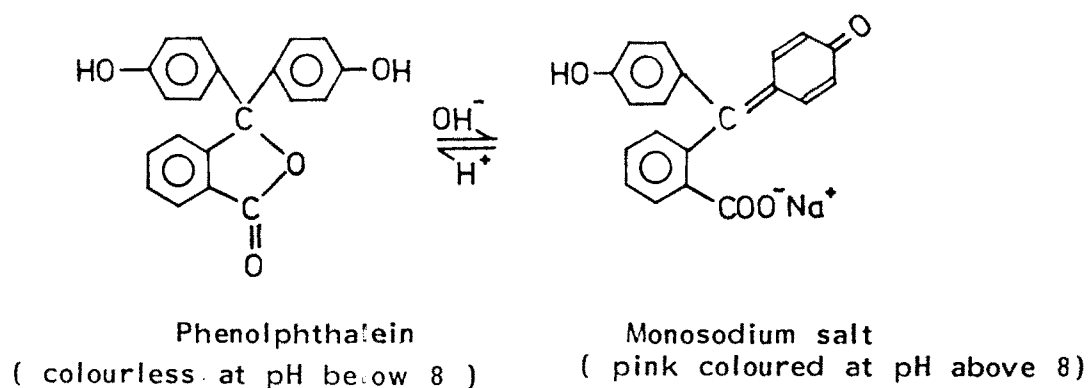


**CHAPTER-I**

**INTRODUCTION**

## INTRODUCTION

1.1 Phenolphthalein and polyarylates : Phenolphthalein was first prepared(1) by Bayer in 1871 by heating phthalic anhydride (1 mole) with phenol (2 moles) in the presence of concentrated sulphuric acid. It is a white crystalline solid, M.P. 260°C., insoluble in water but soluble in alkalies to form deep red solutions. It is used as an indicator in acid-base titrations because it is colourless below pH-8 and pink above pH-8. The pink colour is due to the quinoid structure produced in alkaline medium. However, in excess of alkali, again it becomes colourless due to loss of quinoid structure.



Phenolphthalein is also used as a purgative in medicine. In addition to the acid-base indicator and purgative applications, phenolphthalein plays a very important role in the synthesis of various polymers.

As early as the 1930s, the use of phenolphthalein for the synthesis of polyesters in an American patent was reported (2).

The synthesis of alkyd polymers using fluorescein and phenolphthalein was then published (3). Polymerisation of diallylphenolphthalein dicarbonate (4) and the semiconductive properties of polymers prepared by heating phenolphthalein with  $ZnCl_2$  at 256/306°C (5) as well as epoxy polymers based on phenolphthalein have been reported (6-7). However, a characteristic feature of all these studies is that phenolphthalein was used simply as one of the representatives of the enormous number of diols/bisphenols, without taking into account its specific contribution to the properties of the polymers.

Polyarylates, heterochain polyesters of dihydric phenols, possess film and fibre forming properties. In order to exhibit film forming properties, they must have an intrinsic viscosity at least of the order of 0.4-0.5 dL/g while the value required for fibre formation is approximately 1.0 dL/g. The breaking stress on extension of non-oriented polyarylate films is 600-1000  $kgf\ cm^{-2}$ . The orientation of films in both directions can increase this value to 1500-2000  $kgf\ cm^{-2}$ . A valuable property of polyarylate films is their ability to retain effective mechanical parameters after prolonged heating at elevated temperatures. Polyarylates have effective dielectric parameters, which do not change over a wide temperature range; and are resistant to the prolonged action of inorganic and organic acids (with the exception of sulphuric acid), oxidants and dilute alkalis but are inadequately resistant to the action of concentrated solutions of alkali and ammonia.

The polyarylates of aromatic dicarboxylic acids are characterised by high thermal stability. The polyterephthalates of

2,2'-bis (4-hydroxyphenyl) propane, phenolphthalein, phenolanthrone and phenolfluorene under an inert atmosphere begin to lose mass at 350-360°C. The decrease in the mass of the phenolphthalein-diphenyl-4,4'-dicarboxylic acid polyarylate during isothermal heating in air at 400°C for 1 hr is about 7%. Polyarylates burn but do not support combustion whereas the polyarylates containing chlorine (upto 13%) and phosphorous exhibit an enhanced fire resistance and also a high resistance to the action of ionising radiation.

