CHAPTER 1
INTRODUCTION
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1.1 Polymeric Materials

Polymeric materials are used in a wide range of applications ranging from general purpose large volume commodity household articles to low volume, speciality, load bearing components. The prime considerations for materials selection in any application are the performance requirements versus the material properties and the cost effectiveness of the material. The performance specifications may include mechanical properties such as strength, rigidity, toughness, abrasion and wear resistance, thermal characteristics, chemical resistance and electrical properties. A few typical consumer and industrial applications of polymeric materials include packaging films, luggage, toys, textile fibres, paints, lighting fixtures, electrical connectors, auto tyres and gears, bearings.

The materials are generally classified in terms of their applications as plastics, elastomers, synthetic fibers, protective coatings and adhesives. Polymers are also used as matrix material for reinforcing fillers/fibres in high performance composites for defence, aerospace and industrial applications.

Engineering thermoplastics are increasingly replacing conventional materials primarily because of their greater ease of processing into products of complicated shapes and the economics of the high productivity conversion processes such as injection moulding. The other advantages offered by thermoplastics include light weight, corrosion resistance/long life expectancy, versatility of product design
and the ease of maintenance of the product. The property requirements for a specific new application can be met through modification of the base polymer with fillers, reinforcing fibres, grafting, blending etc.

The thermoplastic materials may be categorized into three groups based on their volume of production, cost and thermal performance.

(a) Bulk or commodity plastics: Low priced, high volume polymers such as polyethylene, polyvinyl chloride, polypropylene and polystyrene. The maximum use temperature of these materials is \( \leq 100^\circ C \).

(b) Engineering plastics: These are polymers exhibiting higher thermal and mechanical performance. In this class, polymers such as polyamides (Nylons), polycarbonates, polyacetals, polyphenylene oxide, thermoplastic polyesters, polyurethanes and polyphenylene sulfide may be included. On a production/cost basis, these materials are medium volume and medium priced plastics. The consumption of these materials is significantly lower than that of the commodity plastics. The use temperature of these materials is in the range 150-200\(^\circ\)C. They display better thermomechanical properties such as high HDT and modulus, wider end use temperatures, chemical resistance and excellent load bearing characteristics. These are used in metal replacement applications. Some of the major applications for engineering plastics include pump impellers and housings, low friction components, heat and chemical resistant units, electrical parts and materials for construction industry.
### TABLE 1

**CONSUMPTION FIGURES OF ENGINEERING PLASTICS**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Consumption x1000 tons</th>
<th>Market share %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total polyamides including</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nylon-6, nylon-66, speciality nylon</td>
<td>436</td>
<td>39.71</td>
</tr>
<tr>
<td>Polycarbonates</td>
<td>250</td>
<td>22.77</td>
</tr>
<tr>
<td>Polyacetals</td>
<td>186</td>
<td>16.94</td>
</tr>
<tr>
<td>Modified PPO</td>
<td>140</td>
<td>12.75</td>
</tr>
<tr>
<td>Thermoplastic polyesters (PBT, PET)</td>
<td>75</td>
<td>6.83</td>
</tr>
<tr>
<td>Polysulfones</td>
<td>6</td>
<td>0.55</td>
</tr>
<tr>
<td>Polyphenylene sulfide</td>
<td>5</td>
<td>0.45</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1098</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
Speciality polymers: Polymers that can be grouped in this category are low volume/high priced speciality materials and would include polymers such as fluoropolymers, polysulfones, polyether ketones, polyimides etc. which cater to specific property combinations defined to meet product performance. The polymer can be used at temperatures upto 270°C.

The conventional processing methods such as extrusion and injection moulding can be used for processing of engineering plastics with modification of the equipment.

The increasing use and acceptance of engineering plastics can be gauged from the reported sales of engineering plastics. This has crossed the one million 'ton mark.' The contribution of various polymers with their market share is shown in Table 1. The table excludes commodity polymers modified to meet property requirements for engineering applications. Polymers such as polypropylene and acrylonitrile-butadiene-styrene (ABS) copolymers could be used for specific engineering applications.

A number of high performance engineering plastics, with the exception of nylon 6, nylon 66 and polyacetals, are based on aromatic monomer units. The advantages of incorporating para phenylene moities in the polymer backbone are well documented. The physical properties of a large number of such condensation polymers can be correlated to their chemical structure. These polymers are often used with glass fibres for engineering applications.

Some of the outstanding and commercially useful aromatic polymers include the thermoplastic polyesters (PET and PBT), poly-
## Table 2

