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# Synthesis and Characterization of a Novel Heterocyclic Poly(Schiff Base Sulfide) Polymer: Nucleophilic Displacement Polymerization of N,N'-Bis(p-chlorobenzylidine)-2,6-diaminopyridine with Sodium Sulfide

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NOTE

# SYNTHESIS AND CHARACTERIZATION OF A NOVEL HETEROCYCLIC POLY(SCHIFF BASE SULFIDE) POLYMER: NUCLEOPHILIC DISPLACEMENT POLYMERIZATION OF N,N'-BIS(P-CHLOROBENZYLIDINE)-2,6-DIAMINOPYRIDINE WITH SODIUM SULFIDE

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Key Words: Azomethine, Poly(Schiff Base Sulfide) Polymer, Nucleophilic Displacement Polymerization, Diaminopyridine, Thermal Behavior, X-Ray Diffraction

## ABSTRACT

Novel synthesis of a new poly(Schiff base sulfide) (PSBS) polymer by nucleophilic displacement polymerization of N,N'-bis(p-chloro-benzylidine)-2,6-diaminopyridine with sodium sulfide was carried out. The resulting polymer was soluble in some polar aprotic sol-vents having inherent viscosity of 9.01 dl/g in Dimethyl sulfoxide (DMSO) at 30°C. The monomer and the polymer were characterized by elemental analysis, IR and $^1$HNMR spectroscopy.

The temperature of 10% wt loss under nitrogen and glass transition tem-perature ($T_g$) of the polymer were found out to be 380°C and 74.6°C, respectively. The semicrystalline nature of polymer was evidenced from its X-ray diffraction study.

## INTRODUCTION

The basic properties of Schiff base polymers (polyazomethines) are due to the linkage C=N in the backbone . Studies on Schiff base polymers have been a subject of interest because of their high thermal stability [1, 2] chelating ability [2, 3] and semi-conducting property [4, 5]. There have been several reports concerned with the doping and conductivity of Schiff base polymers [6]. Poly(arelyne sulfide)s such as poly(phenylene sulfide) are an important class of high performance polymers . The synthesis of poly(xylenylsulfide ) with good flexibility and electrical characteristics have been reported by a group of Japanese workers [7]. Synthesis and characterization of some new Schiff base polymers have been reported [8, 9] recently. Kondo *et al*. [10] have reported the nucleophilic substitution of hetero-arylene systems instead of non-activated benzene rings to prepare sulfur-containing aromatic polymers. Dutta and Mait [11] have reported the reaction of 2,6-dichloropyridine with anhydrous sodium sulfide for the synthesis of poly(pyridinylene sulfide).

Recently, we [12] have reported the synthesis of a new poly(Schiff base sulfide) (PSBS) polymer through nucleophilic displacement polymerization of N,N'-bis(p-chlorobenzylidine)-4,4'-diaminodiphenyl methane with sodium sulfide. In this communication, we wish to report the synthesis of a heterocyclic Schiff base monomer i.e. N,N'-bis(p-chlorobenzylidine)-2,6-diaminopyridine and it's subsequent nucleophilic displacement polymerization with sodium sulfide in anhydrous condition and the characterization of the said monomer and the polymer.

## EXPERIMENTAL

### Materials

2,6-diaminopyridine (E. Merck, Germany) was used after sublimation under reduced pressure. 4-Chlorobenzaldehyde (E. Merck, Germany) was used without further purification. The hydrated sodium sulfide (E. Merck, Germany) was dehydrated as described later. N-methyl-1-2-pyrrolidone (NMP) (SRL, India) was purified by distillation prior to use. All other solvents, such as toluene, xylene, and methanol (all AnalaR/GR grades) were also distilled prior to use.

