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NUCLEOPHILIC SUBSTITUTION POLYMERIZATION OF 2,6-DICHLOROPYRIDINE WITH BISPHENOL A

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ABSTRACT

Polypyridine ether (PPyE) is synthesized by the nucleophilic substitution polymerization between 2,6-dichloropyridine and Bisphenol A (BPA) in polar aprotic solvents at 160° C. The polymer is soluble in aprotic solvents and is characterized by elemental analysis, IR and ¹H-NMR spectroscopies and viscometry. Thermal behavior of the polymer is studied by TGA, DSC and TMA. The polymer shows moderate thermal stability and LOI value of about 40. X-ray analysis reveals that PPyE is partial crystalline.

KEYWORDS : Nucleophilic substitution polymerization, dichloropyridine, polypyridine ether.

INTRODUCTION

Polyheteroarylene ether such as poly (ether -1,4 -iso quinolinediyl) is an important class of new polymer¹. Recently considerable attention has been given to nucleophilic substitution of nonactivated benzene rings. Recently Kondo et al^{2,3} reported the nucleophilic substitution of heteroarylene systems instead of nonactivated benzene rings to prepare sulfur containing aromatic polymers. Kricheldorf et al⁴ also reported the reaction of 2,6-dichloropyridine (DCP) with methylated bisphenol A (BPA) for synthesis of polypyridine ether.

Since the pyridine derivatives undergo nucleophilic substitution reaction more readily than the benzene derivatives ⁵, it is expected that halopyridines will be more reactive than halobenzene systems. This has prompted me to investigate nucleophilic substitution polymerization of 2,6-dichloropyridine (DCP) and bisphenol A (BPA) in anhydrous condition.

EXPERIMENTAL PROCEDURE

Materials : 2,6-dichloropyridine (DCP) (Fluka, Switzerland), Bisphenol A (BPA) (BDH, India), dimethyl sulfoxide (DMSO), (BDH, India), N, N-dimethyl acetamide (DMAC) (BDH, India), N-methyl pyrrolidone (NMP) (E. Merck, Germany) were used. They were used after either crystallization or purification following standard procedures ⁶.

Measurements : Elemental analysis for carbon, hydrogen and nitrogen was done by a Heraeus Carbo Erba 1108 elemental analyzer. IR spectra were recorded with a Perkin-Elmer (Model 577) spectrophotometer by using KBr discs ¹H-NMR spectrum was run on a Varian EM-390, 90 MHz NMR spectrometer at room temperature in deuterated dimethyl sulfoxide (DMSO-d₆) using tetramethylsilane (TMS) as the internal reference. The inherent viscosities of the polymer solutions (0.5% w/v) in N,N-dimethylformamide (DMF) were determined at 30°C by using an Ubbelohde suspended level viscometer. The solubilities of the polymer were examined by using 0.02 g of polymer in 3.5 mL of solvent at room temperature. X-ray diffraction was obtained with a Philips X-ray diffractometer (Model Ph 1710) using Ni-filtered CuK α radiation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a Stanton Redcroft 625 thermal analyzer at a heating rate of 10 K/min. The thermomechanical analysis (TMA) measurements were recorded on a Shimadzu, TMC-30 at a heating rate of 10 K/min in air and with a load of 20 cN on the sample. The limiting oxygen index (LOI) measurement was done by following the technique described by Kishore et al⁷.

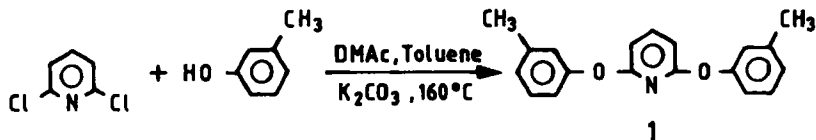
Model reaction : A mixture of m-cresol (2.16 g, 0.02 M), potassium carbonate (1.75 g, 0.0125 M), DMAC (20 mL) and toluene (10 mL) was stirred at room temperature in nitrogen atmosphere and finally refluxed for 2 h. The water was removed by azeotropic distillation until the temperature rose to 140°C. After that 2,6-

dichloropyridine (DCP) (1.48 g, 0.01 M) was added and allowed to react for 24 h at 160°C. The reaction mixture was poured into a large amount of water, the precipitate obtained was extracted with methylene chloride and dried under vacuum at 60°C for 6 h. yield : 2.53 g (87%), m.p. : 260° C.

