SYNOPSIS

SYNTHESIS AND CHARACTERIZATION OF SOME COPOLYMERS

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SYNOPSIS OF THE THESIS TO BE SUBMITTED TO SAURASHTRA UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

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GENERAL INTRODUCTION

A summary of the work to be incorporated in the thesis entitled “SYNTHESIS AND CHARACTERIZATION OF SOME COPOLYMERS”

Modern era is polymer era. The end uses of polymers are unlimited. Today polymers have replaced many traditional engineering materials like metal, wood, cement, etc. Polymers are used in various forms such as fibers, films, coating material and various fabricated or molded articles, which exhibit a wide range of properties in terms of strength, rigidity, flexibility, toughness, elasticity, resilience, optical clarity, chemical and solvent resistivity, etc.

Polyether sulfones, polyether ketones, polyether-ether ketones and polysulfonates are well known as engineering plastics and find their usefulness in various fields [1, 2]. Aromatic cardo (Latin meaning a loop) polymers are well known for their excellent solubility, excellent thermo-mechanical and electrical properties and easy processibility [3-6] and hence they are of an industrial importance.

Polyesters are widely used commercially as fibers, plastics, and coatings and other fields [7, 8]. Commercially terephthalate polyesters are well known as engineering thermoplastics due to their good chemical resistance, high thermal and dimensional stability, high strength and rigidity coupled with good surface hardness and gloss [9]. Copoly(ester-sulfonates) possess outstanding balance mechanical properties and excellent hydrolytic stability [10-12].

3. D. J. Liaw, “Synthesis and characterization of sulfones containing polyesters derived from 4,4’-dicarboxydi phenyl sulfones by direct
Summary...


4. S. S. Vibhute, M. D. Joshi, P. P. Wadgaonkar, A. S. Patil, N. N. Maldar,

characterization of new soluble polyesters derived from various cardo

Synthesis and properties of novel poly(arylene thioether)s based on 2,2-

7. X. Han, A. B. Padias, H. K. Hall. “Syntheses of polyarylates by

and properties of aliphatic spirodilactam diphenol containing polyesters”
Polymer, 46(12), 3971-3974, 2005.

9. F. Pilati “Polyesters” in: Comprehensive Polymer Science, 5, G Allen

Chem. Ser. No.91, 70,3,1969; C.A. 72,21,966,1970

11. B. G. Manwar, S. H. Kavthia, P. H. Parsania “Synthesis and physico-
chemical properties of copoly(ester-sulfonates) of 1,1'-bis (3-methyl-4-
hydroxyphenyl) cyclohexane with 2,4-toluene disulfonyl and terephthaloyl

and S. Kaliaguineb “Synthesis and characterization of sulfonated
poly(ether ether ketone) for proton exchange membranes” J. Membr.
The work to be incorporated in the thesis is divided into five chapters:

CHAPTER 1: LITERATURE SURVEY
CHAPTER 2: SYNTHESSES OF MONOMERS AND COPOLYMERS
CHAPTER 3: CHARACTERIZATION OF COPOLYMERS
CHAPTER 4: THERMO-MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLYMERS
CHAPTER 5: SUMMARY

CHAPTER-1: LITERATURE SURVEY
This chapter of the thesis describes the up to date literature survey on syntheses, characterization and applications of bisphenols, acid chlorides, disulfonyl chlorides, polysulfonates, polyesters and copoyester-sulfonates.

CHAPTER-2: SYNTHESSES OF MONOMERS AND COPOLYMERS
This chapter is further subdivided into two sections:

Section-1: Syntheses of monomers

(A) Synthesis of 1, 1'-bis (R-4-hydroxy phenyl) cyclohexane
1-1'-Bis(4-hydroxy phenyl)cyclohexane (BC) and 1-1'-bis(3-methyl-4-hydroxy phenyl)cyclohexane (MeBC) were synthesized by Friedel–Crafts condensation of phenol / o-cresol and cyclohexanone in the presence of HCl: CH₃COOH (2:1 V/V) as a catalyst at 50-55°C for 4h and were repeatedly crystallized from methanol-water system prior to their use.

\[
\text{BC: } R=\text{H} \quad \text{and} \quad \text{MeBC: } R=\text{CH}_3
\]
(B) Synthesis of terephthaloyl chloride / isophthaloyl chloride.

A mixture of terephthalic acid/ isophthalic acid (10 g, 0.06 mole), thionyl chloride (30.52 ml, 0.41 mole) and 1 ml pyridine was refluxed (75-80 °C) for 12 h. The excess of thionyl chloride was distilled off and TC/ITC was crystallized from n-hexane-chloroform system to get fine white, shining crystals.

(C) Synthesis of 4, 4′-diphenyl ether disulfonyle chloride

4,4′-Diphenyl ether disulfonyle chloride (DSDPE) was synthesized by reacting diphenyl ether (0.05 mol), chlorosulfonic acid (1.5 mol) and urea (0.2 mol) as a catalyst with stirring at 50-60°C 4½ h. DSDPE crystallized from chloroform-n-hexane system. The yield and mp were 75% and 122-126°C, respectively.
(D) Synthesis of 4, 4'-diphenyl disulfonyl chloride (DPSC)

\[
\begin{align*}
\text{Cl} & \quad \text{SO} \\
\text{SO} & \quad \text{Cl}
\end{align*}
\]

DPSC

4,4'-Diphenyl disulfonyl chloride (DPSC) was synthesized by reacting diphenyl (0.1 mol) and chlorosulfonic acid (0.7 mol) urea (0.2 mol) as a catalyst with stirring at 50-60°C for 3 hours. DPSC crystallized from the 1,4-dioxane-water system. The yield and mp were 62% and 200-202°C, respectively.