1.2 Applications of Polyarylates :Polyarylates are worked to produce articles by cast moulding, moulding under pressure, extrusion, vortical sputtering and in case of soluble polyarylates also by employing their solutions (8, 9). It was found that an infusible and insoluble polyarylate such as 'Econol' can be used successfully to produce monolithic articles. These articles possessed high thermal resistance, considerable mechanical strength and good dielectric characteristics at high temperatures.

The combined effect of high heat resistance and effective strength parameters of polyarylates led to the use of these polymers as constructional articles (components for automation and other mechanism). By virtue of their effective insulating properties, they are used successfully in radio engineering and electrical engineering (shells for coils, plugs, disconnecting devices etc.) and in the electronic industry. Heat resistant polyarylate films obtained by extrusion or castings from solution are used as electrically

insulating materials. Polyarylates are also employed for the preparation of varnishes and by virtue of their high solubility and compatibility with various polymers, cardo and other polyarylates are used successfully for the preparation of valuable composite materials.

The introduction of a polyester such as the terephthalic acid-phenolphthalein polyarylate into an epoxide composition leads to the formation of not only strong and lighter materials but also of materials capable of being employed over a wide range of temperatures and loads (10). Filled materials such as antifriction products which have a low coefficient of friction are obtained from polyarylates and they can be employed for a long time without a lubricant at high temperature (250°C) in vacuo and for high velocity gradients between friction surface (sliding and roller bearings). It has been noted that compositions containing polyarylate, polyester imide and a filler are technologically suitable for moulding and the preparation of impact-resistant articles. Impact resistant compositions with improved low temperature properties are obtained from mixtures of polyarylates with poly(alkylene terephthalates) and other polymers. The resulting polymers are used to manufacture motor car components. Electrically conducting transparent polymer compositions have been developed; by the crystallisation in situ of tetraselenatetracene chloride in a polyarylate matrix (10).

1.3 Solubility and thermal characteristics : There are number of factors which increase the heat resistance of linear polymers, viz. introduction of different cycles to the main chain of macromolecules, increasing the intermolecular interaction due to polar groups and hydrogen bonds, introduction of side cycle groups, polymer crystallisation, ordering the structure, use of monomers with a symmetrical structure (for instance terephthalic acid instead of isophthalic acid), formation of chemical cross-links between linear macromolecules, regular arrangement of units in the chain, preparation of stereoregular polymer and so on.

The following factors are mainly responsible for better solubility -

Preparation of amorphous polymers, decrease of the rigidity of the macromolecular chain, introduction of polar groups showing affinity for the solvent, introduction of various substituents containing polar groups showing affinity for the solvent, random position of various units in the backbone and introduction of dissimilar units.

Comparison of the factors increasing heat resistance and solubility shows that some of them improve one property but impair the other (e.g. a decrease in rigidity lowers the heat resistance while increasing the solubility). Most interesting are the factors leading simultaneously to increase in the heat resistance and solubility of polymers. Among these is the introduction of cyclic side groups into the macromolecule. The introduction of such cyclic side groups is very effective if one of the elements

of the cyclic group belongs to the main chain of the macromolecule (that is the cardo group) (Table-I).

Polyarylates derived from phenolphthalein and aromatic dicarboxylic acids were first systematic purposeful investigations in the field of cardo polymers (11,12). In case of cardopolymers, attention was drawn to the specific role of the cardophthalide group in the development of the properties of the heterochain polymers. The unit containing at least one element in the repeating unit that is included in the cyclic side group is called cardo unit from the Latin word 'Cardo'(a loop); whereas the corresponding polymers are called cardo polymers because such cyclic side groups can be regarded as loops in relation to the main chain of the macromolecule. By using phenolphthalein many cardopolymers such as polyesters, polyamides, polyimides, polyethers, polycarbonates, 1, 3, 4 oxadiazoles, heterochain polymers, carbochain polymers and other polymers have been synthesised and the number is growing each year. The introduction of cardo groups in the polymer endows them with some specific properties such as increased thermal stability & effective solubility in organic solvents.

Cardo polymers have high glass transition temperatures which increase with the size of the cardo group. Jackson and Caldwell(13) explain the high glass transition temperature by the fact that the noncoplaner structure of the bulky groups cannot be oriented in one definite direction and consequently, can not move in the close space between the molecule chains. Due to this cardo polymers have higher thermal transitions.

