hexamethylene spacer.

Conclusions

The polymeric sulfides have been established to be useful catalysts for the chlorination of various phenols using sulfuryl chloride in the presence of a Lewis acid. An increase in para selectivity compared with cases where no catalyst was used has been achieved with most catalysts for most phenols. This can be understood in terms of the mechanistic rationalization put forward by Watson in his original report of catalysis by diphenyl sulfide, wherein he proposed that the actual electrophilic agent was bulky chlorodiphenylsulfonium tetrachloroaluminate, which therefore favoured attack at the less hindered para-position of *o*-cresol.^{10, 11} However, the more subtle effects observed in the present study are more difficult to rationalize on this simple basis alone.

For example, the ring size of polymeric sulfide played an important role in terms of selectivity in the chlorination of some phenols. In particular, polysulfides 3 and 4 gave better para-selectivity compared to for the chlorination of *o*-cresol and phenol. The ring size was found to have almost lower para-selectivity in the chlorination of *m*-cresol and *m*-xylenol. Also, poly sulfides 3 showed a higher selectivity than poly sulfide 4 for the chlorination of phenol, *m*-xylenol and *o*-cresol, while both polymeric sulfides showed similar selectivity for the chlorination of *m*-cresol. At this point it is not clear what causes these subtle effects, but we are currently undertaking studies with other catalysts, which may help to clarify the issue.

Experimental

General

Chemicals and phenol derivatives were purchased from Aldrich and Lancaster chemicals and mostly used without further purification. Sulfuryl chloride was distilled at ambient pressure under an inert atmosphere. All GC analyses were carried out on a Shimadzu GC-2014 Gas Chromatograph using a capillary ZB Carbowax column (30 m, 0.32 mm ID). The GC conditions used for analysis were 40 °C for 3 min, ramped to 220 °C at 10 °C/min and held for 8 min. The injection temperature was 300 °C and the detection temperature 250 °C. Tetradecane was added as an internal standard to allow quantification. All of the expected products from chlorination of phenols were purchased from Aldrich Chemical Company and used to determine retention times and response factors for each product. ¹H and ¹³C NMR spectra were recorded on a Bruker AV500 spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C measurements. Chemical shifts δ are reported in parts per million (ppm) relative to TMS and coupling constants J are in Hz and have been rounded to the nearest whole number. Assignments of signals are based on integration values, coupling patterns and expected chemical shift values and have not been rigorously confirmed. Gel permeation chromatography (GPC) was carried out using a GPC MAX variable loop equipped with two KF-805L SHODEX columns in THF, with a RI(VE3580) detector using a GPC MAX pump operating at a flow rate of 1 ml/min. Calibration was achieved using a series of Viscotek polystyrene standards up to Mw = 9.4 \times 10⁵.

Typical experimental procedure for the preparation of 2-amino-5-mercapto-1,3,4-thiadiazole (1). A mixture of thiosemicarbazide (20g, 0.24 mol), absolute ethanol (70 ml), anhydrous sodium carbonate (10.6 g, 0.10 mol), and carbon disulfide (18.2 g, 0.24 mol) was warmed with continuous stirring at 60 °C for 1 hr. Then refluxed for 4 hrs, the mixture cooled down to room temperature. It was then filtered and the solvent was removed under reduced pressure. The residue was dissolved in distilled water, and acidified with conc. HCl to give a yellow precipitate.

The crude product was filtered and recrystallized from water as yellow needles (1; Scheme 1) in 58 % yield¹⁹.

2-amino-5-mercapto-1, 3, 4-thiadiazole (1), Mp 230–232 °C (Lit¹⁹. 232); ¹H-NMR (d-DMSO) δ (ppm): 7.80 (s, 2 H, NH₂), 9.85 (s, 1 H, NH), ¹³C-NMR (CDCl₃) δ (ppm): 152 (C=S), 181 (CNH₂).

Typical experimental procedure for the preparation of N,N- Terephthalalylidene di-[2-amino-5-mercapto-1,3,4-thiadiazole] (2). A mixture of 2-amino-5-mercapto-1, 3, 4-thiadiazole (2.66 g, 0.02 mol), and terephthalaldehyde (1.34 g, 0.01) in absolute ethanol (30 ml) was refluxed for 5 hrs. After cooling to room temperature the precipitate was filtered and recrystallized from ethanol in 85 % yield.

N,N-Terephthalalylidene di-[2-amino-5-mercapto-1,3,4-thiadiazole] (2). 85%, Mp 156–158 °C; ¹H-NMR (d-DMSO) δ (ppm): 8.10 (d, 4H, Ar-H), 8.50 (t, J = 7 Hz, 2 H, CH=N), 9.85 (s, NH), ¹³C-NMR (d-DMSO) δ (ppm): 129, 139 (Ar-C), 152 (C-N thiadiazole), 163 (CHN), 184 (C=S thiadiazole).

