


I N T R O D U C T I O N

Since the pioneering researches of H. Staudinger (1920-1930),^{has} the subject of polymer science and technology ~~have~~ been through many spectacular developments along several well identified regions. One of these regions covers work on the theoretical and mechanistic understanding of the polymer system concerned - viewed or reviewed through novel experimental approaches ushering in new ideas and concepts, and reinterpretations of facts in the light of new experimental revelations. A second region of no less importance is concerned with the increasing demand for application oriented research. The realization that a polymer molecule can be tailored in a large variety of ways to various useful end products, has opened up the general field of synthesis and modification of polymers through novel chemical reactions. The key factor in such synthesis is, however, the selection of the appropriate materials used in copolymerization or polycondensation or nuclear substitution reactions. Despite the fact that a mammoth literature already exists in the latter field - new research is warranted to explore the syntheses of more interesting and novel products by choosing monomeric entities with structural novelties and potentialities to result in new polymers with many improved physico-chemical properties. At the same time, availability of a large variety of chemical reactions in organic molecules opens up the possibility of synthesizing chemically modified new polymer systems with outstanding physico-chemical properties.

The present work on the synthesis and chemical modification of polymers with carbazole units in the main chain and as pendant groups attempts to highlight the role of the heterocyclic moiety, carbazole, in the manifestation of improved properties such as thermal, electrical, photoconductive etc. in the resultant polymers relative to the polymer systems containing conventional aromatic moieties.

In order to grasp the significance of the work thus accomplished, it is necessary to keep abreast of the present developments in the related field. Accordingly, section 1.I of this chapter presents an upto date resume of the developments in the synthesis, chemical modification and characterization of the carbazole based polymer systems. Section 1.II gives a general account of the classification, syntheses and properties of polyarylates, polyimides and polyazo-compounds based on aromatic and heterocyclic ring systems. Section 1.III presents some general aspects of chemical modification of polymers, and section 1.IV highlights some general aspects of the synthetic cation-exchange resins through chemical modification of polymers and their characterization. Finally, in the light of all these informations, the object and scope of the present research work have been highlighted in section 1.V of this chapter.



SECTION 1.1 : A REVIEW OF THE SIGNIFICANT DEVELOPMENTS
IN THE SYNTHESIS, CHEMICAL MODIFICATION
AND CHARACTERIZATION OF CARBAZOLE BASED
POLYMER SYSTEMS

During recent years, some attention appears to have been drawn to the syntheses of a few interesting polymers including carbazole units in the main chain or as pendant groups. This review attempts to highlight the available literature in this field. In the preparation of this review, emphasis has been given mainly to focus the synthetic approaches and the property evaluations in outline and to identify the domains which call for more concerted research involving the field of carbazole based polymer systems.

The review to be presented in the following pages forms the subject of a recent article by the author being published in 'Polymer', England(1982).

SECTION 1.II : RECENT DEVELOPMENTS IN POLYARYLATES,
POLYIMIDES AND POLY-AZO-COMPOUNDS BASED
ON AROMATIC AND HETEROCYCLIC RING SYSTEMS

The survey of the carbazole based polymer systems as described in Section 1.I reveals that no significant effort has been put to search over the possibility of introducing carbazole ring systems in the syntheses of polyarylates, polyimides and poly-azo compounds, whose applications are of paramount importance in the various branches of engineering viz. aviation, cosmonautics, electronics, solid-state, thermal resisting processes etc. The scientific weightage of these ideas ^{can be} adjudged properly only after having a thorough appraisal of the more important major developments in these particular synthetic polymer systems, which is therefore attempted in the present context. X

POLYARYLATES

Polyarylates are conventionally known as polyesters from diphenols and dicarboxylic acids. They are aromatic or partial aromatic polyesters. When ^{with} aliphatic dicarboxylic acids such as succinic acid or adipic acid, mixed aromatic-aliphatic polyesters are obtained with low glass transition temperature ; however, a higher glass transition temperature is achieved with purely aromatic polyesters prepared from terephthalic, isophthalic or a similar acids. This subsection is mainly concerned with the polyesters of purely aromatic nature. X

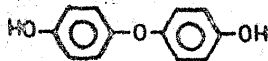
The literature on polyarylates based on aromatic dicarboxylic acids is substantial. In a book by Korshak and Vinogradova¹ on polyesters about 80 pages have been devoted to polyarylates. In another book by Korshak², 140 different formulae of polyarylates are listed and described citing 279 references, 110 of them having been originated from Korshak's laboratory. In addition, the reports by Conix³, Levine and Temin⁴, Morgan^{5,6}, Eareckson⁷ and Weyland et al.⁸ on polyarylates should also be mentioned. From the patent literature it can be seen that in the western world many companies have been actively engaged in polyarylates research. In 1970, Carborundum⁹ marketed a poly(p-hydroxybenzoate) under the name 'Ekonol (R)'.

Some conventional diphenols¹⁰ which are used for the syntheses of polyarylates, are (1-4) and some of the numerous diphenols with a more complicated structure, particularly studied by Korshak et al.¹¹, are (5-9). Bier¹⁰ mostly worked with diphenols of simple structure such as (4) (bisphenol A, dian) which along with its chlorinated products such as dichloro-dian(10) and tetrachloro-dian(11), and with the dihydroxytetraphenylethane(12) are produced in large quantities by several companies.

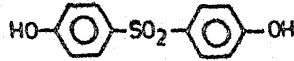
As reported by earlier workers¹⁰, among the aromatic dicarboxylic acids employed for the preparation of linear aromatic polyesters, terephthalic and isophthalic acids are most important, especially their derivatives such as the acid chlorides or diphenylesters of the acids.



