SCOPE OF THE RESEARCH WORK
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Poly(p-phenylene sulfide) (PPS) is a versatile engineering plastic with excellent thermal/chemical resistance and mechanical performance. It is used for moulding of engineering components and also as a corrosion resistant coating on various substrates. The polymer was first commercialized in late 1972. The combination of properties offered by the material has made it an important engineering thermoplastic for metal replacement.

The polymer has great commercial significance. However, there is little published literature on the kinetics and structural development during the polymerization. A study of the polymerization to generate PPS is also of fundamental interest. This precipitation polycondensation reaction is a novel heterogeneous process. The commercially significant polycondensation reactions which are homogeneous systems are the production of unsaturated polyesters,nylons, phenolic resins, polyurethanes etc. Thus, the study of PPS synthesis would also elucidate aspects of the effect of solubility of reactants in the reaction medium on kinetics, the growth/propagation of the polymer chain in the solid phase after precipitation and the interrelation of the chemical reaction kinetics and physical processes such as precipitation and crystallization. It is this line of thinking that prompted the present investigation of the kinetics and structure development during the synthesis of PPS.

The polymerization to PPS involves the reaction of 1,4-dichlorobenzene (PDCB) with sodium sulfide in N-methyl pyrrolidone (NMP),
a highly polar solvent. The reaction may be represented as:

\[
\text{heat} \quad \text{n Cl} \quad \text{Cl} \quad + \text{nNa}_2\text{S} \quad \rightarrow \quad \text{ }(\text{Cl} \quad \text{S})_n \quad + \quad (2n-1) \quad \text{NaCl}
\]

The reaction is usually carried out in a polar solvent at high temperature (265°C) and pressure (≈ 160 psi). In the present work, the reaction was studied at 195°C and at a pressure of ≈ 35 psi. The system involved the use of PDCB in a slight excess.

The scope of the doctoral research touched on the following aspects concerning the polymerization to generate PPS.

i) Polymerization kinetics

ii) Mechanistic studies by varying the reactants and catalyst.

iii) The effect of physical reaction parameters such as stirring speed and dilution, on the yield and degree of polymerization.

iv) Characterization of the degree of polymerization with reaction time by microanalysis and dilute solution viscosity measurements.

v) Characterization by differential scanning calorimetry, the physical structure of the polymer generated at different conversions.

vi) Morphological characterization by x-ray diffractometry and scanning electron microscopy.

The kinetics and structure development during the polycondensation to PPS were investigated by collecting and analysing polymer samples generated at different reaction times. The conversions were evaluated by volumetric analysis, the amount of sodium chloride formed
and the unreacted sodium sulfide present. The polymer yields were determined gravimetrically. The polymer formed at different reaction times were characterized by chlorine end group analysis, dilute solution viscosity, thermal evaluation, x-ray diffractometry studies and particle size determination by scanning electron microscopy. In this manner, the interrelationships between kinetics and structure development were studied.

The following experiments were carried out to elucidate the polycondensation mechanism and to propose a probable reaction scheme. These involved the use of:

(a) Sodium para chloro thiophenoxide as initiating species
(b) Excess PDCB to accelerate the initial reaction steps
(c) Sodium hydroxide as probable catalyst
(d) 1,4-dibromo benzene instead of 1,4-dichloro benzene

In most precipitation polymerization reactions, the polymer precipitates out after a critical degree of polymerization is attained. In such heterogeneous systems, the transport of reactants exerts considerable influence on the reaction rate. In order to study the diffusional limitations on the polycondensation to PPS, the yield data at fixed reaction time were obtained at different stirring speeds and different dilutions. The results of the study were analyzed to interrelate kinetics with structure development.