Section-2: Syntheses of copolymers

(A) Syntheses of copolyester-ether-sulfonates

Copolyester ether-sulfonates (CPEES) of varying compositions were synthesized by interfacial polycondensation technique according to following reaction scheme:

\[
\begin{align*}
\text{MeBC} & \quad \text{MeBC} \\
\text{O} & \quad \text{O} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

DSDPE

Copolyester ether-sulfonates (CPEES) were synthesized by reacting MeBC (0.007 mole) with an equimolar amount of TC and DSDPE in chloroform : water (1:2 v/v) system. The reaction was carried out in the presence of NaOH (0.007 mole), CTAB (45-60 mg) and SLS (15-30 mg) at 0-5°C for 4 hours. The copolymers were obtained as white powders with high yields.
CPEES-1 to CPEES-5 was purified from using chloroform-methanol system. Films were cast from 5% chloroform solutions.

(B) Synthesis of copolysulfonate

Copolysulfonate of MeBC, BA and DPSC was synthesized according to the following reaction scheme:

CPMCAD was purified using chloroform-methanol system. Films of CPMCAD were cast from 5% chloroform solution.

(C) Synthesis of copolyestersulfonate

Copolyester-sulfonate of MeBC, DPSC and ITC was synthesized according to the following scheme:
CPMCDI was purified using chloroform-methanol system. CPMCDI films were cast from 5% chloroform solution.

CHAPTER-3: CHARACTERIZATION OF MONOMERS AND COPOLYMERS

This chapter is further subdivided into seven sections:

Section-1: Solubility

Solubility is an interesting aspect of the polymer system, which diminishes with increasing molecular weight of the given polymer in a solvent under consideration. The polymer dissolution is extremely slow process. A special feature of polymer solution is high magnitude of positive excess entropy and large negative deviations from Raoult’s law. Solubility of copolymers was tested in various organic solvents at room temperature and thermodynamic goodness of the solvents is reported.

Section-2: Spectral characterization

The structures of the copolymers are supported by the IR and NMR spectral data.
Section-3: Film preparation

In order to exploit mechanical and electrical properties and hydrolytic stability of the copolymers, tough and transparent films were prepared from concentrated solutions.

Section-4: Density measurements

The densities of copolypolymer films were determined by flotation method at 30°C by using CCl_4- n-hexane system and compared.

Section-5: Viscosity measurements

Viscosity measurements were made in four different solvents: chloroform, 1,2-dichloroethane, tetrahydrofuran and 1,4-dioxane at 30°C. The intrinsic viscosity and Huggin’s constant are determined and are discussed in light of thermodynamic goodness of the solvents.

Section-6: Molecular weight determination

When characterizing polymers, it is important to consider polydispersity index (PDI) as well molecular weight. Polymers can be characterized by a variety of definitions for molecular weight including number average molecular weight ($M_n$), weight average molecular weight ($M_w$), size average molecular weight ($M_z$), or viscosity molecular weight ($M_V$). $M_w$, $M_n$ and PDI of copolymers were determined by gelpermeation chromatography using THF as a solvent and mixed bed styra gel as a column material at 30°C and discussed [13-14].

Section-7: Chemical resistance

Chemical resistance of copolymers was determined against water and 10% each of acids, alkalis and salt at room temperature for varying time interval. The effect of acids, alkalis and salt on hydrolytic attack is discussed.
CHAPTER-4: THERMO-MECHANICAL AND ELECTRICAL PROPERTIES OF POLYMERS

Physico-chemical properties of polymers mainly depend on the molecular architecture. Thermo-mechanical and electrical properties of polymers are of great importance from both scientific and practical point of views. Thermal analysis of polymers is useful in the design and synthesis of new materials to meet specific requirements in polymer technology such as high temperature resistance, synthetic fibers, transportation industries, electrical instruments, etc. On practical side thermal analysis of polymers not only explain the behavior of polymers under conditions of high temperature but also helps in selecting the right kind of materials for the specific uses where high temperatures are encountered. The usage of plastics for mechanical applications offers the parts through design, elimination of finishing operations, simplified assembly, reduced maintenance, weight saving, noise reduction, and freedom from corrosion. The kinetic parameters provide usefulness of the potentially unstable nature of the materials under investigation.

Both DSC (Differential scanning calorimetry) and TGA (Thermo gravimetric analysis) are complementary of each other and the combined analyses provide much information on physico-chemical changes in a system during heating.

This chapter of the thesis is further subdivided into two sections:

Section-1: Thermal analyses of copolymers

Copolymers are analyzed by DSC and TGA at a single heating rate in an N₂ atmosphere. The glass transition temperature, thermal stability and kinetic parameters of the copolymers were determined and discussed in light of molecular structure and copolymer composition.
Section-2: Mechanical and electrical of copolymers

High polymers are well known for their engineering applications as films, fibers, sheets, composites, etc [15]. The use of polymers in engineering as dielectric is becoming increasingly important because dielectric property is a sensitive method of studying polymer structure. The tensile strength, electric strength, dielectric constant and volume resistivity of copolymer films were determined according to standard test methods and compared possible industrial importance of the copolymers is discussed.


CHAPTER 7: SUMMARY

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

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