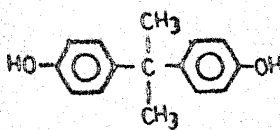
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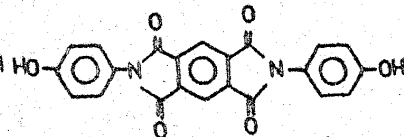
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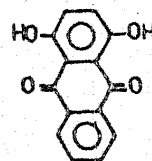
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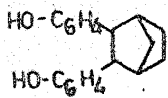
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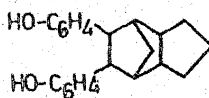
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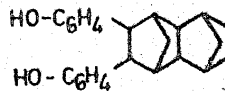
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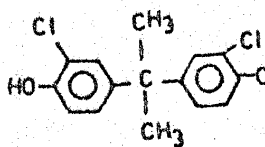
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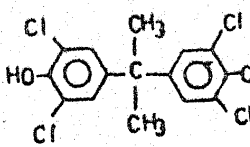
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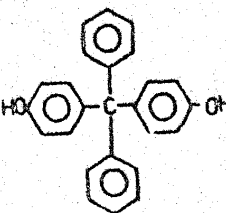
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In general, there are two chemical routes¹⁰ for producing the polyarylates. One route goes through the reactive acid chlorides and the other goes through special re-esterification reactions.

Acid chloride route

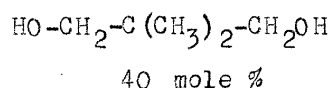
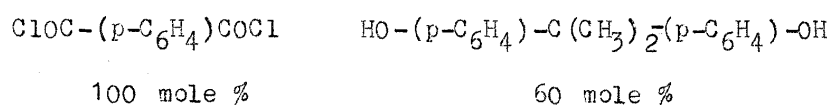
It is the mostly applicable route for the syntheses of polyarylates and employed through the reaction of the chlorides of the dicarboxylic acids with the diphenols. Most of the numerous polyarylates produced by Korshak have been prepared by this technique. In this route, the reaction can be performed by three different processes.¹⁰

Interfacial polycondensation : This is a two-phase process and performed at room temperature. The technique has been described by Morgan¹² and Korshak et al.¹³⁻¹⁵ with the use of acid chlorides and diphenols as reactants. The interfacial polycondensation method has been realized on a commercial scale by Bayer AG¹⁰ in the production of polyarylates.

Solution polycondensation : (a). At normal temperature^{10,16} — this process requires stoichiometric or superstoichiometric amounts of HCl acceptors^{10,16} such as pyridine or triethylamine. The advantage of this process is that the low boiling solvents such as chloroform, methylene chloride etc. and normal pressure can be applied. It, however, results in high molecular weights of the polyarylates but it is difficult to obtain products with good colour after processing, (b) At high temperatures¹⁰ — the process is carried out in the presence of catalysts¹⁰ such as

amines or metallic magnesium. In this process, it is necessary either to use solvents of high boiling points or to work under pressure with solvents having low boiling points.

Melt polycondensation : Gouinlock et al.¹⁷ did some trials by the interfacial method in a batch equipment and by the melt method in an extruder and condensed¹⁶ the following products :

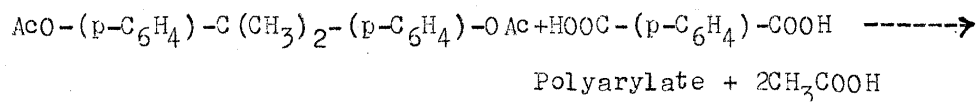


The neopentene glycol reduces the melt viscosity. In the melt process, first a prepolymer was made in a batch reactor, which was then fed ^{to} an extruder for finishing the condensation. Significant differences of properties between the interfacial and melt polyarylates were observed¹⁷. In fact, with high degree of condensation, there has been a problem of high viscosity and the additional problem of having a reactor surface stable against the combined attack of hydrogen chloride generated in the reaction and the phenolic groups at high temperatures.

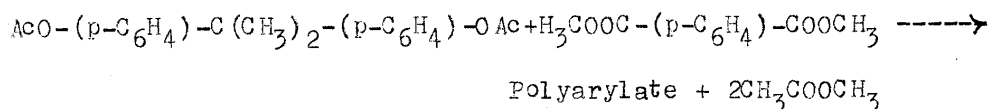
Re-esterification routes

The following routes are described in the literature¹⁰ :

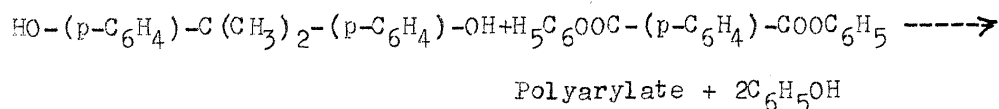
(a) ester of diphenol + acid



(b) ester of diphenol + ester of dicarboxylic acid

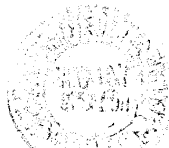


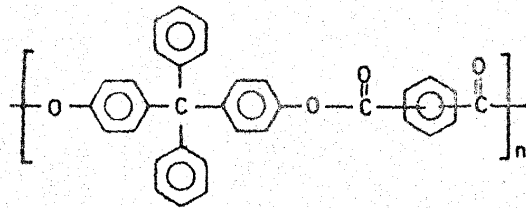
(c) diphenol + diphenylester of dicarboxylic acid



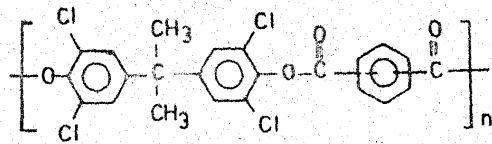
The equation (a) has been described by Levine and Temin⁴. Only a little is known about the equation (b) for producing polyarylates. The ester exchange process via the diphenyl ester of the aromatic dicarboxylic acid can be performed easily [equation(c)]⁷. This process is known from the polycarbonate synthesis¹⁸ on the basis of bisphenol A. A remarkable aspect of the process (c) is that approximately the same weight quantity of phenol has to split off, as bisphenol A is needed. Notably, the reaction of the ester exchange via diphenyl ester cannot be applied¹⁸ to all diphenols, e.g. not to the tetrachloro-dian. It is likely that in this case, the hydroxy groups are sterically blocked¹⁸ so that a reaction with the phenyl-ester cannot take place.