### Monomer Synthesis

1.0913 gm (0.01mol) of 2,6-diaminopyridine (DAP) and 20 ml of methanol were placed into a three-necked flask. 2.814 (0.02 mol) of P-Chlorobenzaldehyde (PCB) dissolved in 10 ml of methanol was added to it. The reaction was carried out at 20°C for 1 hour under nitrogen atmosphere. The product (monomer) then poured into distilled water and the precipitated crystals then separated by filtration. The monomer was recrystallized from toluene, washed with methanol and finally dried at 80°C under vacuum for 6 hours the yield was 91%.

### Preparation of Anhydrous Sodium Sulfide [12]

In a three-necked flask fitted with a water condenser, nitrogen inlet tube and a mercury pocket, 20 ml of NMP and 10 ml of xylene were mixed. Then, 2.40 gm (0.01 mol) of hydrated sodium sulfide was added to the flask and the solution mixture was heated under a slow stream of nitrogen for 1.5 hours and the distillate was removed by nitrogen flushing. Xylene was added occasionally into the reaction mixture to maintain concentratioin of the solution, and thus, the distillate containing water was removed until the temperature rose to 140°C. The dehydrated sodium sulfide in NMP thus prepared was used for polymer synthesis.

### Polymer Synthesis

The reaction of monomer, PCBDAP 3.54gm (0.01 mol) with dehydrated $Na_2S$ was carried out in NMP (30 ml) at 200°C for 24 hours with constant stirring under nitrogen. The reaction mixture was then collected and poured into large excess of ice-cold water. The precipitated product was isolated by filtration, thoroughly washed with hot water and then with hot methanol. Finally the polymer was dried in vacuum at 80°C for 6 hours. The yield of the polymer was 82%.

### Measurements

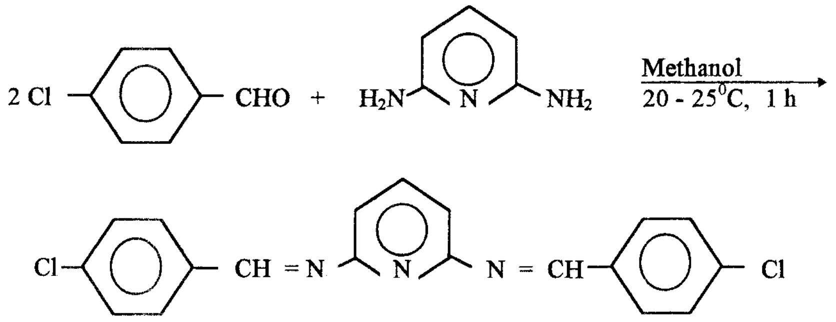
IR spectra (in KBr) were recorded with a Perkin-Elmer 337 model spectrophotometer. $^1$H-NMR spectra were run on a Bruker AC 300 F NMR (300 MHz) spectrometer at room temperature using tetramethylsilane (TMS) as the internal reference. While taking $^1$H NMR spectra the solvents used for the monomer and the polymer were deuterated chloroform ($CDCl_3$) and deuterated sulfoxide (DMSO-$d_6$), respectively. The inherent viscosity of the polymer solution (0.5% w/v) in DMSO was determined at 30°C by using an Ubbelohde suspended level viscometer. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were recorded on a V2.2A Dupont 9900 thermal analyzer in nitrogen at a heating rate of 10°/min up to 600°C. X-ray diffraction was obtained with a

Phillips X-ray diffractometer (model pw 1710) using Ni-filtered Cu-$K_\alpha$ radiation (30 kv 20mA).

