SUMMARY AND RECOMMENDATIONS
SUMMARY AND CONCLUSIONS

The polycondensation reaction to generate PPS involves the reaction of 1,4-dichlorobenzene (PDCB) and sodium sulfide in a highly polar solvent like N-methyl pyrrolidone (NMP). The reaction could be represented as,

\[
\text{n} \quad \text{Cl} \quad \text{Cl} \quad + \quad \text{n} \quad \text{Na}_2 \quad \text{S} \quad \xrightarrow{\text{heat}} \quad \text{(solvent)} \quad \left(\begin{array}{c}
\text{S} \\
\end{array}\right)_{\text{n}} \quad + \quad \left(2\text{n}-1\right) \quad \text{NaCl}
\]

In the actual commercial process of Phillips Petroleum, the reaction temperature is set at 265°C which generates a pressure of \( \geq 160 \) psi.

In the present investigation, the reactions were conducted at 195°C and a pressure of about 35 psi. The following aspects concerning the polycondensation reaction were investigated.

(1) Kinetics of polycondensation with concurrent characterization of the degree of polymerization with reaction time by microanalysis and dilute solution viscosity measurements.

(2) The effects of physical reaction parameters such as stirring speed and dilution on the yield and degree of polymerization.

(3) Thermal characterization by differential scanning calorimetry and thermogravimetric analysis to elucidate structure development in polymerization.

(4) Morphological characterization by x-ray diffractometry and scanning electron microscopy to illustrate interaction between kinetics and structure development.

(5) Mechanistic studies involving the variation of reactants to postulate a possible mechanism for the reaction.
The polycondensation kinetics were studied with the reaction of PDCB with sodium sulfide at a molar concentration of 1.064:1. This was used as the reference set. The synthesis of PPS was found to differ from the conventional polycondensation reactions in the following aspects.

(i) The polymer yield was significant even at very low conversions.

(ii) The presence of unreacted monomers was noted even at conversions as high as 97 percent.

(iii) The polymer precipitated during the course of the reaction. However, the molecular weight of the polymer was found to increase continuously with reaction time indicating that the polymerization continued even after precipitation of the low molecular weight oligomer.

(iv) The kinetic data showed a second order dependance with two distinct regions of reaction rates. The initial reaction rate was slower upto 50 percent conversion. This was followed by a faster rate from 50 to 97 percent conversion.

The effect of physical and chemical parameters on the kinetics and molecular weight development was studied by conducting the following experiments.

(a) Variation in reactor geometry. Teflon versus stainless steel reactor.

(b) Variation in the speed of agitation and extent of dilution under the standard set of conditions.

(c) Use of sodium parachloro thiophenoxide (SPCTP) as initiating species.

(d) Use of large excess of PDCB.

(e) Use of paradibromobenzene (PDBB) in place of PDCB.
The kinetic data obtained in the stainless steel and Teflon reactor were comparable. In experimentations to evaluate the effect of stirring and extent of dilution, the reaction time was fixed at 6 hours while the other parameters were unaltered from those in the reference set. The polycondensation reaction was found to be extremely sensitive to the extent of dilution. Variance in stirring affected the reaction, in comparison, only marginally. The yield and degree of polymerization dropped significantly with increasing dilution.

In the case of the experiments where SPCTP was used, no significant change in the rate was observed. The variation in rate was within experimental limitation. However, the regimes over which two different rates were observed did vary. The initial slow rate was observed up to 36 percent conversion when SPCTP was used versus 50 percent for the reference set.

In reactions wherein a large excess of PDCB was used, the rate was evaluated by using the valid non-stoichiometric equation. The notable feature in this system was the observation that the rate in the later part of the reaction was an order of magnitude slower as compared to the initial rate. The observed trend was thus reversed as compared to the reference set where an initial slower rate was followed by a faster rate in the later stages of the reaction.