Some commercially important polyarylates (PAE-B, PAE-I and PAE-W) prepared by the company 'Dynamit Nobel' have been described by Bier¹⁰. The products PAE-B and PAE-I have been prepared by the high temperature solution polycondensation method via the acid chloride route. The polyarylate PAE-W has been prepared by the melt-polycondensation of the bisphenol A with the diphenyl-ester of the aromatic dicarboxylic acids. These three polyarylates are

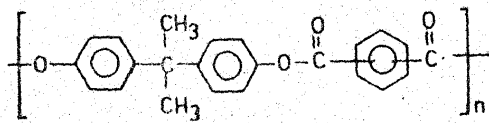




PAE-B*



PAE-I†



PAE W‡

* PAE-B = Polyarylester-Behr, E., Dynamit Nobel.

† PAE I = Polyarylester-Ismail, R., Organ.-Chem. Institut der Universität Bpnn, 53 Bonn, Mackenheimer Allee 168.

‡ PAE W = Polyarylester-Wolfes, W., Dynamit Nobel.

amorphous in nature and ~~have the~~ ^{possess} mouldabilities. The polyarylates ~~are~~ ^{are} more or less soluble or capable of swelling in a series of solvents, halogenated hydrocarbons, esters, ketones, epoxides. In contact with some solvents they also show stress crazing.

Cardo Polyarylates

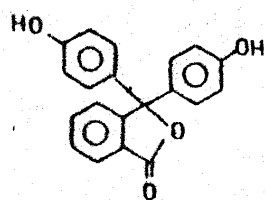
In a review by Korshak et al.¹⁹, a series of polyarylates based on cardo monomers in which either diphenols or diacid chlorides or both possess cardo groups, have been described.

Some common cardo diphenols and cardo diacid chlorides employed by some groups¹⁹ of investigators for the preparation of polyarylates, are (13-18). The methods of preparation of polyarylates described earlier are also applicable for obtaining cardo polyarylates. As is reported¹⁹, most of the cardo polyarylates have been synthesized by high temperature solution polycondensation of diacid chlorides and diphenols in organic solvents. The kinetics of the reaction of terephthaloyl chloride with 9,9-bis(4'-hydroxyphenyl)fluorene (14) and some diphenols of the norbornane type have been studied, which is claimed to run by an ionic mechanism including the formation of an acylium-ion.^{20,21} The synthesis of the cardo polyarylates has been carried out in ditolylmethane^{22,23}, sovol²⁴⁻³⁰ (a mixture of tetra- and penta-chloro diphenyls), α -chloronaphthalene³¹, o-dichlorobenzene³¹, 1,2,4-trichlorobenzene³¹, nitrobenzene³¹, and others at a monomer concentration of 0.6 to 5 moles/liter at 180 - 220°C for several hours. Interestingly, the polycondensation of phenolphthalein and

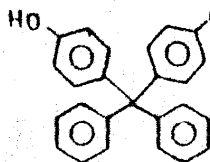
aromatic diacid in ditolymethane leads to a precipitation¹⁹ of polyarylate from the reaction mixture as a thick, poorly soluble bulk. The polyarylates, obtained in this method exhibit good physico-mechanical properties^{24,25,31}, due to the fact that in the synthesis of polyarylates, there is predominant formation of unfolded rigid conformation of macromolecules, which gives rise to fibrillar structures; however, the polymers are composed from not very regular globula of $\geq 1000 \text{ \AA}$ in size. It is responsible for the brittle fracture of such amorphous polyarylates and explains the high impact strength of the polyarylates. Moreover, in the preparation of crystallizable cardo polyarylates^{32,33}, particularly a polyarylate of 9,9-bis(4'-hydroxyphenyl) anthrone-10 (15) and terephthalic acid, the 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 the molecular weight as well as structure of the polyarylate.

Heterocyclic Polyarylates

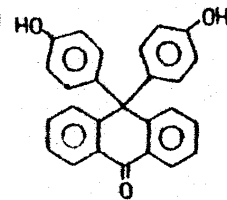
Wilfong³⁴, Drewitt et al.³⁵ and a group of Japanese workers³⁶ reported a series of polyarylates based on heterocyclic monomers, diphenols and dicarboxylic acids containing heterocyclic rings. Some important heterocyclic monomers which have been reported by the same authors for the preparation of commercially useful polyarylates, are (19-23). Recently, Steffen³⁷ reported thermally stable silicone-polyarylates based on heterocyclic diphenols such as 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole. These polyarylates are found³⁷ to possess considerably high glass-transition temperatures.



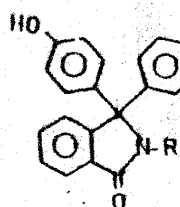
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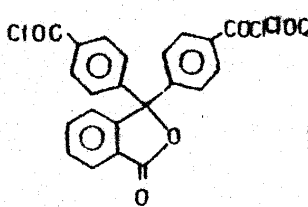
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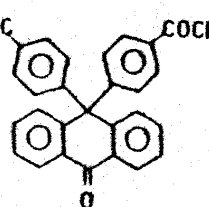
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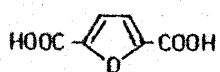


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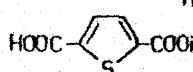


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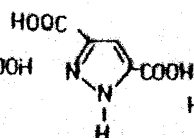
R=H, C₆H₅, HOCH₂CH₂



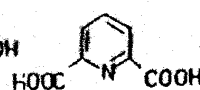
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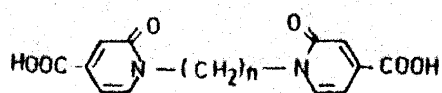
(20)



(21)



(22)



n = 2-10

(23)

POLYIMIDES

The years since 1960 have seen the development of a number of new polymers for which the emphasis has been upon superior thermal stability. Among the known thermally stable polymeric materials, the imide-ring containing polymer systems have occupied³⁸ an outstanding position in the high-temperature performing materials. In this subsection, a general survey of polyimides especially based on aromatic and heterocyclic rings will be discussed.

