# Synthesis of Poly(4,6-Dimethylpyrimidine)sulfide and amine.

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# Abstract:

4,6-Dimethyl2-pyrimidinethiol (DMPT) and 4,6-Dimethyl2-pyrimidineamine(DMPA) react with Alcl<sub>3</sub> to form poly(4,6-dimethylpyrimidinesulfide) (PDMPS), and poly(4,6-dimethylpyrimidineamine) (PDMPA). These are products of electrophilic substitution reaction of the Friedel-Crafts type.

Key Words: Friedel-Crafts Reaction, Poly(4,6dimethylPyrimidinesulfide), Poly(4,6dimethylpyrimidineamine).

#### Introduction:

poly(p-phenylene sulfide) PPS has been commercially produced Organosulphur and organoamine compounds are act as alkaline earth metal<sup>[2-4]</sup> by the Mecallum polymerization.

Condensation of alkali-metal salt of p-halothiophenol has been also reported for the PPS preparation  $[^{3-5]}$ , however these polymerizations proceed at high pressure and temp. PPS -Like polymers have been prepared by oxidizing thiophenol with Aluminum chloride (AlCl<sub>3</sub>) and thionvl chloride<sup>[6]</sup>, or concentrated sulfuric acid, but these preparations result in highly branched cross linked polymers with primary chains of low Molecular weights. Linear PPS and PPSe prepared from the reaction of diphenyl disulphide<sup>[7]</sup> and dichlorodiphenyl diselenide<sup>[8]</sup> respectively with a Lewis acid catalysts to clave it is S-S and Se-Se bonds and are easily polymerized at room temperature and atmospheric pressure.

In this work we report the synthesis of (PDMPS). (PDMPA) from (DMPT) and (DMPA). respectively.





DMPA PDMPA The most important pyrimidine derivatives are the barbituric acid and the prunes such as nucleic acids and uric acid<sup>[9]</sup>, some other pyrimidine derivatives are used as antimalarials such as pyrimidine sulphonamide and aniline amino pyrimidine<sup>[10-20]</sup>.

Sulfadimethoxine(SD) (4-amino-N-)2,6-dimethoxy-4pyrimidinyl)benzene sulfonamide) which has been known as an antibacterial agent for several decades, was modified to a polymerizable monomer(SDM) through a reaction with methacrylonyl chloride, then copolymerized with a water-soluble monomer, N.N-dimethyl acrylamide and a cross-linked, by a conventional free radical solution polymerization method<sup>[21]</sup>. Sulfonated poly (phenylene sulfide) (SPPS) ion exchanger were prepared by sulfonation of the original polymer <sup>[22]</sup>, and PPS called engineering thermoplastic class. Due to its chemical structure, mode of phenyl groups linked by a sulfur atom, it has excellent chemical and thermal properties<sup>[23]</sup>.

from p-dichlorobenzene with sodium sulfide<sup>[1]</sup>, and alkali or antioxidants, anticipate to the decomposition of hydrogen peroxides, sulphide and Disulphide react with hydrogen peroxide to produce sulphoxides and thiosulphinated. organosulphides are important stabilizers agnist the Autooxidation of polymers (such as PVC, and polyolefine....). They are able to decompose hydrogen peroxide into nonradical products. The most important process is oxidation of the sulphide boud connected with the formation of the sulphoxide sulphone and groups<sup>[24]</sup>.



It is believed that sulphides, sulphoxides thiosulphonates, selenides, triamines, phosphines phosphates,....etc, are capable of decomposing hydrogen peroxides without formation of free radicals, and thus they function as stabilizers<sup>[25]</sup>.

# **Experimental:**

## Instrumentation:

Melting points (soft temp.) were determined using Gallen Kamp melting point apparatus.

IR spectra were obtained using Pye Unicam SP 300 spectrophotometer(KBr disc).<sup>1</sup>H-NMR spectra were recorded on the Varian A-60 in d6-DMSO and were recorded in ppm downfild from TMS. For Viscosity used Ubbelohde Viscometer (Polym.conc. 0.5g/dl in DMSO at  $(25.0 \pm 0.1C)$ . Elemental analysis (C,H and N) was recorded on Carlo Erba type 1106.