**Structure and Typical Properties of Aromatic Polymers**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Test Method ASTM No.</th>
<th>Tensile Strength $10^3$ psi</th>
<th>Modulus $10^3$ psi</th>
<th>Impact Strength ft. 15/in</th>
<th>Deflection Temperature °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene terephthalate PET</td>
<td>![PET Structure]</td>
<td>D 638, D 648</td>
<td>8500</td>
<td>400</td>
<td>0.25</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-10,500</td>
<td>-600</td>
<td>-0.65</td>
<td>-106 (annealed)</td>
</tr>
<tr>
<td>Polybutylene terephthalate PBT</td>
<td>![PBT Structure]</td>
<td></td>
<td>8200</td>
<td>280</td>
<td>0.8-1.0</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-9600</td>
<td>-355</td>
<td>5</td>
<td>-185</td>
</tr>
<tr>
<td>Polyphenylene oxide PPO</td>
<td>![PPO Structure]</td>
<td></td>
<td>7800</td>
<td>380</td>
<td>5</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-9600</td>
<td>-355</td>
<td></td>
<td>-265</td>
</tr>
<tr>
<td>Polycarbonate PC</td>
<td>![PC Structure]</td>
<td></td>
<td>9500</td>
<td>345</td>
<td>10-14</td>
<td>270</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>![PS Structure]</td>
<td></td>
<td>360</td>
<td>1.2</td>
<td></td>
<td>345</td>
</tr>
<tr>
<td>Polyphenylene sulfide PPS</td>
<td>![PPS Structure]</td>
<td></td>
<td>9500</td>
<td>480</td>
<td>0.5</td>
<td>275</td>
</tr>
</tbody>
</table>
sulfones, polycarbonates, polyphenylene sulfide, polyphenylene oxide (Noryl). The polymer backbone consists of one or more atoms interposed between the paraphenyiene units. The structure and typical properties of a few aromatic polymers are summarized in Table 2.

1.2 Poly(p-phenylene sulfide)

Poly(p-phenylene sulfide) (PPS) has gained considerable importance as a versatile engineering plastic since 1973 and is predicted to become one of the six major engineering plastics by 1990. The polymer structure consists of para-substituted aromatic rings interconnected by sulfur linkages. Linear PPS has one sulfur atom between the paraphenyiene units. The chemical structure of the polymer is represented as indicated below.

Although the polymer was first reported in 1897, it was not till the mid seventies that PPS could be marketed. The first commercial plant was put up in late 1972 by Phillips Petroleum in USA. PPS has been a monopoly product of Phillips Petroleum and is marketed under the trade name Ryton. Though broadly available in coating and moulding grades, 72 different grades are marketed by various companies using the base resin produced by Phillips Petroleum. The consumption figure during the year 1984 is 5000 tons. Several reviews highlighting the salient features of PPS and its application potential are available.

The repeating paraphenyiene unit imparts rigidity to the polymer chain and the symmetry due to paraphenyiene linkages imparts
a high degree of crystallinity and excellent thermal resistance. PPS is a versatile engineering plastic with a unique combination of properties like high corrosion and solvent resistance, thermal resistance, good mechanical properties, good processability, flame retardance and ability to be compounded with various fillers. PPS has combination properties of thermoplastic and thermosetting classes of materials.

PPS is used in coating and injection molding applications. Coatings based on PPS exhibit better adhesion to metal substrates and better filler acceptability in comparison with fluoro polymer coatings. The coating process is also simpler since the polymer melts during the curing process. The coating applications of PPS include corrosion resistant lining for chemical equipment, pump impellers, flame-proof casing for electrical equipment, non-stick coatings for cookware, low friction rollers for calendering machines etc. For applications involving injection moulding grades, PPS is compounded with glass fibres and fillers (40% glass fibres). Typical applications include ball valves, pump impellers, electrical sockets, gears and housings, microwave oven shelves, telephone components etc.

Sodium sulfide and paradichlorobenzene, the major raw materials used for the synthesis of PPS, are relatively inexpensive.

The early studies on the formation of PPS resins are well reviewed. In these investigations, the polymer was observed as a side product in reactions directed at the synthesis of simple organic compounds.

The first published report on PPS dates back to 1897. The formation of the polymer as a resinous material was observed in the reaction of benzene and sulfur. The polymer generation was also observed
in the Friedel-Crafts reaction \((\text{AlCl}_3)\) involving phenol with sulfur\(^{43}\), of thiophenol\(^{44}\), of thiophenol with thionyl chloride\(^{45}\), self condensation of thiophenol in concentrated sulfuric acid\(^{46}\), reaction of benzene with sulfur\(^{47}\), oxidation of paraphenylene dimercaptan\(^{48}\) and reaction of phenol with sulfur dichloride\(^{48}\).

These studies resulted in polymer yields only in the 50 to 80 percent range. Elemental analyses of the polymer formed in the above investigations corresponded to the empirical formula \(C_6H_4S\). The reported physical characteristics of the formed polymer are conflicting. It was either described as amorphous or as a crystalline material. However, the high softening range of the polymer was uniformly noted. The polymers were perhaps either oligomers or with cyclic structures. The polymers were not extensively characterized.

Reinvestigation of the self polycondensation of thiophenol\(^{49}\) in the presence of sulfuric acid gave high melting (310°C) branched polymer (80.8%) along with toluene soluble low melting (125-130°C) oligomer (11.4%).

Macallum revived the dormant field of PPS synthesis. The Macallum polymerization\(^{50-52}\) involved the melt reaction of para dichloro benzene, sulfur and anhydrous sodium carbonate in varying proportions in a sealed vessel at temperatures in excess of 300°C. The reaction may be represented as,

\[
\text{Cl-Cl} + S + \text{Na}_2\text{CO}_3 \rightarrow \left(\text{S}_x\right)_n + \text{NaCl} + \text{CO}_2
\]

\[
1\text{M : 1.5M : 1.5M} \quad \text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_2\text{C}
\]
The sulfur rank "x" in the above equation (which denotes the average number of sulfur atoms between repeat units) varied from 1 to 5. The chemical composition and the physical properties of the polymer formed were found to be dependant on the relative ratios of the reactants used. Polymers with 'x' close to unity were obtained when the molar ratios of sulfur and sodium carbonate to para dichloro benzene were maintained at 1.5:1.5:1. The number-average molecular weight of these polymers, as determined by chlorine end group analysis was found to be in the range of 35000 to 70000.