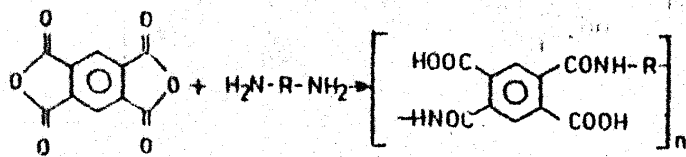
Aromatic Polyimides

The advent of aromatic polyimides with their high level of thermooxidative stability has initiated a surge of research to improve upon the already existing thermal properties of the polyimides reported in the beginning of the last two decades or so. This is more than justified in view of the modern needs of improved polymers for spacecraft and missile thermal protecting materials.

Extensive reports are available on aromatic polyimides³⁸⁻⁴⁵ derived from the pyromellitic dianhydride (PMDA) and various aromatic diamines. Earlier workers⁴⁶⁻⁴⁸ in this field prepared polyimides by polyamide-salt techniques. Thus PMDA was reacted with ethanol to form the diester-diacid, which was treated with diamine to precipitate the monomeric diester-diacid salt. The salt was then heated to form a polymerizing melt, which, on dehydration and dealcoholation in the melt, formed the polyimide.

In 1960, du Pont company^{42,44} disclosed a novel synthetic route for the preparation of polyimides, which was cited by many polyimide researchers in the subsequent literature^{38,41,45,49-52}. Sroog^{38,40} reported such synthetic routes for the polyimides from PMDA and various aromatic diamines, and applications of the polyimides related to their thermal, mechanical and electrical properties. Formation of polyimides (poly-pyromellitimides) by direct polymerization of PMDA and aromatic diamines in solvents such as dimethylacetamide or dimethylformamide to soluble poly(amic acids) of high molecular weight and subsequent dehydration is illustrated in Scheme 1.II.1.^{41,42}

Chudina et al.⁵³ and more recently, Ghatge et al.⁵⁴ reported the syntheses of aromatic polyimides from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and conventional aromatic diamines. They also reported the thermal properties of these polyimides and particularly, Ghatge et al.⁵⁴ studied their electrical properties in view of the structural characteristics related to the various diamines. Imai et al.⁵⁵ reported the syntheses of the polypyromellitimides from a novel dianhydride system, pyromellitic dithioanhydride and conventional diamines. A critical study on the aromatic polyimides synthesized from various diisocyanates has been extensively made by Naoya⁵⁶, Meyers⁵⁷, Carleton et al.⁵⁸ and Ghatge et al.⁵⁹ They proposed the mechanism of formation of aromatic diisocyanate based polyimides in presence of polar solvents such as tertiary amine as catalyst and concluded⁵⁶⁻⁵⁹ the existence of unusual seven membered ring intermediate in the total synthesis.

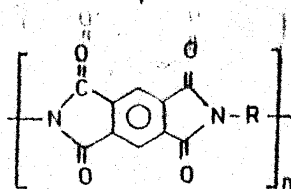


PMDA

Diamines

Poly(amic acids)

$(-2\text{H}_2\text{O})_n$



Polyimides

R = p-Phenylene ; m-phenylene ; p, p'-diphenylene ;
 4, 4'-diphenyl ether/sulphide/sulphone/methylene/
 isopropylidene.

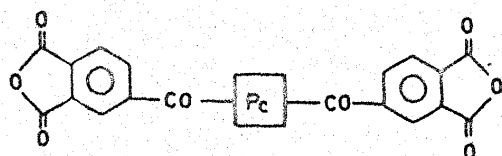
SCHEME 1. II.1



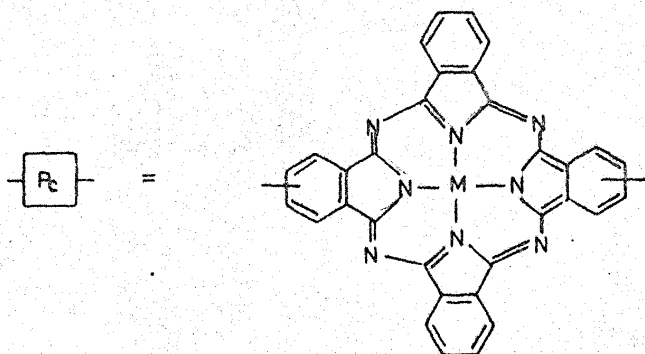
A Russian group⁶⁰ reported a new class of aromatic polyimides from bis(3,4-dicarboxyphenyl)phenylphosphine oxide dianhydride, which reportedly exhibit good dielectric properties. A series of novel aromatic polyimides containing metal \square Co(II), Ni(II) and Cu(II) \square -phthalocyanine rings has been reported by Shirai et al.⁶¹ following the standard synthetic route of Sroog^{42,44} (du Pont) involving solution condensation in N-methyl-2-pyrrolidone of metal (II)- \square 2,9 or 10 (or 2,16 or 17) bis(3,4-dicarboxybenzyl) \square -7 phthalocyanine dianhydride (24) with aromatic diamines such as 4,4'-methylene bis(aniline), followed by thermal imidization.

In general, polyimides are considered⁶² to be an amorphous class of polymers. However, a few crystalline aromatic polyimides have been reported by three groups^{42,63,64}. Clair et al.^{62,65} reported the syntheses of linear aromatic polyimides from a novel dianhydride of 4,4'-bis(3,4-dicarboxyphenoxy) diphenyl sulphide and conventional aromatic diamines such as p-phenylene diamine and benzidine. These polymers have been reported⁶² to exhibit a high degree of crystallinity particularly with p-phenylenediamine.