## RESULTS AND DISCUSSION

### Monomer Synthesis

The reaction Scheme (**I**) for the synthesis of dichloro Schiff base monomer (PCBDAP) may be represented as follows:



(I)

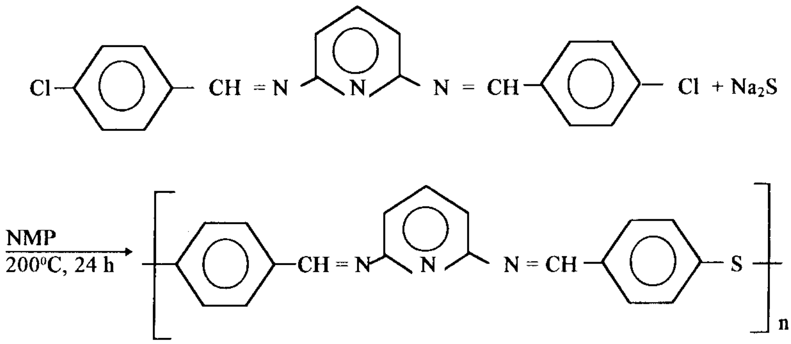
The monomer (PCBDAP) shows canary yellow color. While taking the melting point of the monomer, it was observed that at 220°C the blackening starts (yellow color gradually changes) and at 265°C it completely changes to a black color. The monomer was soluble in common organic solvents like acetone, methanol and chloroform and also in polar aprotic solvents like DMSO, NMP and dimethyl acetamide (DMAC).

From the elemental analysis of monomer ($C_{19}H_{13}N_3Cl_2$), the measured contents of C,H and N agree nearly with the calculated values:

| | | | |
|---|---|---|---|
| Calcd. (%) | C 64.44 | H 3.67 | N 11.86 |
| Found (%) | C 64.28 | H 3.53 | N 11.78 |

### Polymer Synthesis

The reaction Scheme (**II**) for the synthesis of poly(Schiff base) sulfide polymer by the polycondensation reaction between PCBDAP and anhydrous $Na_2S$ may be represented as follows :



(II)

The mechanism is supposed to be the same as that for a nucleophilic displace-ment reaction of dichlorophenylene with sodium sulfide to form polyphenylene sulfide [13].

It is well-known that aromatic nucleophilic displacements occur efficiently only when the aromatic ring is highly electron deficient. This usually requires atleast two electron withdrawing groups as well as the leaving group. In our case, the mechanism proposed is a nucleophilic displacement of chloride by sulfide ion. This requires a fractional +ve charge on the carbon atom to which chlorine atom is attached. Due to +R effect of chlorine atom attached to the benzene ring, there should be carbon-chlorine double bond character which would make nucleophilic displacement reaction rather difficult. However, under drastic conditions as we have adopted in our case (NMP medium 24 hours and 200°C), this reasonance stabilization might have been overcome. Simultaneously, the -I effect of chlorine atom remains unaffected leading to development of fractional +ve charge on carbon atom to which chlorine atom is attached. Similar explanation has also been given earlier [12]. NMP, due to its relatively higher boiling point and better thermal stability than those of similar other aprotic solvents, is used generally in the polymerization reacions of aromatic polysulfides [14]. It is assumed that NMP facilitates the nucleophilic displacement reaction through its dipolar aprotic properties and functions as a catalytic reactant in transforming $Na_2S$ into soluble nucleophile [11, 14]. Dutta and Maiti [11] while reporting the synthesis of poly(pyridinylene sulfide) by nucleophilic displacement polymerization of 2,6-dichloropyridine with anhydrous sodium sulfide have also used NMP as the solvent under drastic reaction conditions (200°C, 10 hours).

The polymer (**II**) $(C_{19}H_{13}N_3S)_n$ as synthesized by us, shows a brown color. The elemental analysis of the polymer agrees well with the proposed structure

(**II**) of the polymer :

| | | | | |
|---|---|---|---|---|
| Calcd. (%) | C 72.38 | H 4.12 | N 13.33 | S 10.15 |
| Found (%) | C 72.45 | H 4.12 | N 12.91 | S 9.87 |

The polymer is soluble in polar aprotic solvents like Dimethylformamide (DMF), DMAc and DMSO, but insoluble in $H_2O$, acetone, methanol, hexane, ether, and chloroform. The inherent viscosity, ηnh (dL/g) of the polymer solution in DMSO (0.5% w/v) is found to be 0.91 dL/g.