Macallum polymerization process was not a commercial success since the polymer properties could not be reproduced. The products obtained ranged in properties from hard polymers softening at high temperatures to rubbery polysulfides, depending on the ratio of the reactants. However, the work prompted further investigation towards an extensive study of the chemistry and structure of the polymers.

At Dow Chemical Co., USA, the research team headed by Lenz reinvestigated the Macallum polymerization process. They observed that the polymer properties and yields were not reproducible. Polymer characterization showed these were either branched or crosslinked. They proposed a probable mechanism for the course of Macallum polymerization.

The Lenz team switched to an alternate synthetic route involving self polycondensation of metal salts of para halo thiophenols. The reaction may be represented as,

\[ nX \rightarrow \text{SM} \rightarrow \left( \text{S} \right)_n + nMX \]
where $M$ is an alkali or alkaline earth cation, while $X$ is a halide, fluorine, chlorine, bromine or iodine.

The polycondensations were carried out either in bulk or in solvent pyridine in ampules sealed under inert atmosphere, at temperatures lower than the melting point of the salt. Among the systems investigated, the commercially attractive one was found to be the system based on cuprous p-bromo thiophenoxide. This reaction could be represented as,

$$nCuSBr \xrightleftharpoons{250-300^\circ C} (\text{thiophene})_n + nCuBr$$

It was found that the rate of solution polycondensation was faster than the solid state polycondensation. The influence of the halogen on the rate was in the order $I > Br > Cl > F$. An overall second order rate was observed for the solution polycondensation in pyridine.

The polycondensations resulted in linear poly(p-phenylene sulfide) with better thermal stability than the polymers produced by the Macallum process. However, the process could not be exploited commercially due to the expensive raw material and inherent difficulty in the complete removal of the side product, cuprous bromide.
Phillips process for PPS:

Phillips Petroleum Co. USA reinvestigated the synthesis of PPS, aiming at a viable commercial process.\textsuperscript{56,57} The work culminated in the successful development of a commercial plant in 1972. The Phillips process involves the reaction of aromatic dihalides with alkali metal sulfides in a polar organic solvent at high temperatures and pressures. The preferred route involves the reaction between para dichloro benzene and sodium sulfide in N-methyl pyrrolidone at elevated temperatures (265°C) and pressure (\(\sim 160\) psi). Linear PPS is obtained almost quantitatively. The reaction can be represented as;

\[
\text{n Cl} \bigg( \text{ } \bigg) \text{Cl} + \text{n Na}_2\text{S} \xrightarrow{\text{heat solvent}} \bigg( \text{ } \bigg)\text{n} + (2\text{n}-1) \text{ NaCl}
\]

Sodium sulfide, a reactant in the synthesis, was obtained in an anhydrous form by reaction between sodium hydroxide and sodium hydrosulfide, followed by the dehydration step to remove water by distillation. The polymer isolation steps include recovery of the polymer from the reaction mixture, extensive washing to remove the side product sodium chloride, and drying.

A number of methods for the synthesis of PPS have been patented by Phillips Petroleum.\textsuperscript{59-94} The common feature in these methods is the reaction of para dichloro benzene in N-methyl pyrrolidone. The methods vary in the nature of sulfide, the co-reactant. Other reported variations of the reaction include incremental addition of one reactant or addition of compounds like thiourea, alkali metal carbonates, mixed dichlorobenzene, lithium halides or carboxylates, etc.

PPS obtained by the Phillips process is a low molecular weight polymer, not suitable for moulding applications. The molecular weight of
PPS was enhanced by the following methods.\textsuperscript{95-113}

(a) recycling of low molecular weight PPS from earlier batches.
(b) use of lithium salts such as chloride, carbonate, metaborate, acetate as catalysts.
(c) using pressurized carbon dioxide atmosphere.
(d) using sodium benzene sulfonate or sodium butane sulfonate.
(e) use of sodium acetate
(f) addition of bifunctional chloride
(g) addition of alkali-metal carboxylate with varying amounts of alkali metal hydroxide, and
(h) co-polycondensation with a comonomer.

The molecular weight of PPS was also enhanced by controlled post polymerization heat treatment. The dry polymer was subjected to a programmed thermal heating cycle below its melting point, till the desired molecular weight was attained. The heat treatments could either be at atmospheric pressure or under pressure with additives\textsuperscript{114} such as sulfur, tetramethyl thiuram disulfide or organic peroxide, quinones, sulfuric acid, peroxide-sulfuric/nitric acid, hexamethoxy methyl melamine, alkali metal carboxylate. The increase in molecular weight was evaluated by measuring the melt flow index and the increase in inherent viscosity of the polymer. The melt flow index decreased with increase in molecular weight.