### Starting materials:

AlCl<sub>3</sub> (reagent grade) was obtained from Fluka and purfied by vacuum sublimation<sup>[26]</sup> before used.

The monomers DMPT and DMPA were recrystallized in a acetone solvent, dried and used<sup>[27]</sup>.

#### **Polymerization of DMPT and DMPA:**

To two necked flask equipped with  $N_2$  gas and condenser, (10 mmole) of each monomers DMPT or DMPA with (10 mmole, 1.333gm) of purifed Aluminum Chloride was changed and 10ml of nitrobenzene was added. The mixture was magnetically stirred and boiled under reflux for (7hr) a viscose products were poured into 150ml of methanol. Polymer was then filtrated. The solid was worked up boiling three times with 150ml of methanol and then three times with 150ml of water. The products were dried over night at 100C to render polymer.

## **Results and Discussion:**

The polymers are prepared by using Aluminum chloride (Lewis acid) as catalyst, which formed the complex and substitutes electrophilically on the pyrimidine ring as Friedel-Crafts reaction. Heterocyclic thiol, and amines are Lewis bases and form complexes with Lewis acids <sup>[28, 29]</sup>.

+ -

$$C_6H_5$$
-SH + AlCl<sub>3</sub>  $\longrightarrow$   $C_6H_5$ -S AlCl<sub>3</sub>H

Sulphinium ion is typically formed in acid-base equilibrium between Lewis acid and electrophilic in Friedel-Crafts alkalization<sup>[30, 31]</sup>.

The IR spectra of both polymers show no absorption band at 3010-3100 cm<sup>-1</sup> range indicates the absence of -C-Haromatic ring ( at the carbon 5-position of the pyrimidine ring). The absence of any absorption band at 2500cm<sup>-1</sup> range indicates the absence of -SH group for the PDMPS and no absorption two bands in the  $-NH_3$  group of PDMPA. The presence the broad band of 2- amine of PDMPA, at 1345cm<sup>-1</sup> and the band of -NH at 3350-3450cm<sup>-1</sup> range. The absorption band at 810cm<sup>-1</sup> indicates the para substitution on the aromatic ring.

The structures of these polymers were confirmed by <sup>1</sup>H-NMR. The absence chemical shifts at 6.5-6.35 ppm for aromatic hydrogen on the polymers respectively indicates alinear or 2-5 conjugated substituted pyrimidine sulfide and amine structure. The NH protons of PDMPA have not been observed. These protons may be either exchanging very rapidly with the solvent, or their peaks may be covered up by the broad solvent resonance line<sup>[32]</sup>.

The elemental analysis that is the C,H, and N contents of polymers (PDMPS, PDMPA) are listed in Table(1). The values are in reasonable agreement with theoretical values confirming the proposed structures.

Table(1): Elemental analysis , viscosity and yields of PPDMPS and PDMPA.

Polymers	Found (calc.%)			Vise		m.p.
	С	н	Ν	.(dl/g)	Yeild	(soft temp.)
PDMPS	34.12(34.68)	3.8(3.7)	13.7(14.0)	1.08	%97	>320
PDMPA	36.73(36.65)	4.59(4.45)	21.3(20.9)	1.05	%95	>300

Reduced Viscosities for both polymers were determined by using a Ubbelohde Viscometer (polymer conc. 0.5g/dl) in DMSO at  $25.0 \pm 0.1C^{\circ}$ . The viscosity for each sample was measured twice and values were averaged.

#### **Conclusion:**

New polymers were prepared by Friedel – Crafts alkylation reaction. The proposed of new polymer are important

antioxidant against the Auto-oxidation of polymers (such as pvc, polyolefine...etc). They are able to decompose hydrogen peroxide (formed from the oxidation) without formation of free radicals.

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#### الملخص:

4,6-Dimethyl 2-pyrimidinethiol (DMPT)and ) يتفاعل كل من

4,6-Dimethyl 2-pyrimidineamine(DMPA

لویس (AICI<sub>3</sub>) لتحضیر ( AICI<sub>3</sub>) وال

sulfide)(PDMPS), and poly(4,6-dimethyl pyrimidine

amine) (PDMPA ويعتبر هذا التفاعل من نوع التفاعلات الباحثة عن الالكترون (فريدل-كرافت).