

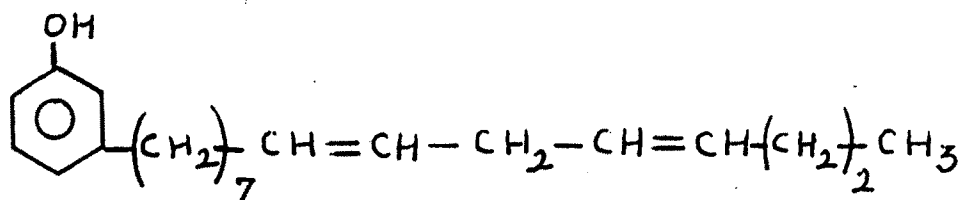
CHAPTER I

INTRODUCTION

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1.1 Cashew Nut Shell Liquid

Cashew nut shell liquid (CNSL) is available as a by product in the cashew processing industry. It is dark brownish black, viscous, vesicant and corrosive liquid. India is one of the major countries of the world producing cashews and CNSL and it is getting good export market. Distillation of commercial CNSL under vacuum gives single phenolic component with an unsaturated side chain in the meta position whose structure is established as below :



The structural features of CNSL, cardanol and its derivatives impart several useful properties to them as a commercially useful intermediates. Manufacture of varnishes and paints, resins, mosquito larvicides, detergents and pesticides, waterproofing materials, adhesives, automobile break linings and plastic components based on CNSL are reported. Azo dyes, rubber chemical, plasticizers, stabilisers, urethanes etc. have been also prepared from cardanol derivatives. Many patents and research articles are available in literature describing CNSL for baking enamels, coating materials,

uv light absorbers and stabilisers for PVC reclaiming agents accelerators and vulcanising agents etc. Thus Cardanol have been utilised for various commercial applications (1).

Polyimides were synthesized from 2-pentadecyl-1, 4-benzene-diamine (derived from cardanol) aromatic dianhydrides (2). These polyimides were sufficiently thermally stable and more flexible films could be cast.

These thermostable polymers derived by polycondensation polyimides, have been the subject of research for many years (3). Aromatic polyimides such as Kapton (Dupont), are used in the aerospace field because they possess high thermal and mechanical properties. However, their high softening temperatures and insolubilities in common organic solvents limit their use. Minimum energy conformation of pyromellitic anhydride - oxyaniline polyimide (Kapton) using molecular mechanics and the quantum chemical method have been performed (4) to probe into structure property relations. We have reported soluble polyimides based on tetraphenylthiophene or CNSL derivatives (2, 5)

McGrath et al reported poly(imide arylene ether sulfone)s from imide containing bisphenol and 4,4- dichlorodiphenyl sulfone (6). Similarly bisphenols containing amide and imide groups were reacted (7) with diaminosilanes giving disilane containing polyamides and polyimides which had rather low inherent viscosity but thermally stable $> 300^{\circ}\text{C}$. Korshak et al have studied the synthesis of copolymer using two different functional groups in

aminoalcohols or aminophenols producing both the ester and imide units linked together in the same repeat unit of polymer termed as poly(ester imide) having increased fire resistance (8).

1.2 Poly(ester imide)s

These wholly aromatic poly(ester-imide)s are an important class of thermally stable polymers (9,10) and they are generally prepared by the direct polycondensation of :

- i] Trimellitic anhydride with a mixture of a diamine and a diol(11).
- ii] A dicarboxylic acid (12) containing preformed imide group(s) with a diol.
- iii] A diphenol containing imide group(s) with diacidchloride (13).
- iv] A dianhydride containing ester group(s) with a diamine (14,15) or a diisocyanate (16) and
- v] A diamine containing ester linkages with a dianhydride (17)

Thus to expand the raw material base of intermediates for heat resistant polymers, bis(hydroxyphenyl) pyromellitimides have been prepared (18) from the reaction of p-aminophenol in DMF with PMDA at the boiling point of solvent. However, these aromatic poly (ester-imide)s suffer from being infusible and insoluble in organic solvents and pose processing difficulties limiting their widespread utility (19). approaches taken to improve upon the processing characteristics of thermally stable polymers include incorporation of flexibilizing linkages, bulky groups, and meta-catenation (20).

Flexibilizing groups such as, oxyethylene (21), sulfone (21), silane (23) etc., have been incorporated conveniently into the polymers via the diisocyanates containing respective functional groups. Korshak et al (24) reported poly(ester-imide) with regular alternation of ester and imide groups, by polymerisation of terephthaloylchloride (TPC) with an imidol prepared from p-aminophenol and pyromellitic dianhydride. However, the resulting polymers were insoluble in organic solvents.

Imidol was also polymerised with bis-phenol A and TPC to give mixed poly(ester-imide) which was soluble in 1:3 phenol: CCl₄ mixture. This class of imidol was also found effective as antidegradent for SKI-3 rubber (25).

1.3 Objectives of Present Investigation

This investigation was undertaken with a view to exploit the use of cardanol in the preparation of aminophenol, imidephenol and polymers there from. Thus present investigation deals with the preparation of novel monomer imide containing bisphenol (II) from 4-amino-3-pentadecyl phenol (derived from CNSL/Cardanol). The monomer (II) has been evaluated in the preparation of heat resistant polyimide esters. Therefore, this modified diols containing imide groups have been polycondensed with diacidchlorides to obtain poly(ester-imide)s, as there is no report on poly(ester-imide) that contain pendant pentadecyl groups. Consequently, in the present studies we describe the synthesis of novel diol containing preformed imide groups viz. N, N1 bis (4-hydroxy-

2-pentadecylphenyl) pyromellitic diimide(II). The polycondensation of this aromatic diol (II) with isophthalic acid chloride (IPC) and terphthalic acid chloride (TPC) to obtain new aromatic poly(ester-imide)s is also reported. The incorporation of preformed imide structure in monomer(II) and then polycondensation to high molecular weight avoided the problem of "off-gas" in final step of imidisation (cyclisation) of amide acid by conventional "two step aromatic polyimide" synthesis.