PPS is normally produced by a batch process. Phillips Petroleum Co. USA, have recently filed process patents for a continuous production of PPS.\textsuperscript{124-127}

Thus Phillips Petroleum Co. USA have carried out extensive work in the synthesis of PPS. Open literature on the synthesis of PPS is rather limited.\textsuperscript{128-137} Reported work by others is exclusively covered by patents.
1.3 Kinetics of polycondensation reactions

The kinetic analysis of a reaction involves monitoring the rate and order of disappearance of the reactants as measured by the change in their concentration. This is evaluated by analysing samples drawn intermittently during the course of the reaction.

The first objective in any kinetic study is to determine the rate of the reaction. Simple reaction schemes and their corresponding rate expressions are represented as:

\[ \begin{align*}
\text{Reaction} & \quad \text{Rate expression} \\
P & \rightarrow \text{products} \quad \quad \quad - \frac{d[P]}{dt} = k[P] \\
P + P & \rightarrow \text{products} \quad - \frac{d[P]}{dt} = k[P]^2 \\
P + Q & \rightarrow \text{products} \quad - \frac{d[P]}{dt} = -\frac{d[Q]}{dt} = k[P][Q]
\end{align*} \]

where P and Q are the reactants.

The constant \( k \), the rate constant, is also known as the specific reaction rate constant. Its dimensions depend on the order of the reaction. The generalized expression between \( P \) and \( Q \) may be represented in the form,

\[ -\frac{d[P]}{dt} = -\frac{d[Q]}{dt} = k[P]^x [Q]^y \]

The indices \( x \) and \( y \) are defined as the order of the reaction with respect to the individual reactants and the overall rate of the reaction is represented as \( [x + y] \).
Polycondensation reactions

Polycondensation reactions occur between difunctional reactants through a series of stepwise reactions to form dimer, trimer, tetramer, pentamer and so on, with or without the elimination of side products such as water, hydrochloric acid or sodium chloride. The molecular weight of the polymer builds up gradually. Certain polycondensation reactions such as polyesterifications are reversible. In such cases, the side product formed during the reaction has to be removed from the system to shift the equilibrium towards product formation to obtain high molecular weight polymer. In addition, reactants should be pure to prevent side reactions and the molar ratios of the reactants must be maintained in stoichiometric proportions.

Polycondensation reactions are not generally classified into different groups. The commercially important polycondensation reactions include esterification to form polyesters, amidation reactions to produce polyamides, the reaction between diols and diisocyanates to synthesise polyurethanes and nucleophilic substitution reactions resulting in the formation of polymers like polysulfones and polyphenylene sulfide. Polycondensation reactions of industrial importance are generally homogeneous systems while polymer formation to PPS is a heterogeneous one.

The various stages that occur during a polycondensation reaction can be represented as,

Monomer + monomer → Dimer + Sm
Monomer + dimer → Trimer + Sm
Trimer + monomer → Tetramer + Sm
Trimer + Dimer → Pentamer + Sm
where \( S_m \) denotes the small molecule (side product) that is formed during the reaction.

At any given reaction time 't', molecules of different degrees of polymerization are present and any two species can react for the growth of the polymer chain. The overall rate expression would be the summation of the individual rates of formation of the various species. The kinetic analysis of such a system poses a very difficult task. This uncertainty is overcome by assuming that the reaction rate between two functional groups is independent of the chain length of the reacting species and that the effect of a similar functional group present elsewhere in the molecule on the rate is negligible. The validity of these assumptions have been experimentally confirmed. Investigations on esterification reactions as a function of chain length have shown that the rates of disappearance of \(-\text{COOH}\) groups in dibasic acids become independent of chain length \( n \), for \( n \leq 4 \).\(^{191-193}\) Thus, the kinetic analysis is simplified to that observed in simple organic esterification reactions and the rate of reaction can be related to the rate of disappearance of a reactant or a functional group. The degree of polymerization or the chain length increases gradually as the reaction proceeds. In a heterogeneous system such as PPS synthesis, the general features of the process and the operating parameters have not been investigated systematically.

Polyesterifications are the most extensively studied of all polycondensation reactions. The different rate expressions that emerge can be classified as under:

(i) Internal or self catalysed reactions.
(ii) Externally catalysed reactions.
(iii) Non-\textit{stoi}chiometric ratio of reactants.
The kinetic expressions differ and are discussed separately.

In the internal or self catalysed polyesterification reactions, the rate expression can be represented as,

$$- \frac{d[COOH]}{dt} = k'[COOH]^2[OH]$$ \hspace{1cm} (5)

Since stoichiometric concentrations of functional groups is taken for the reaction, the rate equation becomes,

$$\frac{d[COOH]}{dt} = ka^3$$ \hspace{1cm} (6)

where, 'a' denotes the concentration of the functional groups.

