SYNOPSIS

STUDIES ON SOME SPECIALTY CARDOPOLYMERS

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SYNOPSIS OF THE THESIS TO BE SUBMITTED TO SAURASHTRA UNIVERSITY FOR THE DEGREE OF PHILOSOPHY IN THE FACULTY OF SCIENCE - CHEMISTRY

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PLACE OF THE WORK

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A summary of the work to be incorporated in the thesis entitled, “Studies on some specialty carbo polymers”.

GENERAL INTRODUCTION

Among nitrogen containing compounds, amino compounds are more useful. They find their usefulness as intermediates for synthetic fibers and medicines. Aromatic diamines are the important constituents for the syntheses of dyes, agrochemicals, varnishes, adhesive, and coating materials, pesticides, fertilizers and in other applications. They are widely used in manufacturing thermally stable polyamides, amino and epoxy resins. They are also used as curing agents for epoxy resins and in the synthesis of variety of Schiff bases for various purposes. [1-4]. Schiff bases are most widely used as fine chemicals [5] medical substrates and ligands for metal complexes [6].

They are also useful as starting materials for the synthesis of important drugs like antibiotics, antiallergic, antiphlogistics and antitumor [7-9] and components of rubber compounds [10]. Schiff bases based on salicylaldehyde and other hydroxy aldehydes possess unique characteristic properties of improving both antiwear and corrosion inhibition of synthetic lubricating oils and greases. [10]


Synopsis

The work to be incorporated in the thesis is divided into five Chapters:

CHAPTER 1: INTRODUCTION
CHAPTER 2: SYNTHESIS OF DIAMINES, SCHIFF BASES AND THEIR POLYMERS
CHAPTER 3: CHARACTERIZATION OF POLYMERS
CHAPTER 4: ULTRASONIC STUDY OF EPOXY AND BISBENZOXAZINES
CHAPTER 5: SUMMARY

CHAPTER 1: INTRODUCTION

This chapter of the thesis describes the up to date literature survey on syntheses, applications and characterization of diamines, Schiff bases, epoxy and bisbenzoxazines.

CHAPTER 2: SYNTHESIS OF DIAMINES, SCHIFF BASES AND THEIR POLYMERS

This chapter is further subdivided in to three sections:

SECTION-I: Synthesis of 1-1’ bis(4-aminophenyl)cyclohexane

Aromatic diamines can be synthesized by acid catalyzed condensation of hydrochloride salt of aromatic amines and cyclic ketones. Thus, appropriate amount of aniline and cyclohexanone were condensed at 150°C in presence of hydrochloric acid for 24h. The resultant solution was cooled and made alkaline by using 10% NaOH solution, separated diamine was filtered, washed well with distilled water and crystallized repeatedly from chloroform–n-hexane system. The yield was 39% and mp 162°C. Purity was checked by TLC in ethyl acetate-n-hexane (50:50 v/v) solvent system.

\[
\text{H}_2\text{N}-\begin{array}{c}
\text{Z} \\
\text{R}
\end{array}-\text{CH} = \text{N} \quad \text{NH}_2
\]

SECTION-II : Synthesis of symmetric double Schiff bases

Schiff bases of general structure (Scheme-2) were synthesized by condensing diamine and substituted aldehydes in ethanol by using glacial acetic acid as a catalyst at reflux temperature. Schiff bases were isolated from excess of chilled water, filtered, washed well with sodium bisulphite, distilled water and dried at 50°C in an oven. Schiff bases are soluble in common solvents and were crystallized at least three times from appropriate solvent system. Their purity was checked by TLC in appropriate solvent system.

\[
\text{R} \quad \begin{array}{c}
\text{CH} = \text{N} \\
\text{Z} \\
\text{N} = \text{HC} \\
\text{R}
\end{array}
\]

Where, \( Z = \text{-CH}_2, \text{-O, -SO}_2 \),

\( R = 4-\text{OH, 4-Cl, 4-F} \)
SECTION-III: SYNTHESSES OF POLYMERS

(A) Synthesis of epoxy resins and their curing study

Epoxydation was carried out by using 4-hydroxy symmetric double Schiff bases with epichlorohydrine by using isopropanol as a solvent and alkali as a catalyst at reflux temperature for 2 h. Epoxy resins were isolated from excess water, filtered, washed well with distilled water and purified using DMF-Water system. The epoxy equivalent of the resins was determined by pyridinium method. The resins were cured by phthalic anhydride as a hardener.

