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Synthesis and Characterization of New Polyetherimide Containing Bulky Pendant Group

M. Anitha Malbi

Department of Chemistry, Holy Cross College (Autonomous), Nagercoil, India

G. Leema Rose

Department of Chemistry, Holy Cross College (Autonomous), Nagercoil, India

Y. Christabel Shaji

Department of Chemistry, Holy Cross College (Autonomous), Nagercoil, India

Abstract:

The present study is focused on the synthesis and characterization of organo soluble and thermally stable polyetherimide (PEI) containing bulky pendant group (Veretraldehyde). The polyetherimide was prepared by nucleophilic aromatic substitution reaction with a bisdiol salt and a strongly activated bis-aromatic halo monomer containing precyclized imide moiety in a dipolar aprotic solvent. The products were characterized by FT-IR, ¹H-NMR and ¹³C-NMR spectroscopy. The properties such as inherent viscosity, melting point and solubility of the PEI were studied and they possess interesting features like good processability, high inherent viscosity, increased solubility and high melting point.

Keywords: Veretraldehyde, Pyromellitic dianhydride, Chlorine terminated tetrimide, Polyetherimide

1. Introduction

Aromatic Polyetherimide (PEIs) is an important class of high performance polymer having excellent resistance to high temperatures, better processing characteristics and favourable balance of other physical and chemical properties.¹ They have both imide and ether functional groups in the polymer backbone, thus having the merits of both the functional groups such as high thermal stability, good mechanical properties better solubility as well as easy processability and greater tractability. This paper reports the synthesis of new PEI.

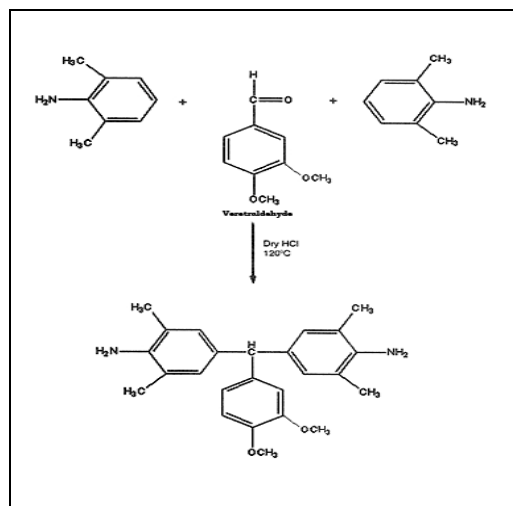
2. Experiment

2.1. Materials Used

2,6-Dimethylaniline, veretraldehyde, pyromellitic dianhydride, p-chloro aniline, dimethyl formamide, dimethyl acetamide, N-methyl pyrrolidone, dimethyl sulphoxide, toluene, acetone, chloroform, dichloromethane, tetrahydrofuran, ethanol, methanol, sodium hydroxide and anhydrous potassium carbonate.

2.2. Synthesis of Monomer [Bi s (4-amino-3,5-dimethylphenyl) 3',4'-dimethoxy phenyl methane]

2,6-Dimethylaniline (12.1g, 0.1 mol) was charged into a 250 ml three necked round bottomed flask equipped with nitrogen inlet, an addition funnel and a reflux condenser. Concentrated hydrochloric acid (8 ml) was added drop-wise to the reaction vessel for 30 minutes. The solid substance obtained was melted by heating to 100 °C. To this veretraldehyde (8.3 g, 0.05 mol) was added. After complete addition the temperature was raised to 120 °C and the reaction mixture was stirred at this temperature for 12 hrs, cooled and neutralized with sodium hydroxide solution. The solid product obtained was filtered, washed with methanol, recrystallized in ethanol and finally dried in vacuum at 70 °C for 12 hrs (Scheme - 1).²