Equation 6 on integration and use of initial conditions such as at $t=t_0$, $a=a_0$ becomes,

$$2kt = \frac{1}{a^2} - \frac{1}{a_0^2}$$ \hspace{1cm} (7)

The fractional conversions of the reaction could be expressed as a function of the fraction of the hydroxyl or carboxyl groups reacted at time 't'. If $p$ denotes the fractional conversions, the concentration 'a' of carboxyl or hydroxyl group, at time 't' can be expressed as,

$$a = a_0(1-p)$$ \hspace{1cm} (8)

Substituting the value of $a$ from the above equation in equation 7, results in

$$2a_0^2kt = \frac{1}{(1-p)^2} - 1$$ \hspace{1cm} (9)
The reaction follows third order kinetics and a plot of \( \frac{1}{(1 - p)^2} \) against reaction time should be linear. However, the uncatalysed polycondensation reaction has been found to follow third order kinetics only after 80 percent conversion. The deviation from third order in the early stages has been described to be due to large polarity changes in the medium as a result of the disappearance of the hydroxyl and carboxyl groups.

In externally catalysed polyesterification reactions the concentration of the strong acid, added as the catalyst, remains constant during the reaction. The rate expression in this case is represented as,

\[
- \frac{da}{dt} = ka^2
\]

(10)

In forms of fractional conversion 'p', the rate expression is given as,

\[
C_0 kt = \frac{1}{(1 - p)} - 1
\]

(11)

The reaction follows second order kinetics for most polyestersifications and a plot of \( \frac{1}{(1 - p)} \) against reaction time is linear over a wide range of conversions. The form (11) represents the average number of structural units per chain and is defined as the number-average degree of polymerization (\( DP_n \) or \( \bar{x}_n \)). Equation 11 therefore becomes,

\[
\bar{x}_n = 1 + kC_0 t
\]

(12)

The number-average molecular weight in catalysed polyesterification increases linearly with reaction time.

In catalysed reactions with non-stoichiometric ratio of reactants
used, the rate expression is expressed in the form,

\[- \frac{d[P]}{dQ} = k[P][Q]\]  \hspace{1cm} (13)

where P and Q are the reactants.

Although one of the reactants is in excess, for the reacting functional groups, the stoichiometric relation is given by,

\[[P_0] - [P] = [Q_0] - [Q]\]  \hspace{1cm} (14)

where \([P_0]\) and \([Q_0]\) represent the initial concentrations and \([P]\), \([Q]\), the concentrations at time 't'.

Combining the equations 13 and 14 and integrating equation 13, the following expression is obtained,

\[\ln \frac{[Q]}{[P]} = - \ln r + \frac{Q_0}{[P]} [1 - r] kt\]  \hspace{1cm} (15)

where \(r = \frac{[P]}{[Q_0]} < 1\) is the molar ratio of the reactants.

A plot of \(\ln \frac{[Q]}{[P]}\) against reaction time is linear and the reaction follows second order kinetics.

Published information on heterogeneous polycondensation is rather limited. The only published work on the kinetics of polycondensation to generate PPS is that of Lenz and coworkers. 55

Due to a sequence of reactions in the early stages of the PPS polycondensation the following species could be formed.
The reactivities of the different species I, II, III, IV and V would be expected to be different. Thus the rates of formation of the monosubstituted moiety and its rate of growth would be different. No published information exists on elaborate kinetic evaluation of this system.

In reactions involving diisocyanates, the reactivity of the isocyanate group is affected by the structure of the organic moiety to which it is attached. In aromatic diisocyanates reactivity is influenced by the position of attachment of the second isocyanate group to the benzene ring. The reactivity of the two isocyanate groups are not equivalent and the disappearance of one isocyanate group through urethane formation reduces the reactivity of the other. The reaction follows an overall second order kinetics and the rate expression can be represented as,
### TABLE 3
**REACTIVITY OF DIISOCYANATES**

<table>
<thead>
<tr>
<th>Diisocyanate</th>
<th>Structure</th>
<th>Rate constant $k \times 10^{-4}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
</tr>
<tr>
<td>m-phenylene diisocyanate</td>
<td>OCN-[H]_2NCO</td>
<td>6.0</td>
</tr>
<tr>
<td>p-phenylene diisocyanate</td>
<td>OCN-[H]_2NCO</td>
<td>5.7</td>
</tr>
<tr>
<td>1-chloro, 2,4-phenylene diisocyanate</td>
<td>OCN-[Cl]_2NCO</td>
<td>13.0</td>
</tr>
<tr>
<td>2,4-toluene diisocyanate</td>
<td>OCN-[H]_2NCO</td>
<td>2.0</td>
</tr>
<tr>
<td>2,6-toluene diisocyanate</td>
<td>OCN-[H]_2NCO</td>
<td>0.8</td>
</tr>
<tr>
<td>4,4'-bis(2-methyl isocyanato phenyl)</td>
<td>OCN-[H]_2NCO</td>
<td>0.11</td>
</tr>
</tbody>
</table>
The reactions of aromatic diisocyanates and diols leading to the formation of polyurethanes have been published.

In the case of the most widely used aromatic diisocyanate, namely, 2,4-toluene diisocyanate (TDI), the inductive effect of the isocyanate group is moderated by the steric effect of the methyl group. It was observed that in the early stages of the reaction, the isocyanate moiety para to methyl group contributes to the rate observed and in the latter stages of the reaction, the rate decreases to a great degree due to the lesser reactivity of the isocyanate group at the ortho position. Table 3 shows the change in both the rate constants with the structural variations in different diisocyanates.