\[
\begin{align*}
    \text{H}_2\text{C} & \text{CH} \text{CH}_2 \left[ \text{O} - \text{CH}_2 \text{CH} \text{CH}_2 \text{O} \right]_n \text{CH}_2 \text{CH} \text{OH} \\ 
    \text{Where, } & \quad \begin{array}{c}
    \text{Z} = \cdot\text{CH}_2 \cdot, \cdot\text{O} \cdot, \cdot\text{SO}_2 \cdot \\
    \text{Z} & = \cdot\text{CH}_2 \cdot, \cdot\text{O} \cdot, \cdot\text{SO}_2 \cdot
\end{array}
\end{align*}
\]

III (Epoxy resins of symmetric double Schiff bases)

(B) Synthesis of bisbenzoxazines and their ring opening polymerization

Bisbenzoxazines were synthesized by condensing aniline, formaldehyde and a Schiff bases using dioxane as a solvent, at reflux temperature for 15 h and isolated from chilled water filtered, washed well with water and dried at room temperature. Bisbenzoxazines were crystallized four times from dioxane-water system. It is proposed to polymerize bisbenzoxazines via ring opening polymerization.

\[
\begin{align*}
    \text{Where, } & \quad Z = \cdot\text{CH}_2 \cdot, \cdot\text{O} \cdot, \cdot\text{SO}_2 \cdot \\
    \text{IV(Bisbenzoxazines)} & \quad \begin{array}{c}
    \text{Where, } Z = \cdot\text{CH}_2 \cdot, \cdot\text{O} \cdot, \cdot\text{SO}_2 \cdot
\end{array}
\end{align*}
\]
(C) Synthesis of polySchiff bases

PolySchiff bases were synthesized according to following polymerization Schemes V-VII. Resultant polySchiff bases were isolated from water, filtered washed well with water and dried at room temperature. The yields were 90-96%.

Scheme-V

Scheme-VI
CHAPTER 3: CHARACTERIZATION OF POLYMERS

This chapter is further subdivided into four sections:

SECTION-I: SOLUBILITY OF POLYMERS

Solubility of polymers was tested in various organic solvents at room temperature and thermodynamic goodness of the solvents is reported.

SECTION-II: SPECTRAL CHARACTERIZATION OF POLYMERS

Formation of different linkages in the monomers and polymers are supported by IR and NMR spectral data.

SECTION-III: THERMAL ANALYSIS OF POLYSCHIFF BASES

Thermogravimetry can precisely describe the degradation of polymers under varying temperature range and atmosphere. Various kinetic parameters provide usefulness of the potentially unstable nature of materials under investigation. Polymers are characterized by DSC and TGA techniques at 10°C/min heating rate under nitrogen atmosphere. Thermal stability and various kinetic parameters are determined and discussed in this chapter.
CHAPTER 4: ULTRASONIC STUDY OF EPOXY AND BISBENZOXAZINES

Recently ultrasonic has become the subject of extensive research because it finds applications in numerous fields of science like consumer industries, medical fields, engineering, process industries, etc. Knowledge of acoustical properties of solutions furnishes a wealth of information on molecular interactions occurring in the solutions, the nature and the strength of interactions. The density, viscosity and ultrasonic speed measurements of epoxy resins and bisbenzoxazines solutions in different solvents were carried out at 30°, 35° and 40°C. Various acoustical parameters such as isentropic compressibility ($\kappa_s$), specific acoustical impedance ($Z$), Rao’s molar sound function ($R$), Van der waals constant ($b$), internal pressure ($\pi$), classical absorption coefficient ($\alpha/f^2$)$_c$, viscous relaxation time ($\tau$), solvation number ($S_n$), free volume ($V_f$) and intermolecular free length ($L_f$) are determined and discussed in light of effect of solvent, temperature, concentration, etc.

CHAPTER 5: SUMMARY

This chapter describes a brief summary of the work investigated during the tenure of the research programme.

Signature of the guide  Signature of the candidate

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