As is evident from earlier discussion, the investigations on the aromatic polyimides have dealt almost exclusively with five-membered imide ring systems, including heat-resistant polypyromellitimides. More recently, Ueda et al.⁶⁶ reported the syntheses of novel aromatic polyimides with six-membered imide rings through polycondensation of a six-membered tetracarboxylic dianhydride, 2,5-di(carboxymethyl)terephthalic dianhydride,



(24)



$M = Co(II), Ni(II), Cu(II)$

prepared from pyromellitic dianhydride with aromatic diamines and compared⁶⁶ their properties with conventional polypyromellitimides.

Bell⁶⁷ extensively studied the effects of stereoisomeric variations in aromatic polyimide structures on the properties of polyimides. The polymerizability of aromatic diamines of the $H_2N-Ar-R-Ar-NH_2$ type with aromatic dianhydrides to high molecular weight poly(amic acids) has been related to the basicities (and therefore, reactivities) of the amino groups. Even diamines containing an amine group at a position ortho to the R group connecting the phenyl rings have been successfully polymerized to high molecular weight polymers for which the R groups are not of an amine-deactivating type. Of all the aromatic polyimides prepared from a family of stereoisomeric diamines differing with each other only in the positions of attachment of the amine groups, those synthesized from the para oriented diamines have the highest glass transition temperatures (T_g). The use of m-diamines has been effective for producing polyimides with markedly lower T_g values than those from p-diamines. However, except for several very specific cases, the polyimides prepared from o-diamines have T_g as high as those from the p-diamines. These isomeric effects of structural changes upon polymer properties are observed to be general for all classes of aromatic diamines. However, the polyimides prepared from the diamino-diphenylmethanes require special care in drawing conclusions

about their structure-property relationships due to susceptibility of the methylene moiety to oxidation and crosslinking under the thermal conditions needed for complete imidization. The polyimides prepared from isomeric diaminobenzophenones are more thermooxidatively stable, as a class, than those polymers prepared from the diaminodiphenylmethanes. While there is little difference in stability between isomeric polyimides from the diaminobenzophenones, marked differences between the various polyimides prepared from diamines of the diphenylmethane series are observed.

Cardo Polyimides

Korshak et al.¹⁹, in a recent review, described the synthetic developments of 38 cardo polyimides in which either diamines or dianhydrides contain cardo groups, and their structure-property relationships.

In the series of cardo polyimides¹⁹, cardo polypyromellitimides of anilinephthalein and anilinephthalimidine are the first soluble compounds among those extremely heat-resistant cardo polyimides.^{68,69} As with other polyimides described earlier, they can be synthesized by a two-stage process with thermal cyclodehydration of the previously prepared poly(amic acids).^{68,69} Korshak et al.⁷⁰⁻⁷² also suggested that the one-step high temperature polycyclization in an organic solvent (nitrobenzene, benzonitrile, 1-chloronaphthalene, sulpholane, cresol and others) is a better method for the preparation of high molecular weight soluble cardo polyimides. It is also suggested⁷¹⁻⁷³ that the formation of

cardo polyimides from dianhydrides and diamines is an equilibrium process. Therefore, to prepare high molecular weight polyimides, the water isolated in cyclization should be removed⁷¹⁻⁷³ from the reaction mixture as fully as possible. Cardo polyimide can also be successfully prepared^{74,75} by the two-stage polycyclization of tetraacid dichloride diesters and primary amines. The cyclization of intermediates, poly(amic esters) [hydrolytically stable derivatives of poly(amic acids)]₇, leads to the formation of cardo polyimides with higher molecular weights than those obtained by cyclodehydration of the corresponding poly(amic acids). In general, cardo polyimides are classified^{76,77} according to the effect of substituted groups on heat resistance. The polyimides of PMDA and naphthalenetetracarboxylic dianhydride are characterized by the highest heat resistance.

Significantly, cardo polyimides are found^{71,76} to exhibit high thermal stability as compared to the conventional aromatic polyimides. It is explained⁷⁸ by the fact that the thermal stability of cardo polyimides depends to a greater extent on the cardo groups which produce rigidity in the overall macromolecules due to hindered rotation around the main chain bond and thus restrict the mobility of the polymeric segments. These polyimides are stable^{79,80} to acidolysis and exchange reactions at the imide cycle, but decompose^{79,80} under the action of amines and other bases.

Heterocyclic Polyimides

Most of the polyimides known at present have been obtained from purely aromatic monomers (dianhydrides and diamines); however, in recent years polyimides based on heterocyclic monomers have received considerable attention. More recently, Rusanov and Batirov⁸¹ published a review on polyimides based on heterocyclic monomers including 189 references.

The great variety of the known heterocycles leads to the possibility of formulating completely different projects designed to modify the properties of polyimides in the following way⁸¹ :

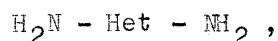
1. The introduction of highly condensed heterocyclic fragments permits an increase in the thermal stability and heat resistance of the polyimides.

2. The introduction of heterocycles containing bulky side groups makes the polyimides soluble in organic solvents^{19,82-84}.

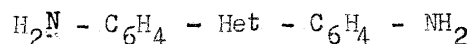
3. The inclusion of heterocyclic rings in the polyimides increases considerably the hydrolytic stability of the polymers.

In general, heterocycles can be introduced⁸⁵⁻⁹¹ into the polyimides by employing monomers containing the required heterocycles and also monomers containing groups capable of cyclizing to the required heterocyclic system. The former system has significant advantage^{85,86} over the latter as because of imidization processes, which proceeds under milder conditions than the processes leading to the formation of required heterocyclic systems.