When all the factors affect both isocyanate groups equally, the reactivities of both the isocyanate groups are equal. This is observed of methylene diisocyanate (MDI) or substituted MDI having equivalent isocyanate groups. However, in the absence of the steric effects, the reactivity of bifunctional monomers is reduced significantly as a result of the reaction of one isocyanate group.

Polycondensation reactions leading to the formation of PPS follow aromatic nucleophilic substitution mechanism. Aromatic polyethers are commercially prepared by aromatic nucleophilic substitution reactions between a diphenoxide and a aromatic dihalide. The reactions are carried out in a highly polar organic solvents. It can be represented in the form,
Denoting [ArO] as the phenoxide and [Ar’X] as the aromatic dihalide in the form of functional moieties, the rate equation can be expressed as,

\[
- \frac{d[\text{ArO}]}{dt} = k[\text{ArO}][\text{Ar’X}]
\]  

(18)

The above expression on integration becomes,

\[
\frac{1}{c} = k t + \frac{1}{c_o}
\]  

(19)

where \( c \) is the concentration of phenoxide [ArO] or the dihalide [Ar’X] functional group at time ‘t' and \( c_o \) the initial concentration.

A second order reaction kinetics with respect to the concentration of functional groups is observed. The reaction rate was however bimodal. The uniform initial rate observed was followed by a slower rate beyond 50% conversion. In the investigations of Lenz et al. towards synthesis of PPS, an overall second order reaction rate was observed. In the present investigation, a bimodal rate was observed.

To summarise, polycondensation reactions fall into three categories.

(i) Uncatalysed reactions that occur with reasonable rate (formation of polyesters and polyamides).

(ii) reactions that require external addition of catalyst to have reasonable rates of reaction (formation of phenol-formaldehyde resins).

(iii) reactions with optional addition of catalyst (formation of polyurethane).

The reactions could either be homogeneous or heterogeneous in nature. Most commercially important polycondensation reactions are homogeneous while the generation of PPS is heterogeneous in nature.
1.4 Physico-chemical characterization of polymers

A variety of techniques are available for the physico-chemical characterization of polymers. The widely used techniques and the information generated are summarized below.

<table>
<thead>
<tr>
<th>Analysis technique</th>
<th>Information generated</th>
</tr>
</thead>
<tbody>
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The following techniques have been used in the present investigation.

(i) Infrared spectroscopy
(ii) Volumetric analysis
(iii) Microanalysis
(iv) Dilute solution viscosity
(v) Differential scanning calorimetry (DSC)
(vi) Thermogravimetric analysis (TGA)
These techniques are discussed briefly in the following sections.

1.4.1 Infrared spectroscopy

Infrared (IR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm\(^{-1}\) by polymer molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are indicative of the bond strengths and structural geometry in the molecule. Absorption in the range 1100 cm\(^{-1}\) to 600 cm\(^{-1}\) is specific to each molecule and is termed as 'finger print' region. General infrared spectroscopy is useful to determine functional groups present in the polymer molecule. The substitution pattern in aromatic polymers can also be predicted.

1.4.2 Volumetric analysis

Specific volumetric analysis can be used to evaluate concentrations of reactants and products generated in a reaction. The method involves collection of samples at intermittent reaction times and estimation of the concentration of a reactant. Usually titrimetric methods are followed. In the present investigation, the concentrations of unreacted sodium sulfide and the moles of sodium chloride formed were determined at different reaction times by iodometric and argentometric titrations.

1.4.3 Microanalysis

The method is generally used to evaluate the chemical composition. This estimate can be related to the number average molecular
weight of a polymer, provided the end group differs from the repeating structure of the polymer. The polymer sample is digested with a strong acid in a sealed ampule. The digested sample is then analysed either by gravimetric or volumetric analysis. In the present system, the PPS samples were analysed for chlorine end groups; a gravimetric method was followed, the details of which are given in section 2.

1.4.4 Dilute solution viscosity

Dilute solution viscosity measurement is a widely used indirect method for evaluating the molecular weight of a polymer. The incremental increase in the viscosity of a solvent brought about by the addition of small amounts of polymer forms the basis for intrinsic viscosity determination. It is indicative of the size of the solvated polymer and can be related to the polymer molecular weight by comparison with data based on direct methods such as membrane osmometry and light scattering. A number of capillary viscometers that can be used for the determination of viscosity of dilute polymer solutions exist such as Ostwald, Cannon-Fenske and Ubbelohde viscometers. The viscometers are mounted in precisely-constant temperature bath. The procedure involves the measurement of the flow times of an exact volume of the solvent as well as of polymer solutions of different concentrations at the specific preset temperature. The following viscosity parameters can be determined from the measurements:

\[
\begin{align*}
\text{Relative viscosity } (\eta_r) & = \frac{t}{t_0} \quad (1) \\
\text{Specific viscosity } (\eta_{sp}) & = (\eta_r - 1) \quad (2) \\
\text{Intrinsic viscosity } ([\eta]) & = \left(\frac{\eta_{sp}}{c}\right)_0 \quad (3)
\end{align*}
\]
where $t$, $t_o$ are flow times for polymer solution and solvent respectively and $c$, the concentration of the polymer in gm/deciliter.