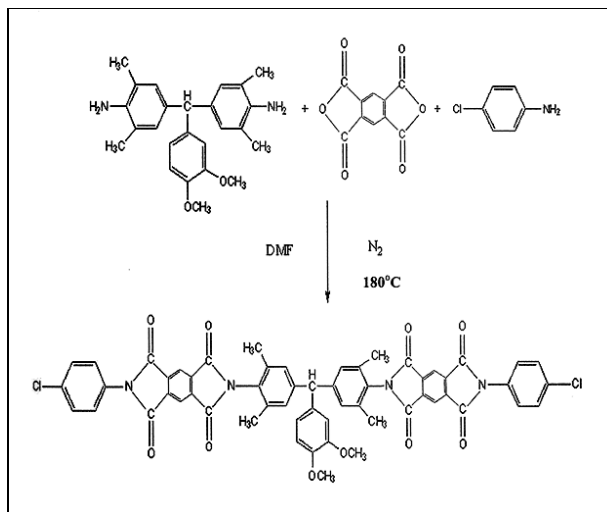
Scheme 1: Synthesis of bis(4-amino-3,5-dimethylphenyl) 3',4'-dimethoxy phenyl methane

2.3. Synthesis of Chlorine terminated tetrimide

2.16g (0.01ml) of bis(4-amino-3,5-dimethylphenyl) 3',4'-dimethoxy phenyl methane was dissolved in 10 ml DMF and was charged in to a three necked round bottomed flask equipped with a nitrogen inlet, mechanical stirrer, reflux condenser and Dean-Stark trap.

To this 4.36g (0.02 mol) of pyromellitic dianhydride (PMDA) and 38 ml of toluene were added. The reaction was carried out for 3 hours at 160 °C in N₂ atmosphere. The water formed as a result of condensation reaction was removed by forming azeotropic mixture with toluene using Dean Stark apparatus. Then the reaction mixture was raised to 180 °C and the residual toluene was distilled off under reduced pressure. To this dianhydride terminated diimide 2.54 g (0.02 mol) of p-chloro aniline and 35 ml of toluene were added and the reaction was carried out in N₂ atmosphere for another 3 hours at about 180 °C.

The water formed as a result of condensation reaction was removed by forming azeotropic mixture with toluene using Dean Stark apparatus. After the reaction was over, the residual toluene was distilled off under reduced pressure. Then, the solution was cooled and precipitated in water. The precipitate obtained was washed with hot water and dried in vacuum oven at 60 °C for 12 hours (yield 93.5%) (Scheme 2).



Scheme 2: Synthesis of chlorine terminated tetrimide containing verteryl moiety

2.4. Synthesis of Polyetherimide

Polyetherimide was synthesized from the prepared chlorine terminated tetrimide and a bisdiol by one step aromatic nucleophilic substitution reactions in DMF in the presence of K₂CO₃.

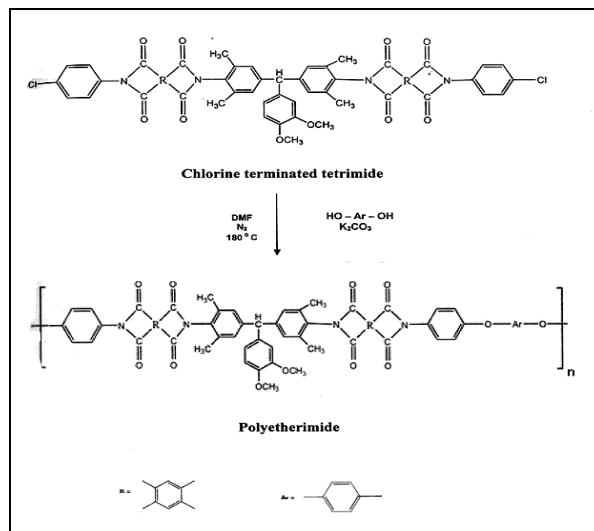
About 0.01 mole (6.28g) of the synthesized chlorine terminated tetrimide was dissolved in DMF and to this 0.02 mole (4.32g) of 1,4-dihydroxy benzene was added. To the above reaction mixture, 0.02 mole (1.57g) K₂CO₃ and about 40 ml of toluene were added. The reaction mixture was heated to 140 °C for 6 hours in N₂ atmosphere with continuous stirring. The water formed as a result of condensation reaction was removed by forming azeotropic mixture with toluene using Dean - Stark apparatus. The reaction temperature was raised to 180 °C and kept at the same temperature for 5 hours. During this time, progress of the reaction was monitored by thin layer chromatography (TLC).