Table-1 : Factors responsible for Physico-Mechanical Properties and Solubility

Sr. No.	Retention of Physico-mechanical properties at elevated temperature	Better solubility
1.	High molecular weight	Oligomers
2.	Use of monomers with symmetrical structures .	Introduction of dissimilar units.
3.	Rigid/Stiff polymer backbone	Decrease in rigidity
4.	<u>Introduction of side cyclics</u>	<u>Introduction of side cyclics</u>
5.	Regular arrangement of units in the chain i.e. ordering	Random positions of various units in the backbone.
6.	Polymer crystallisation	Amorphous Polymer
7.	Increasing the intermolecular interaction due to polar groups and hydrogen bonding	Introduce polar groups in main chain and side substituents showing affinity for the solvent.



It is observed that the polyarylates of phenolphthalein containing phthalide groups are amorphous and non-crystallizing polymers. This is due to the fact that cardo polymers with phthalide groups have randomly placed asymmetrical substituent. However it is believed that under certain conditions the stereoregular placement of the phthalide group can be achieved and this will enable the preparation of a crystalline polymer.

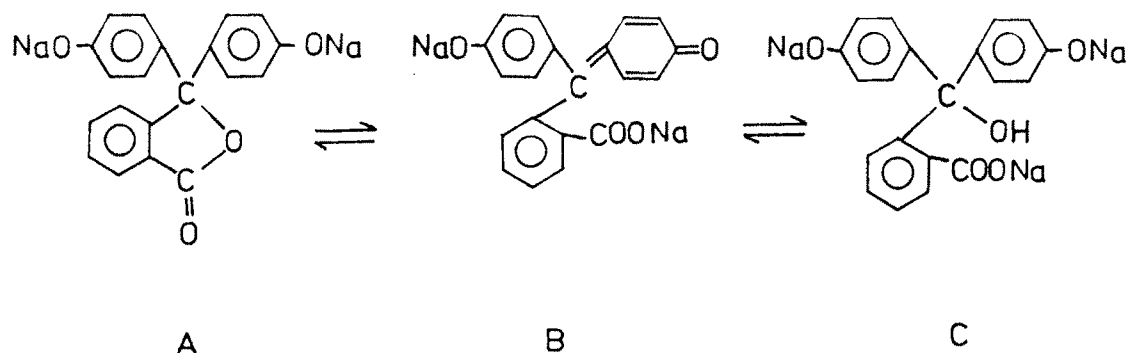
Thus, in terms of their theoretical and practical importance, cardo polyesters as well as other cardopolymers occupy an important place among synthetic high polymers. The solubility of cardo-polyarylates leads to the possibility of their successful conversion from a solution into films and fibrous materials which are used for the purification of gases and liquids and for the trapping of aerosols. Depending on the operating conditions such filter materials can be employed at temperatures upto 300°C.

#### 1.4 Synthetic Methods for Polyesters :

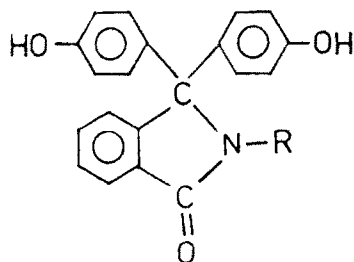
These aromatic cardo polyesters can be prepared by following techniques :-

- a) Interfacial polycondensation
- b) High-temperature solution polymerisation
- c) Low - temperature (acceptor-catalytic) solution polycondensation.

1.4.1 Interfacial polycondensation : It is known that the structure of phenolphthalein in aqueous alkaline solution depends on the base content.



Formation of polyarylates containing no quinone structure by the interfacial polycondensation of phenolphthalein and acid chlorides points to the fact that during the reaction the rearrangement or equilibrium shift between the A and B forms takes place which holds the lactone cycle in phenolphthalein (14,15). As compared to polyarylates of bisphenol obtained by interfacial polycondensation the polyarylates of phenolphthalein are low molecular weights. This is probably due to the slow rates of the rearrangements or equilibria. The presence of cardo bisphenols such as fluorescein or phenolsulfophthalein as a mixture of isomers (in a quinoid or lactone form) hinders the formation of high molecular weight polymers even in a neutral medium. On the other hand the following bisphenols-



i.e. substitution of the NR group (where R = H, EtOH, Ph etc) for the lactone oxygen in phenolphthalein (that is transition from phthalide derivatives to phthalimidine derivatives) leads to compounds which reveal no changes in the alkaline medium associated with the formation of a quinone structure. Therefore, it is possible to synthesize high molecular weight polyarylates from such compounds by interfacial polycondensation under usual conditions.