Typical experimental procedure for the preparation of poly sulfides 3 and 4. Poly sulfide polymers 3 was synthesized by dissolving Na (0.84g, 0.035 mol) in 25 ml of absolute ethanol. Compound 2 (6.18 g, 0.017 mol) was added, and the solution was heated. To the resulting boiling solutions benzene was added (45 ml) and 1, 3-dibromopropane (3.4 g, 0.017 mol). After the vigorous and spontaneous reaction subsided, 45 ml of benzene was added and the mixture was refluxed overnight. After mixture was cooled, it was filtered. The solution was evaporated under reduced pressure to give the corresponding polymeric sulfide 3 in 67% yield. Poly sulfide polymer (4; 70% yield) was synthesized by a similar procedure except using 1,6-dibromohexane (4.1 g, 0.017 mol) instead of 1,3-dibromopropane.

Poly sulfide 3. Yield 67%, Mp 246–248 °C; ¹H-NMR (CDCl₃) δ (ppm): 2.10 (t, 2 H, SCH₂CH₂CH₂S), 3.10 (m, 4H, SCH₂), 8.10 (d, 4H, Ar-H), 8.50 (t, J = 7 Hz, 2 H, CH=N), ¹³C-NMR (CDCl₃) δ (ppm): 28.8 (SCH₂CH₂CH₂S), 35.3, (SCH₂), 129, 139 (Ar-C), 163 (CHN), 152 (C-N thiadiazole), 184 (C-S thiadiazole). Mn (GPC): 6519.

Poly sulfide 4. Yield 70%, Mp 267–269 °C; ¹H-NMR (CDCl₃) δ (ppm): 1.35 (m, 4 H, CH₂CH₂CH₂S), 1.50 (m, 4 H, CH₂CH₂S), 3.10 (t, J = 7 Hz, 4 H, CH₂S) 8.10 (d, 4H, Ar-H), 8.50 (t, J = 7 Hz, 2 H, CH=N), ¹³C-NMR (CDCl₃) δ (ppm): 28.4 (CH₂CH₂CH₂S), 29.5 (CH₂CH₂S), 32.4 (CH₂S), 129, 139 (Ar-C), 163 (CHN), 152 (C-N thiadiazole), 184 (C-S thiadiazole). Mn (GPC): 6321.

Typical experimental procedure for the chlorination of *m*-xylenol. *m*-Xylenol (6.11 g, 50.0 mmol), FeCl₃ (25 mg), DCM (25 ml) and the catalyst (50 mg) were added to a dried 50 ml round bottom flask. Freshly distilled sulfonyl chloride (4.66 ml, 57.7 mmol) was added slowly over 2 h via a pressure equalizing dropping funnel. The reaction was stirred at room temperature for a further 2 h. The mixture was quenched with water (20 ml) and the organic components were extracted with diethyl ether (3 × 30 ml). The ether layers were removed, combined and dried over MgSO₄. The drying agent was filtered and the solvent was removed under reduced pressure. The crude product was weighed and then analyzed by quantitative GC.

Typical experimental procedure for the chlorination of *o*-cresol and *m*-cresol. *o*-Cresol (melted) or *m*-cresol (5.41 g, 50.0 mmol), AlCl₃ (0.25 g) and the catalyst (100 mg) were added to a dried 50 ml round bottomed flask. Sulfonyl chloride (4.66 ml, 57.7 mmol) was then added slowly over 2 h via a pressure equalizing dropping funnel. The reaction mixture was stirred for 2 h before being quenched with water (20 ml). The reaction mixture was worked-up and the crude products were weighed until constant mass and then analysed by quantitative GC.

Typical experimental procedure for the chlorination of phenol. Phenol (melted; 4.71 g, 50.0 mmol), AlCl₃ (0.25 g) and a catalyst (50 mg) were added to a dried 50 ml round bottomed flask. Sulfuryl chloride (4.66 ml, 57.7 mmol) was added slowly over 2 hours via a pressure equalizing dropping funnel. The reaction mixture was stirred for 4 h then quenched by the addition of water (20 ml). The reaction mixture was worked-up and the crude products were weighed until constant mass and then analysed by quantitative GC.

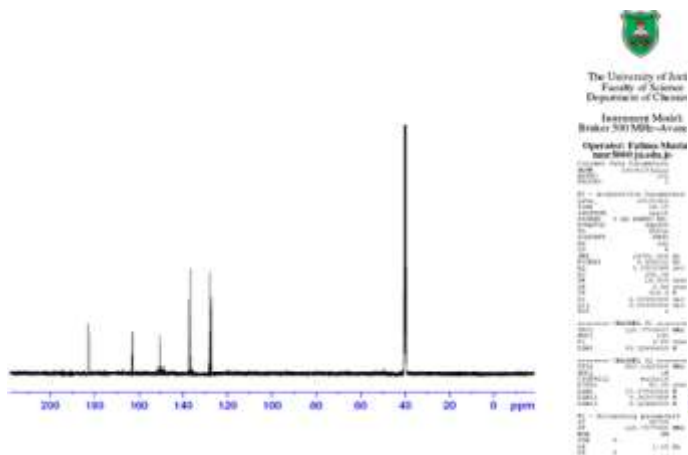


Figure 1: The ¹³C NMR spectra of *N,N*-Terephthalalylidene di-[2-amino-5-mercapto-1,3,4-thiadiazole] (2)