After the reaction was over, the residual toluene was distilled off under reduced pressure. Then, the solution was cooled and precipitated in methanol. The precipitate obtained was washed with hot methanol and dried in vacuum oven at 100 °C for 12 hours. The yield of the reaction was 88.5%.

The polyetherimide was formed by one step aromatic nucleophilic substitution reaction and it proceeded at a faster rate because the strongly activated bis aromatic chloro monomers containing precyclized imide moieties (ie) the chloro terminated tetrimide was reacted in a dipolar aprotic solvent DMF with 1,4-dihydroxy benzene.

This synthesis proceeded via an intermediate, which is the Meisenheimer type complex and it is effectively stabilized through resonance of the imide system.³

The leaving group- 'Cl' is highly activated by two imide carbonyl group as they are locked in a coplanar conformation in relation to the imide rings. During the displacement reaction, the negative charge on the expected Meisenheimer type transition state is well delocalized by resonance effect. This effect significantly lowers the activation energy of the displacement reaction and the reaction proceeded at a faster rate (Scheme 3).



Scheme 3: Synthesis of Polyetherimide

3. Characterization Techniques

The synthesized diamine and the chlorine terminated tetrimide were characterized by elemental analysis, FT-IR, ¹H-NMR and ¹³C-NMR spectroscopy. The synthesized polyetherimide was characterized by elemental analysis, FT-IR, ¹H-NMR spectroscopy.^{4,5}

The inherent viscosity value of polyetherimide is determined in dimethyl acetamide using Ubbelohde viscometer. The solubility of the polyetherimide is tested in various solvents such as N-Methyl Pyrrolidone (NMP), dimethyl sulphoxide (DMSO), Dimethyl Acetamide (DMAc), Pyridine, Chloroform (CHCl₃), Tetrahydro Furan (THF), Toluene, m-cresol and Xylene. The melting point is also determined.^{5,6}

4. Results and Discussion

The elemental analysis data of the monomer, chlorine terminated tetrimide and the polyetherimide are in good agreement with the calculated values. The spectroscopic data obtained from FT-IR, ¹H-NMR and ¹³C-NMR agree well with the proposed structures.⁷

The inherent viscosity of the synthesized polyetherimide is high and it is found to be 0.72 dL/g. This high value may be due to the bulky pendant group incorporated in the polymer back bone, which results in close packing of the polymer chain.^{8,9}

The polyetherimide is readily soluble in aprotic solvents such as NMP, DMAc, DMSO, and m-cresol at room temperature and in organic solvents such as THF, CHCl₃, Xylene and Toluene on heating. The good solubility of the polyetherimide may be attributed due to the presence of flexible ether linkage which enhance the rotational freedom in the polymer backbone and so the solubility is increased and hence the processability is also enhanced.¹⁰

The melting point of the polyetherimide is 267°C. This is due to increased rigidity, better packing ability and grater polymer chain density. Incorporation of methyl substituent ortho to the imide ring in the polymer chain tends to segmental rigidity of the polymer thereby, enhancing the melting temperature. The presence of bulky pendant phenyl unit also tends to enhance the melting temperature by restricting the segmental motion of the polymer chain.^{11,12}

5. Conclusion

By adopting single step aromatic nucleophilic substitution reaction, a new PEI was synthesized and it posses greater solubility, high melting point and greater viscosity due to the incorporation of bulky pendant group in the polymer backbone. Therefore this PEI can be used for high temperature applications.

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