Synthesis of polymer : An equimolecular mixture of DCP and BPA in 50 mL aprotic solvent was charged in a 3-necked flask, equipped with a water condenser, a stirrer and a nitrogen inlet tube. The solution mixture was heated to 160°C under a slow stream of nitrogen for 20 h with stirring. After the reaction was over, the reaction mixture was cooled and poured over ice/water. The precipitated polymer was separated by filtration and repeatedly washed with water. The separated product was reprecipitated with water from ethanol solution. Again the polymer was filtered, washed with hot water, then washed with hot n-hexane to remove unreacted DCP and dried under vacuum at 40° C.

RESULTS AND DISCUSSION

Model reaction : The effectiveness of a pyridine ring system as an electron-withdrawing group can be estimated by the chemical shift of the aromatic protons ortho/para to the position of hetero atom of the pyridine ring. The ¹H-NMR spectrum shows the deshielding of the aromatic protons para to hetero atom of the pyridine ring ⁸ (δ 7.65) is almost same with that of a ketone group ⁹ (δ 7.90) (Fig. 1) and thus portends the likelihood of facile nucleophilic substitution at the 2 and 6 position. The model reaction between DCP and m-cresol resulting in the formation of bis (3-methyl phenoxy) pyridine under higher temperature and longer reaction conditions demonstrated the suitability of halopyridines in the substitution reaction with a phenoxide.



Characterization : The product, bis (3-methyl phenoxy) pyridine obtained by the model reaction was characterized by elemental analysis and IR study.

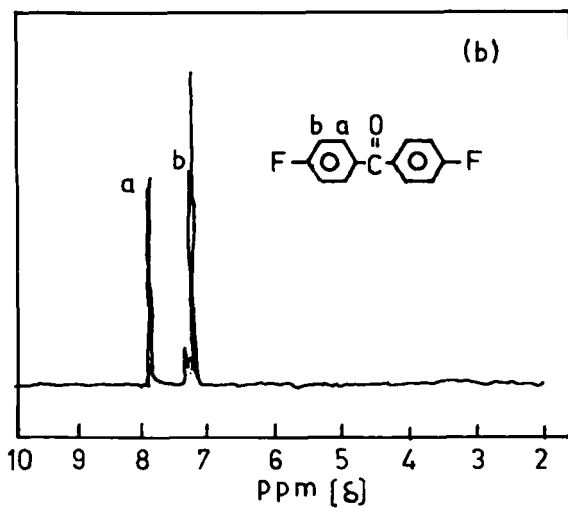
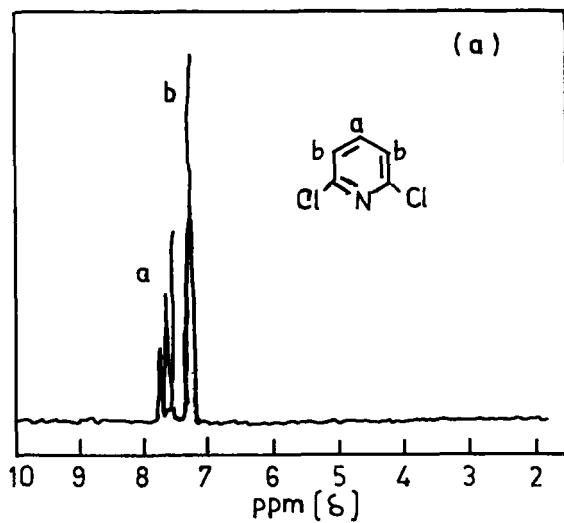


FIG. 1 (a) ^1H -NMR SPECTRUM OF 2,6-DICHLOROPYRIDINE
(b) ^1H -NMR SPECTRUM OF 4,4'-FLUOROBENZOPHENONE

The elemental analysis shows Calcd. for (C₁₉H₁₇O₂N): C, 78.35; H, 5.87; N, 4.79. Found: C, 79.15; H, 6.10; N, 4.62.