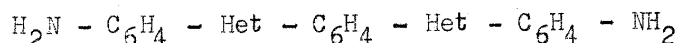
The simplest diamines containing azole rings are of the type -



some of which (Het = 1,3,4-oxadiazole, 1,2,4-triazole, 1,3,4-thiadiazole, etc.) have attracted the attention of the investigators^{92,93} because of the possibility of synthesizing from them (by reaction with the dianhydride of pyrazine-2,3,5,6-tetracarboxylic acid) polyimides without free hydrogen atoms and possessing as a result an increased thermal stability.⁹⁴⁻⁹⁶ More unambiguous results are obtained by using azole-containing diamines of the type -



In the series of compounds of this kind, the isomeric 2,5-(diaminophenyl)-1,3,4-oxadiazoles⁹⁷⁻¹⁰⁴ and 3,5-(diaminophenyl)-4-phenyl-1,3,4-triazoles^{98-102,104} are the most common diamines used for the preparation of polyimides. Three groups¹⁰⁵⁻¹⁰⁷ reported the syntheses of polyimides from diamines containing 1,3,4-oxadiazole and thiazole rings of general formula -



Het = 2,5-(1,3,4-oxadiazole)- ; 2,4-(thiazole)-

A series of polyimides have been reported^{85,105,108-113} through reactions with diamines containing three types of the most common benzazole rings—benzoxazole, benzimidazole and benzothiazole. The polymers are found to exhibit high melting point (260 - 570°C) and high temperatures for the onset of degradation in the range 560 - 595°C.

Korshak et al.¹¹⁴ recently reported the syntheses of polyimides based on symmetrical diamines containing N-phenyl-benzimidazole rings using dianhydrides of aromatic tetracarboxylic acids under the conditions of one- and two-stage polycondensation.¹¹⁵⁻¹¹⁷ An unambiguous influence of the introduction of a bulky substituent into the diamine molecules on the solubility of polyimides has been also explored by Korshak et al.^{118,119} by synthesizing the polyimides from diamines containing substituted quinoxaline rings. Furthermore, the polyimides containing quinazolinone ring systems reported by Wolf et al.^{120,121} are found to exhibit excellent thermal, electrical and mechanical properties, and are useful in electrical insulation applications. Some group of workers^{92,93,122,123} also reported the syntheses of polyimides based on diamines containing symmetrical triazine rings, but the thermal stability of these systems are not found to be much attractive.

The structural set of dianhydrides of heterocyclic tetracarboxylic acids, used to synthesize polyimides, is much smaller than the set of heterocyclic diamines discussed earlier. In the series of dianhydrides of the tetracarboxylic acids derived from the simplest heterocycles, the dianhydrides of furan-2,3,4,5-tetracarboxylic¹²⁴ and thiophen-2,3,4,5-tetracarboxylic acids¹²⁴⁻¹²⁷ received attentions; however, the properties of the polyimides based on these monomers have not been studied in detail. In the series ofazole-containing dianhydrides of tetracarboxylic acids, only 1,3,4-oxadiazole

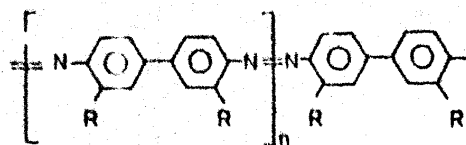
containing compounds^{101,128,129} and in the series of benzazole-containing dianhydrides¹³⁰⁻¹³², the benzoxazole, benzimidazole and benzthiazole containing compounds have been widely used for the preparation of polyimides.

Besides incorporation of five-membered heterocycles in the polyimides so far discussed, the dianhydrides of heterocyclic tetracarboxylic acids containing six-membered heterocycles, e.g., pyridine-2,3,5,6-tetracarboxylic^{124,133} and pyrazine-2,3,5,6-tetracarboxylic dianhydrides, have received^{92-96,124,125,134-141} considerable attention of many investigators in the polyimides syntheses.

POLYAZO-COMPOUNDS

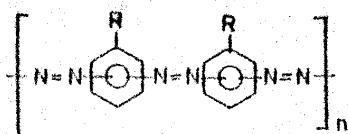
Polymers incorporating the azo groups, -N=N-, in the main chain have been of particular interest¹⁴² in recent years because of their significant semiconducting and photoconducting properties and capability of producing different colour shades over the various polymeric materials.

Berlin et al.¹⁴²⁻¹⁴⁵ reported the syntheses and properties of various polyphenylazo-compounds (25). The polymers are found to exhibit excellent semiconducting properties. Sandholm et al.¹⁴⁶ synthesized three semiconducting polyazophenylenes (26), viz. poly(2,5-diaminotoluene), poly(2,4-diaminotoluene) and poly(2,4-diaminoanisole), by oxidative coupling. Löfgren et al.¹⁴⁷⁻¹⁵⁰ extended the investigation over these polyazophenylenes by studying their electrical conductivity and dielectric properties. Recently, Stöcker et al.¹⁵¹ reported 11 poly(azo-amides) (pigments) (27). These pigments have been used¹⁵¹ for colouring



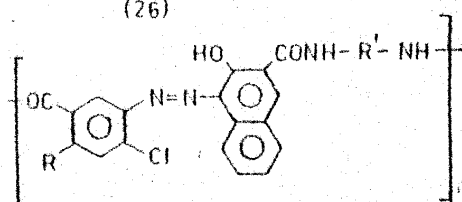
(25)

R = H, COOH, CH₃, SO₃H.



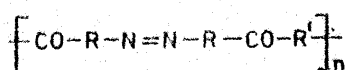
(26)

R = CH₃⁻, CH₃O⁻



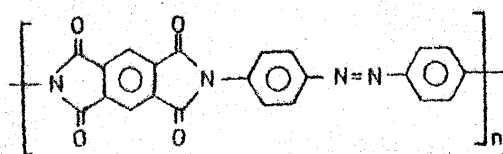
(27)

R = H, Cl; R' = Substituted 1,4-phenylene, 4,4'-diphenylene, 1,5-naphthylene.



(28)

R = m-, p-C₆H₄; R' = 1,6-diaminohexane, piperazine, trans-2,5-dimethylpiperazine



poly(vinyl chloride), poly(propylene) and stoving enamel fast red to brown shades. Riordam and Blair¹⁵² further extended the investigation over poly(azo-amide) systems by synthesizing 6 similar polyazo-compounds (28).