#### 1.4.2 High-temperature solution polycondensation :

Cardo polyarylates have been synthesised by high-temperature polycondensation of diacid chlorides and bisphenols in organic solvents. The kinetics of the reaction of terephthaloyl chloride with some bisphenols was studied, which suggested ionic mechanism including the formation of an acylium ion (16) for the above mentioned reactions. It was established that the properties of the polyarylate obtained from isophthalic acid and phenolphthalein varied appreciably depending on the nature of the solvent in which the process was carried out (17). In the synthesis of phenolphthalein polyarylates in ditolylmethane, which is not a solvent for the polymer obtained the free energy of formation of the coiled macromolecules should be smaller than the free energy of formation of the uncoiled macromolecules. This results in the formation of globular type of the supermolecular structure of the polymer synthesized in ditolylmethane. On the other hand, for the synthesis of the phenolphthalein polyarylate in 1-chloro-naphthalene or nitro-

benzene which are solvents also, for the polymer formed, uncoiled (extended) macromolecules are formed preferentially. As a result of this fibrillar super molecular structures are formed. The polymers with such supermolecular structure have a better set of physico-chemical properties. Hence to synthesize polymers with rigid chains of macromolecules it is necessary to choose the proper reaction medium with regard to its influence on the formation of one or the other conformation of the macromolecule during synthesis.

In the preparation of crystallizable cardo polyarylates by high temperature polycondensation reaction conditions such as the reaction temperature, the rate of heating and cooling of the reaction mixture and the concentration of the reaction mixture affect not only the molecular weight of the polyarylate but also its structure. It should also be noted that the synthesis of polyarylates by high temperature poly condensation based on bisphenols with functional group numbers greater than three e.g. the imide of the phenolphthalein, results in insoluble cross-linked products because of the reaction of the acid-chloride with the lactam-NH group which occurs at elevated temperatures.

#### 1.4.3 Low-temperature solution polycondensation :

In the last few years the method of low-temperature solution polycondensation which yields high molecular weight polymers under mild conditions, has found ever-increasing applications in the synthesis of cardo polyarylates (18, 19). Mechanism and common reaction parameters such as temperature, type of solvent,

mode of addition of reagents etc. have been studied. It is known that the formation of polyarylates from phenolphthalein and terephthaloyl chloride takes place at a high rate both in dichloroethane, which dissolves the polymer and in acetone, from which the polymer precipitates during its formation. In this case the yield of the polyarylate in the first minute of polycondensation was as much as 95% and the reduced viscosity of 0.5% solution in sym-tetrachloroethane (TCE) is  $\gg 1.0$  dL/g and the yield & the molecular weight depended largely on the order of monomer introduction. The best results may be achieved by the addition of diacid chloride to the solution of phenolphthalein and triethylamine in an organic solvent. The results obtained from the study of formation of polyarylates of phenolphthalein (20) were successfully applied to the synthesis of various polyarylates. In great part this can be attributed to the fact that unlike the interfacial polycondensation in which phenolphthalein behaviour is distinctive, in an acceptor-catalytic polycondensation in non-aqueous solvents it does not change the structure even in the presence of strongly basic tertiary amines. Upto now no method has given crystalline polyarylates of phenolphthalein (20). This is probably due to the asymmetry of the both i.e. phenolphthalein itself and the polymer based on it. However under mild conditions of low temperature solution polycondensation, it was possible to obtain crystalline polyarylates based on bisphenols with symmetric substituents such as 3, 3' dichloro-BPA, because these polyarylates were stereoregular.

In the present investigation, we have followed the technique of the low-temperature solution polycondensation for the synthesis of new cardo polyarylates from phenolphthalein derivatives. We report synthesis, characterisation and properties of novel phenolphthalein derivatives such as 3' or 4'-N-tolyl phthalide of phenolphthalein which are reported for the first time. Polymerisation of these new cardo N-aryl substituted bisphenol monomers derived from phenolphthalein with terephthaloyl chloride has been performed by interfacial and low-temperature solution polycondensation method. Resulting polymers have been characterised by IR, NMR spectra. Solubility, viscosity and thermal properties of these polymers have been investigated and structure-property correlation have been discussed.