The two most widely used equations in relating the intrinsic viscosity with concentration are known as the Higgins\textsuperscript{197} and Kramer\textsuperscript{198} equations given below:

\begin{align}
\eta_{sp}/C &= \eta_0 + k' [\eta]^2 C \\
\frac{(\ln \eta_r)}{C} &= [\eta] + k'' [\eta] C
\end{align}

where $k'$ and $k''$ are constants.

A plot of $\eta_{sp}/C$ against concentration on extrapolation to infinite dilution ($C=0$) gives the intrinsic viscosity $[\eta]$, as the intercept. It has units of deciliters per gram. Intrinsic viscosity $[\eta]$ can be related to the polymer molecular weight by the Mark-Houwink equation\textsuperscript{199}

\begin{equation}
[\eta] = K M^a
\end{equation}

where $K$ and $a$ are constants characteristic of a polymer and solvent combination at a given temperature and $M$, the molecular weight.

Knowing $K$ and $a$, the polymer molecular weight can be calculated.

An easier, faster method known as the single point intrinsic viscosity measurement has found wide industrial acceptance. Two equations, one proposed by Schultz and Blaschke\textsuperscript{200} and the other by Solomon and Ciuta\textsuperscript{201} are represented below.

\begin{equation}
[\eta] = \frac{\eta_{sp}}{C} \frac{1}{1 + K \eta_{sp}}
\end{equation}
where \( K \) is constant.

\[
[\eta] = \frac{\sqrt{2}}{C} \sqrt{\eta_{\text{sp}} - \ln \eta_r} \tag{8}
\]

The method involves the evaluation of relative viscosity at a single polymer concentration at an exact temperature. The polymer concentration generally chosen for high molecular weight polymers is 0.5 gm/dl. The intrinsic viscosity is then calculated from equations 7 and 8.

Equation 7 has been derived from equations 4 and 5 implying that Higgin's and Kramer's equations are obeyed by polymer solutions. However, equation 8 does not involve any constant. Intrinsic viscosity determined from equation 8 match experimental results of Naar et al. They proposed that the right hand side of equation tends to the intrinsic viscosity \([\eta]\) at infinite dilution (\(C=0\)). The equation of Solomon and Ciuta (eq.8) was found to be in good agreement with intrinsic viscosity determined by graphical extrapolation method for polycarbonate, poly(phenylene oxide) and poly(ether imide) at polymer concentrations, of \(\eta_{\text{sp}} \ll 1\). Palit and Kar reported that equation can generally be applied for polymer solutions with \(\eta_{\text{sp}} < 0.6\).

Other equations for single point intrinsic viscosity determination have also been proposed. A method proposed by Mortin has been extensively tested. The equation is represented below.

\[
\log \left( \frac{\eta_{\text{sp}}}{C} \right) = \log (\eta) + k (\eta) C \tag{9}
\]

Deb and Chatterjee proposed an equation in the form,
and have shown the usefulness for a number of polymer-solvent systems. Khan and Bhargava have also proposed an equation for evaluating intrinsic viscosity from single point determinations. The method is sensitive to polydispersity and chemical composition in the case of copolymers.

1.4.5 Thermal analysis

Important thermal analysis techniques include thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The characteristic parameters determined by thermal analysis include, the glass transition temperature, the crystalline melting point in the case of crystalline polymers or softening point in the case of amorphous polymers and the thermal stability of the polymer which determines the temperature and rate of thermal degradation. Several reviews are available.

The thermal analysis techniques involve continuous monitoring of a physical property such as the change in mass, enthalpy or specific heat over a temperature range. The techniques offer the advantages of speed, sensitivity and precision. Preliminary thermal analysis would include qualitative determinations such as the use of a simple hot stage microscope. It is used to determine the thermoplasticity, softening temperature, crystalline melting point, flow temperature, adhesive properties and thermal stability.

In differential scanning calorimetry (DSC) the physical or chemical

\[ [\eta] = \frac{1}{C} \sqrt[3/2]{3 \ln \eta_r + \frac{3}{2} \eta_{sp}^2 - 3 \eta_{sp}} \] (10)

and have shown the usefulness for a number of polymer-solvent systems. Khan and Bhargava have also proposed an equation for evaluating intrinsic viscosity from single point determinations. The method is sensitive to polydispersity and chemical composition in the case of copolymers.
changes that occur as the polymer sample is heated and cooled at a programmed rate is evaluated. The method is quantitative as the thermogram (the output of this technique) can be directly related to the thermodynamic parameters such as changes in specific heat, enthalpy and entropy of the polymer under investigation. The polymer sample and a reference materials (usually aluminium upto 600°C) are separately subjected to a programmed heating. The thermogram is indicative of the excess differential power required to maintain the sample holder at the same temperature as the reference material when the temperature is increased/decreased at a constant rate. A typical thermogram of commercial PPS (Ryton) is shown in figure 1.

The enthalpy of a polymer is calculated from a knowledge of the area under its first order transition. Similarly, area under the first order transition of a reference of known enthalpy of fusion is determined (Indium). The enthalpy of fusion of the polymer sample is then calculated.