The elemental analysis agrees well with the experimental result. The IR spectrum shows the aromatic C-N stretching vibration of pyridine ring at 975 cm⁻¹ and C-H stretching vibrations at 3070 and 2950 cm⁻¹ for aromatic system and methyl group respectively. The stretching vibration at 1245 cm⁻¹ was in good agreement with the formation of ether linkage.

Polymer synthesis : The synthesis of polyheteroarylene ether demonstrated that the heteroarylene system is an effective activating group for nucleophilic substitution polymerization¹⁻⁵. Since the pyridine system contains a hetero atom, it is expected to play the role of an activating group for nucleophilic substitution reaction. The model reaction describes the suitability of the nucleophilic substitution reaction.

The nucleophilic substitution polymerization between DCP and BPA²⁻ may be represented as follows:

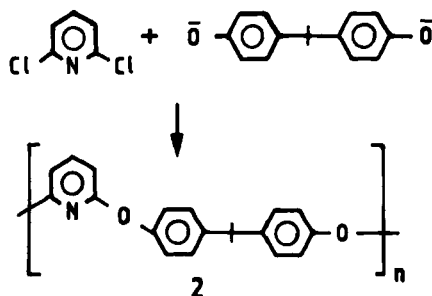


Table 1 presents details of the reaction conditions, yield and inherent viscosity of the polypyridine ether (PPyE). The DMAC solvent by K₂CO₃ method effectively solvates the monomers, polar intermediates, and in most cases the subsequent polymer. The inherent viscosity of the polymer (0.30 dL/g) in this method is moderately high (Table 1). Further, formation of the Meisenheimer complex is strongly influenced by the solvent, polar solvent stabilize the complex and facilitate the substitution reaction^{10,11}. The DMSO solvent by NaOH method is the best among all the solvents studied (Table 1). This is because the formation of BPA²⁻ in the DMSO-toluene solvent is the best than the DMAC-toluene and NMP-toluene solvents¹¹.

TABLE 1 Chloro Displacement Polymerization of DCP and BPA²⁻ in Aprotic Solvents

Sl.No.	Reaction conditions			Polymer		
	Method ^a	Solvent	Temperature (°C)	Time (h)	Yield (%)	η_{inh}^b (dL/g)
1	NaOH	DMSO	160	20	78	0.15
2	NaOH	NMP	160	20	70	0.08
3	K ₂ CO ₃	DMSO	160	20	62	0.04
4	K ₂ CO ₃	DMAC	160	20	90	0.30
5	K ₂ CO ₃	NMP	160	20	82.5	0.12

a Ref. 11

b 0.5% solution (w/v) in DMF at 30°C

Characterization : The chemical structure of the polymer was established on the basis of elemental analysis, IR and ¹H-NMR spectroscopies, and X-ray diffraction study.

The elemental analysis of the polymer is in good agreement with proposed structure of the polymer.

Calcd : C, 79.20; H, 5.60; N, 4.62
 Found : C, 79.56; H, 5.48; N, 4.10.

The IR spectrum of the polymer (Fig.2) shows sharp peaks at 2969 cm⁻¹ and 1245 cm⁻¹. This result agrees well with the stretching vibration of methyl groups and ether linkages of the polymer.

The ¹H-NMR spectrum of the polymer (Fig. 3) shows that the protons of the tertiary carbon atom are aliphatic and all the other protons are aromatic. The aromatic and aliphatic protons have signals in the region 6.2 - 7.8 δ and 1.5 - 1.6 δ , respectively. The ratio of the number of aromatic and aliphatic protons accordingly to the proposed structure 2 of the polymer is 11:6. This agrees well with the ratio of the integration heights of the aromatic and aliphatic protons obtained from the NMR spectrum of the polymer (1.81:1).