### Characterization of the Monomer and the Polymer

The IR spectrum of the monomer (PCBDAP) shows a strong characteristic azomethine (-CH=N-) peak at 1590 $cm^{-1}$ and a strong C-Cl peak at 1070 $cm^{-1}$. The IR spectrum of the polymer also shows strong azomethine peak in the region 1580-1600 $cm^{-1}$. Again, it shows a peak at 790 $cm^{-1}$ confirming C-S linkage in the polymer. From the $^1$H-NMR spectrum of the monomer different proton sets on heteroaromatic and aromatic rings appear as well-resolved peaks in the region δ5.651 to δ7.521 and azomethine (-C=NH) protons absorb at δ7.825. The $^1$H-NMR spectrum of the polymer shows broad and ill-resolved aromatic and hetero-aromatic proton peaks in the region δ5.752 to δ7.510, and a peak δ7.986 for azomethine protons. The first indication of the material to be polymer comes from highly broad and ill-resolved peaks. This is due to the entanglement of macro-molecular chains to distort the shielding effect.

### Thermal Behavior

The TGA curve of the polymer shows that the polymer is quite stable up to 200°C. It undergoes 10% and 20% wt loss at 380°C and 460°C, respectively. From DTG (Derivative Thermogravimetry), the maximum decomposition temperature (TD) of the polymer is found out to be 519.80°C. From DSC studies, the $T_g$ (glass transition temperature) of the polymer is found out to be 74.6°C. The detailed thermal and conductivity characteristics of the polymer are in progress.

### X-ray Diffraction

From the X-ray diffraction pattern of the polymer, the degree of crystallinity ($X_{cr}$) as measured adopting the classical method [15] is found to be 0.23. This value of $X_{cr}$ suggests that the polymer is semicrystalline in nature.

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## REFERENCES

[1] C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc., 80*, 832 (1958).

[2] C. S. Marvel and P. V. Bonsignore, *J. Am. Chem. Soc., 81*, 2668 (1959).

[3] W. E. Rudzinski, S. R. Guthrie, and P. E. Cassidy, *J. Polym. Sci., Polym. Chem. Ed., 26*, 1677 (1988).

[4] Y. Saegusa, K. Sekiba, and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed., 28*, 3647 (1990).

[5] Y. Saegusa, T. Takashima, and S. Nakamura, *J. Polym. Sci. Polym. Chem. Ed., 30*, 1375 (1992).

[6] X. Li, Y. Jiao, and S. Li, *Eur. Polym. J., 27(12)*, 1345 (1991).

[7] JP 63, 243, 135 (1988), Toray Industries, Inc., Japan, invs.: A. Suzuki, M. Umezawa, S. Imai., *Chem. Abstr., 111*, 50144 (1989).

[8] M. Y. Khuhawar and A.H. Channar, *Macromolecular Reports., A32* (Suppl. 4), 523 (1995).

[9] S. Banerjee, C. Saxena, P. K. Gutch, and D. C. Gupta, *Eur. Polym. J., 32(5)*, 661 (1996).

[10] S. Kondo, T. Yamamoto, H. Kunisada, and Y. Yuki, *J. Macromol. Sci., Chem., A27*, 1513 (1990).

[11] P. K. Dutta and S. Maiti, *Makromol. Chem., Rapid Commun. 13*, 505 (1992).

[12] A. K. Mohanty, M. Misra, and B. Misra, *Eur. Polym.J., 33(7)*, 1087 (1997).

[13] X. Li, Y. Jiao, and S. Li, *J. East. China Univ. Chem. Techn., 13*, 586 (1987).

[14] D. R. Fahey and C. E. Ash, *Macromolecules, 24,* 4242 (1991).

[15] P. H. Hermans, *J. Appl. Phys., 19*, 491 (1948).

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