To achieve significant electrical, thermal and mechanical properties through the polyazo-compounds, Bach and Hinderer^{153,154} incorporated imide rings in the polyazo-systems by synthesizing poly(azo-imides) (29) through polycondensation of various diamines such as azodiphenylamine, azodiphenylamine dimer, 4,4'-bis(4-aminophenylazo)benzene with PMDA. The film and fiber of these polymer systems show good insulation properties¹⁵³ and exhibit high modulus¹⁵³ and high heat-resistivity¹⁵⁴.

Recently, Hirohashi¹⁵⁵ reported the syntheses of some heterocyclic ring based novel polyazo-compounds, e.g. poly(azopyrimidines), and their electrical and photoconductive properties. The electrical conductivity of these polyazo-systems was exhaustively studied¹⁵⁵ by making their charge-transfer complexes with acceptor, iodine.

SECTION 1.III : SOME GENERAL ASPECTS OF THE CHEMICAL
MODIFICATION OF POLYMERS

The developments in the field of chemical modification of polymers based on pendant carbazole units have been specifically reviewed in the Section 1.I. However, there is considerable influence of some important structural characteristics of polymers, such as tacticity, morphology, functionality etc. — on the chemical modifications involving reactions such as the addition or substitution of functional groups in the backbone or pendant systems of the polymers. The chemical modifications are generally governed by the chemical reactivity of the polymer systems, which depends on the structure of the polymer and the functional groups attached to them. The present section, therefore, intends to highlight some of the salient aspects in this context.

Structure of Polymers

Polymers consist of a large number of monomer units. If the monomer originally contains reactive groups which are not involved in the formation of polymers, these groups would still be found in repeating units of the polymer chain. They are still reactive in their own ways and so the polymer would be capable of undergoing further reactions.

For polymers which are chemically identical but differ in physical structure, the reactivity is expected to be different. This is considered as the effect of morphology on reactivity,

which is attributed to steric hindrance. This morphological effect on reactivity is more frequent and pronounced in linear high polymers, e.g. cellulose¹⁵⁶⁻¹⁵⁸, polyethylene terephthalate,^{159,160} polyethylene^{161,162}. In addition to this aspect, morphology of polymers includes factors of fine structure such as fibrils and micelles, accessible and non-accessible regions, amorphous and crystalline areas, and other supramolecular agglomerations. These factors can exist only when the polymer is in the solid state and so the effect of morphology on the reactivity of polymers is restricted to heterogeneous systems. Reactivity is, therefore, the ability of the polymer chain to react with other molecules, while accessibility defines the ease by which the reactant molecules can reach to the functional groups of the polymer molecule.

Reactivity of Functional Groups of Polymers

The functional groups of a polymer molecule retain their own individual reactivities. When a polymer molecule contains functional groups, it undergoes the usual reactions such as esterification, etherification, saponification applicable to organic compounds. These chemical transformation reactions seldom proceed with a quantitative yield on account of the changes of solubility and consequently changes in the accessibility of the functional groups when the degree of conversion increases. Thus, a reaction product usually contains untransformed groups as well as structural units resulting from the interactions of neighbouring groups, all together in one macromolecule.

The organic reactions of high polymers usually depend on functionality of the groups in the polymer, internal structure (isomerism and stereoisomerism) of the polymer and the location of reaction sites in the polymer.

Monofunctional Chemical Reactions

In this type of reactions, only one functional group is involved in the modification of the polymer. Monofunctional polymeric reactions proceed usually through the same mechanism as reactions on similar low molecular weight compounds. The methylation of poly(acrylic acid) with diazomethane, the acetylation of poly(vinyl alcohol) with acetic anhydride, the reduction of poly(methylacrylate) with lithium aluminum hydride, the acidolysis of poly(N-vinyl-tert-butyl methane) with hydrobromic acid are some of the examples of monofunctional chemical reactions of polymers¹⁶³⁻¹⁶⁵. The transformation of a polymeric substance into its derivatives having completely different solubilities, but with unchanged degree of polymerization is considered as the final proof of the macromolecular structure of these substances.

Polyfunctional Chemical Reactions

Polymers containing more than one functional groups in the polymer chain undergo various types of reactions resulting into useful products. When two or more functional groups are affected by a chemical reaction, the relative positions of the reactive groups play an important role in the final degree of conversion. The chemical transformation is influenced by the arrangements of

the monomer units in the polymer, whether head-to-tail or head-to-head or tail-to-tail and also the microtacticity of the polymer. The influence of this chain isomerism is best seen in the dechlorination reaction of poly(vinyl chloride)¹⁶⁶ and also in the pyrolysis of poly(vinyl acetate).¹⁶⁶

Bifunctional reactions are very often accompanied by intramolecular cyclization, which results from interaction between neighbouring reactive groups. Imidization of poly(methacrylamide) and acid hydrolysis of copolymers of maleic anhydride and allyl acetamide typify this type of reaction.¹⁶⁷ Functional group interactions have also been used for the syntheses of new types of polymers which are generally not obtained by direct synthesis. For instance, the condensation of poly(vinyl chloride) with aromatic hydrocarbons in presence of Friedel-Crafts catalysts gives polymers containing styrene units and 1,3-methyleneindane rings¹⁶⁸. In such type of reactions, the strong influence of the solvent on the degradation and discolouration of the products is observed. In the case of poly(ethyl α -chloroacrylate), the reaction proceeds¹⁶⁹ by an intramolecular cyclization, following a nucleophilic substitution mechanism, without incorporating the aromatic rings. The development of ladder polymers¹⁷⁰ is based on a polyfunctional reaction in which adjacent side groups are linked together.

Stereoisomerism of Polymer Chains

The chemical reactions of polymers are also affected by the tacticity of the high polymers. The formation of intramolecular

cyclized intermediates in the hydrolysis of p-nitrophenyl methacrylate units incorporated into a chain of poly(acrylic acid) is attributed to the relative position of the carboxylate and the ester groups towards each other and consequently on the micro-tacticity of the system.¹⁷¹⁻¹⁷³ The dependence of chemical transformation on the tacticity of the chain is further observed¹⁷¹⁻¹⁷³ from the ability of polymeric acids to cyclize to yield the corresponding polyanhydride. The hydrolysis of poly(vinyl acetal) of different degrees of acetalization is a typical example of group interactions¹⁷³ and influence of chain microtacticity¹⁷³ in polymers. Interestingly, chain isomerism not only influences the organic transformations of high polymers but also affects their fundamental physico-chemical properties.