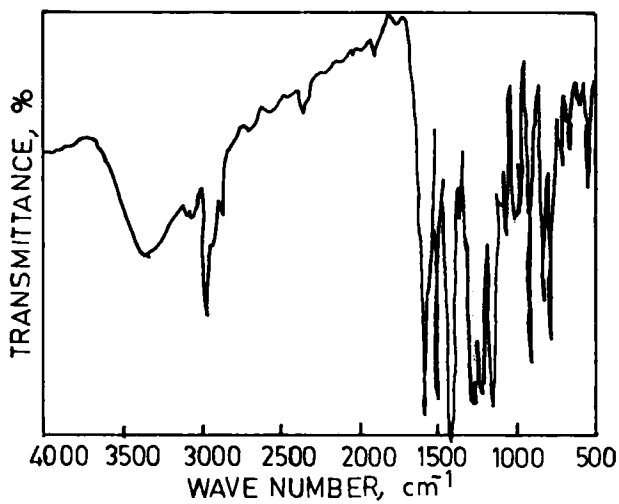
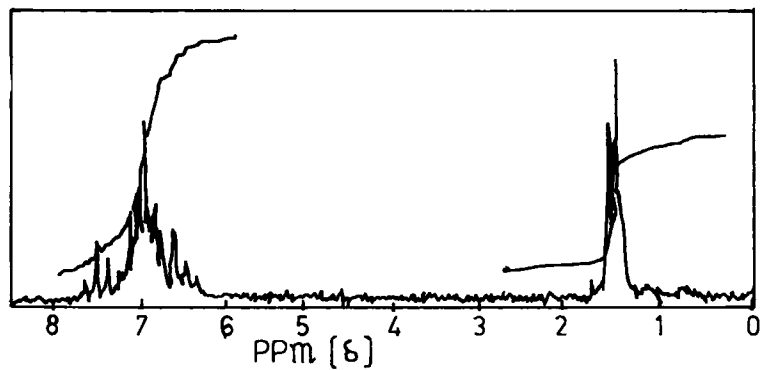


FIG. 2. IR SPECTRUM OF PPyE

FIG. 3 ¹H - NMR SPECTRUM OF PPyE

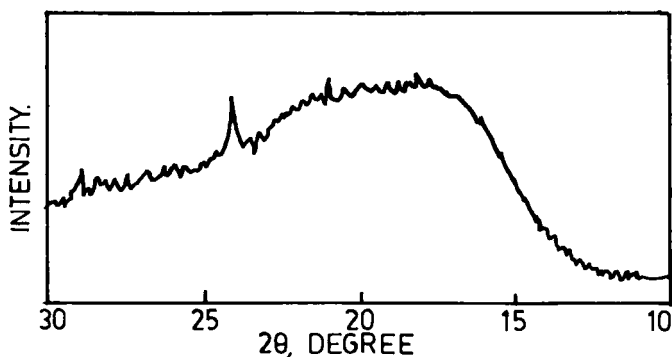


FIG.4. X-RAY DIFFRACTOGRAM OF PPyE.

TABLE 2 Thermal Study of Polypyridine ether

Decomposition temperature, (°C) for weight loss						Char residue % at 600°C		Glass transi- tion temp. Tg(°C)	
10 %		20 %		30%		N ₂	Air	DSC	TMA
N ₂	Air	N ₂	Air	N ₂	Air	N ₂	Air	74.5	76
388	305	414	350	454	390	46	38		

The polymer is soluble in polar aprotic solvents like DMSO, NMP, DMF, DMAC etc., but insoluble in H₂O, hexane and ethers. The X-ray diffractogram (Fig. 4) shows some scattered intense peaks indicating partial crystallinity.

Thermal behavior : TGA study shows the polymer possesses moderate thermal stability. It starts to lose weight after 300°C in air. Some other parameters regarding thermal stability of the polymer is shown in Table 2.

Flammability behavior : Limiting oxygen index (LOI) of this polymer determined by a modified technique⁷ was

found to be 40. It has been reported that polymers with LOI > 27 are related to be non-burning¹². The high LOI value may be due to the presence of nitrogen in the polymer backbone and/or chloro group at chain end of the polymer.

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