Glass transition temperature

The glass transition temperature is an apparent second order transition and signifies the onset of large scale motion of chain segments at the molecular scale. It is the temperature above which amorphous polymers exhibit rubbery characteristics and below which are glassy and brittle. The molecular factors affecting glass transition temperature include, the chemical structure of the monomer(s), tacticity, molecular weight, molecular weight distribution, extent of crosslinking and the presence of plasticizers. In addition to other known methods, glass transition temperature can be determined using a differential scanning calorimeter by monitoring the specific heat change with temperature.
Figure 1: Typical DSC Scan of Rytton V-1

- Crystallisation at 250°C
- Melting at 295°C

Increasing Temp.
Crystalline melting point

The melting point of a semicrystalline polymer is a first order transition. Due to their polydispersity, polymers generally melt over a temperature range, unlike metals. Also the melting point is not sharp. The factors that affect crystalline melting point and its range are, the degree of crystallinity, crystallite size and perfection, molecular weight, molecular weight distribution and orientation. Crystalline melting point of a polymer sample could conveniently be obtained using either a DSC or an optical microscope.

The DSC thermogram of a polymer shows the glass transition temperature as a shift in the base line, crystallization as an exothermic peak and melting as an endothermic peak.

Other applications\textsuperscript{225-229} of the DSC technique include specific heat measurements, estimation of the degree of crystallinity, crystal to crystal transition, liquid crystal transitions, rates of crystallization, crystallization kinetics and curing behaviour of thermosetting polymers.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is used to determine the thermal stability of a polymer. This is a dynamic method and involves the determination of the weight loss of a polymer over a temperature range. The analysis is either conducted in an oxidising or inert (nitrogen) atmosphere. The output is a thermogram which is a plot of the weight of the polymer as a function of temperature, at a programmed heating rate. The technique is used primarily to determine the practical upper temperature limit of use for the polymer. The analysis is very useful in the
selection of processing conditions for the polymer. The dependant variables are the sample size, particle size, the rate of heating and the atmosphere (whether oxidising or inert) during analysis.

Other thermal measurements of practical interest include the vicat softening point useful for comparison of the softening characteristics of thermoplastics and heat deflection temperature signifying the thermo-mechanical response of the polymer under load.

1.4.6 Morphological characterization

Polymer morphology involves the study of the arrangement of polymer molecules into crystalline and amorphous phases, the form and structure of these regions and the manner in which they are organized into larger and more complex domains. The morphology of a polymeric article is the result of the interaction of the chemical structure and physical characteristics of the polymer and the processing conditions. Morphological studies make use of techniques such as density measurements, optical and electron microscopy, x-ray diffractometry, birefringence, scanning electron microscopy etc. The two techniques used in the present work, namely x-ray diffractometry and scanning electron microscopy are discussed below.

X-ray diffractometry

X-ray diffraction studies of polymer are well reviewed. Polymers are either amorphous or semicrystalline. X-ray diffraction studies are extensively used to determine the percentages of the two phases in semicrystalline polymers.

Amorphous polymers can be visualized to consist of molecular
bundles within which some ordered structure is possible. Semicrystalline polymers on the other hand show signs of crystalline order. An increase in crystallinity is signified by denser, stiffer, harder, tougher and solvent resistant characteristics. Amorphous regions offer the advantage of softness and ease in processing.

X-ray diffraction follows Bragg’s law represented by,

\[ n \lambda = 2 d_{hkl} \sin \theta \]

where \( \lambda \) is the wavelength, \( \theta \) the angle of scattering, \( d_{hkl} \) the spacing between the planes that cause diffraction, and \( n \) the diffraction order. X-rays of wavelength \( \lambda = 1.54 \, \text{Å} \) is suitable for x-ray diffraction studies of organic polymers. This is achieved by electron bombardment of a copper target in an evacuated tube and filtration of x-rays generated by using a nickel filter. Normally, the wavelength \( \lambda \) is kept constant and \( \theta \) is varied.

The polymer sample could be in the form of a powder, film or fibre. The diffraction could either be photographed or amplified and recorded by electronic x-ray detectors. A typical output is shown in figure 2 indicating crystalline and amorphous scatterings.

There are a number of methods to determine the percentage of crystallinity by x-ray analysis. The most widely used one involves the measurement of the areas under crystalline and amorphous regions of the x-ray diffraction scans. The degree of crystallinity is calculated from the relation,

\[ C_i = \frac{A_c}{A_c + A_a} \]
FIG. 2: TYPICAL XRD SCAN
where $A_c$ and $A_a$ are the areas of crystalline and amorphous phases and $C_i$, the crystallinity index.

**Scanning electron microscopy (SEM)**

Scanning electron microscopes were first introduced in 1965 and it has since become a very useful tool in polymer research for studying surface morphology. In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and x-rays. These signals are monitored by detectors and magnified. An image of the investigated microscopic region of the specimen is thus photographed.

If the specimen under investigation is not a good conductor, it should be coated with a thin layer of conducting material like gold or platinum. This is done by placing the specimen in a high vacuum evaporator, and evaporizing the conducting material held in a tungsten basket (vacuum deposition).

The output of SEM in the form of a photograph can be used to evaluate the level of dispersion of particles, size and morphological features. SEM can be used with greater success to study the surface morphology of polymers, copolymers, polyblends and polymer networks; microstructure in two phase polymers, filled and reinforced plastics, deformation morphology of fibers, fracture studies and weathering of polymers.