Site of Reaction

In the type of reactions discussed above, one or two functional groups transform independently of their location along the polymeric chain and occur statistically. But in some other reactions, only one particular reactive site is involved and is consequently very selective. This is a very peculiar aspect of the reactivity of high polymers. The presence of a labile site in the macromolecule which is particularly sensitive to a radical attack and also the reactivity of some groups presented as end groups or side groups along the chain are considered responsible for this type of reactivity of the high polymers.

General Methods Employed for the Chemical Modification of Polymers

Conventional reactions such as addition, cyclization, substitution and the reactions of the functional groups are generally performed on the polymers for converting them into appropriate end products. In most instances, the modified polymers are characterized by many improved properties which make them useful for various applications.

(a) Reactions of Unsaturated Polymeric Hydrocarbons

Some important reactions which come under this category, include the following :

1. Cyclization reactions : Cyclization of polymers is effected in presence of catalysts such as H_2SO_4 , $SnCl_4$, BF_3 , $TiCl_4$ and $FeCl_3$. Natural rubber in presence of acids or Friedel-Crafts catalysts and poly(acrylonitrile) on heat treatment undergo cyclizations.¹⁷⁴⁻¹⁷⁶
2. Addition reactions : These comprise reactions including the addition of thiols¹⁷⁷⁻¹⁷⁹ to unsaturated polymers and hydrogenation of unsaturated polymers under suitable conditions of temperature and pressure in presence of suitable catalysts.¹⁸⁰⁻¹⁸² Also addition of halogens to polymers leads to various reactions such as substitutive chlorination, additive chlorination, cyclization and cross-linking in polymers.¹⁸³⁻¹⁸⁷ The solvent and the nature of the halogenating agent influence the extent and order of these reactions.

(b) Reactions of Saturated Polymeric Hydrocarbons

Physical factors such as solubility, permeability and crystallinity, and chemical factors such as cross-linking,

scission and propensity for the desired reaction affect the substitution reactions of polymeric hydrocarbons. For example, fluorination,^{188,189} chlorination,^{190,191} bromination¹⁹¹ of polymers (e.g. polyethylene) bring about changes in the crystallinity of the product (polymer).

(c) Side Chain or Nuclear Substitution Reactions of Poly-vinylaromatics

Vinylaromatic polymers by virtue of the side chain or the aromatic nucleus can undergo varieties of reactions resulting into useful end products. Important chemical reactions which are frequently employed, mainly include the following :

1. Chlorination : Chlorination of aromatic polymers such as polystyrene, in the side chain is usually accompanied by nuclear chlorination ; however, it can be suppressed by complexing with metal ions.¹⁹²⁻¹⁹⁴
2. Chloromethylation : Nuclear substitutions involving chloromethylation reactions are well known.¹⁹⁵⁻²⁰² Chloromethyl ether is a good solvent for vinylaromatics and rapidly swells crosslinked copolymers of vinylaromatics,²⁰³ and consequently, it is used for chloromethylation. It is accompanied by cross-linking²⁰⁴ and catalyst such as $AlCl_3$ or $ZnCl_2$ enhances the process. The substitution of chloromethyl group in a polymer molecule provides some modification of its properties, and because of the high mobility of chlorine atom some further chemical reactions can be carried out ; for example, amination,¹⁹⁵⁻²⁰²

phosphorylation.²⁰⁵ In this way, some ion-exchange resins and thermally more stable materials can be produced.²⁰⁶

3. Amination : Amination of chloromethylated polymers with ammonia or with primary or secondary amines leads to weak-base resins with primary, secondary and tertiary amino groups.^{195,197,199,201,202}

The reaction with tertiary amines yields strong-base resins with quaternary ammonium groups.^{196,198,200,202,207}

4. Sulphonation and related reactions : Sulphonation of polymers is usually carried out²⁰⁸ in halogenated solvents or in carbon disulphide. Sulphonation is also carried out by directly treating the polymer with sulphonating agent without the use of any solvent. The common sulphonating agents used²⁰⁸ are concentrated H_2SO_4 , SO_3 or chlorosulphonic acid. It may not be possible in many instances to introduce more than one sulphonic acid group per benzene ring without going to conditions which decompose the polymer.²⁰⁸

Sulphonation of polyvinylaromatics is usually accompanied by crosslinking due to the formation of sulphone groups.²⁰⁸ The sulphone formation is usually encouraged by the use of chlorosulphonic acid and a Friedel-Crafts catalyst.

If the reactive chlorine of the chloromethylated styrene polymer is displaced by sulphides such as dimethyl sulphide, sulphonium derivatives²⁰⁹ are produced **which** are useful as ion-exchange resins and also as an intermediate for the preparation of chelating ion-exchange resins.

5. Nitration : It is an example of a reaction in which the polymer dissolves with increasing substitution. The nitration and subsequent reduction of vinylaromatic polymers offer several ways to the preparation of electron exchange resins.²¹⁰
6. Phosphorylation : Phosphorylation of polyvinylaromatics such as polystyrene has been reported²¹¹ through reaction with PCl_3 in presence of Friedel-Crafts catalyst. The hydrolysis of the phosphorylated product under mild conditions²¹² gives phosphinic acid groups and the oxidation of the phosphorylated product with chlorine prior to hydrolysis^{213, 214} or with nitric acid after hydrolysis²¹² gives phosphonic acid groups. The alkaline hydrolysis of the phosphorylated product at a higher temperature ($60 - 70^\circ\text{C}$) followed by treatment with 1-2N HCl also gives phosphonic acid groups.^{215, 216}