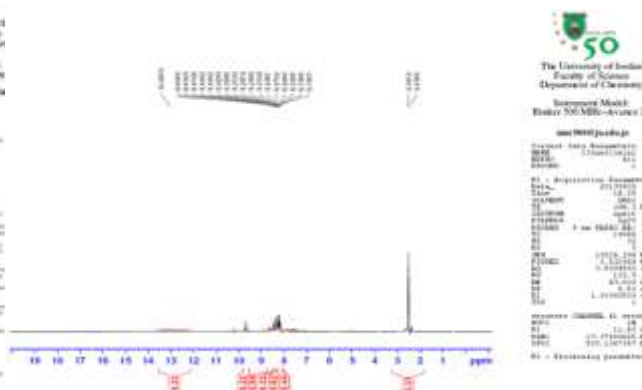


Figure 2: The ¹H NMR spectra of *N,N*-Terephthalalylidene di-[2-amino-5-mercapto-1,3,4-thiadiazole] (2)

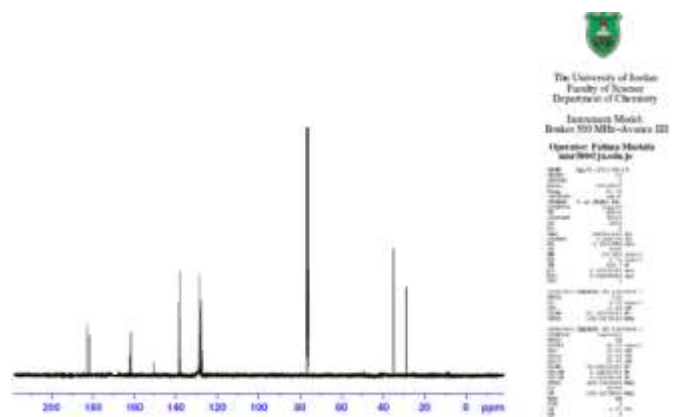


Figure 3: The ¹³C NMR spectra of Poly sulfide 3

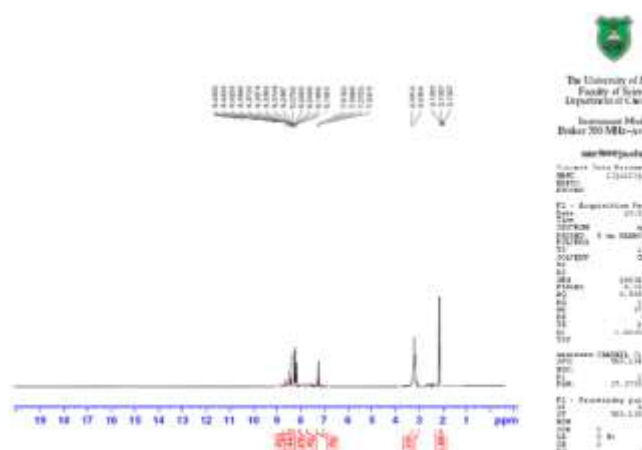


Figure 4: The ¹H NMR spectra of Poly sulfide 3

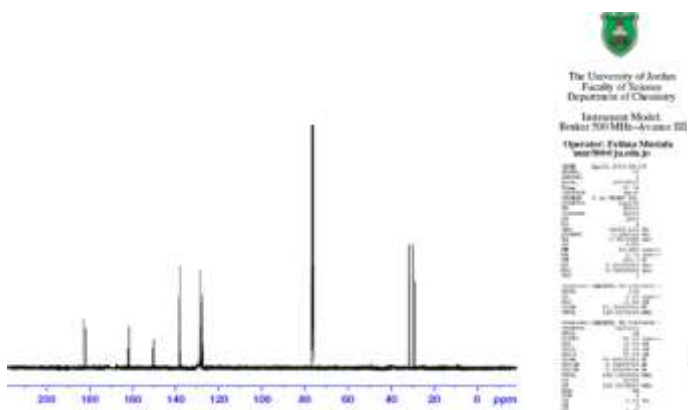


Figure 5: The ¹³C NMR spectra of Poly sulfide 4

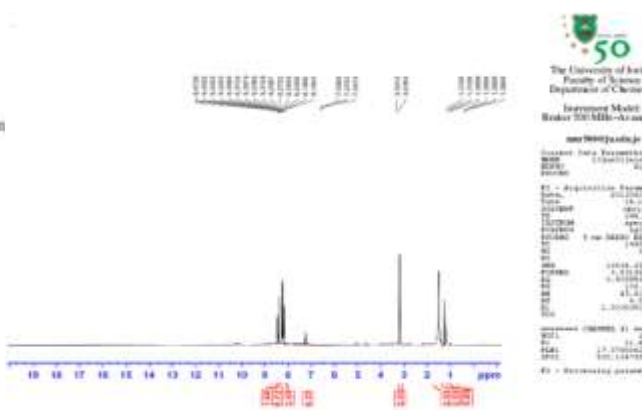


Figure 6: The ¹H NMR spectra of Poly sulfide 4

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