In the experiments wherein PDBB replaced PDCB, a conversion of about 50 percent was achieved after a short reaction time of only 10 minutes, whereas in the reference set with PDCB, the half-way point was reached after 2 1/2 hours. The initial reaction rate in this system was an order of magnitude faster as compared to the reference set. The rate in the later part of the reaction was however identical to that observed for the reference set.
The reference set samples were characterized for the number average molecular weight by microanalysis for estimation of chlorine end groups. It was noted that the polymer molecular weight increased with reaction time inspite of polymer precipitation during the reaction once a critical molecular weight was attained. The intrinsic viscosity measurements in 1-chloronaphthalene were made by a single point relative viscosity determination. The intrinsic viscosity levelled off after a reaction time of 6 hours, but the molecular weight as estimated by microanalysis continued to increase further with reaction time. The polymer thus has a wide molecular weight distribution.

The thermal transitions of the reference set were studied using differential scanning calorimetry. The notable feature of the thermograms was the presence of multiple first order transitions in the first heating cycle, which disappeared in the subsequent heating cycle (from the melt crystallized state). The crystallization peaks were however identical. The thermogram from the first heating cycle corresponds to the morphology of the as-precipitated state versus the morphology in the melt crystallized state in the subsequent scans. The differences due to the change in morphology with thermal conditioning were thus brought out in these studies.

The thermogravimetric analysis of the samples were evaluated in air. The polymer samples differed in the concentration of -SNa end groups. While the polymers formed at low conversions had high concentration of -SNa end groups, those formed at higher conversions would be relatively richer in -Cl end groups. This was reflected in the residue formed as a function of reaction time. The polymer samples formed at lower conversions were thermally less stable. A polymer of thermal stability comparable to commercial sample Ryton V-1 was obtained after a reaction time of 6 hours.
The structure, growth and morphology of the polymers synthesized were investigated by x-ray diffractometry and scanning electron microscopy. It was found that the crystal structure was unaffected while the percent crystallinity decreased marginally with increase in reaction time. The growth of the particle size as well as the total polymer mass formed was found to follow a time dependance of the form,

$$X_t = X_0 (1 - e^{-at})$$

where, $X_t$ represents particle size or mass at time 't', and $X_0$, the value of the parameter at large reaction times.

The total number of particles however decreased as the reaction time was increased. The particle size distribution was found to be dependant on the reaction time, stirring speed and also the concentration of the reactants in the feed. The distribution curve was noted to be sharp, containing at small particle size for short reaction time, high speed and low concentration of the reactants.

The particle morphology showed very strong dependance on reaction parameters. The polymer particles obtained initially have sharp, well defined shapes reminescent of crystalline materials. With increasing reaction time, these develop complex morphologies with sheaf-like structure. This was found to be true for polymer formed at different stirring speeds. Most intricate morphology was noticed in the samples synthesized at very low rpm. The dilution of the reactants in the feed, caused the particles to decrease in size and also to develop an oblong platelet type two dimensional morphology. The results lead to the conclusions that control over reaction time, speed of stirring and concentration of the reactants in the feed are necessary to produce a polymer suitable for specific applications.
RECOMMENDATIONS FOR FUTURE WORK

(1) The effect of halide substituent on the benzene ring could be studied by reacting sodium sulfide with PDCB, PDBB and para diiodo-benzene (PDIB). The trend studied with PDBB and PDCB predict a faster rate at least in the initial stages for the PDIB reaction.

(2) The role of the group at para position to the substitution center could be revealed by the reaction of sodium sulfide with 1-chloro, 4-bromo benzene. The determination of the relative rates of formation of sodium chloride and sodium bromide will be a valuable pointer. Reactions with PDBB indicated a faster rate in the initial stages of the reaction. If this is primarily governed by the bromo group para to the substitution center rather than the leaving group itself, similar trend should be noted for the generation of sodium chloride in this system as well.

(3) Homopolycondensation reactions of sodium parachloro thiophenoxide and sodium para bromothiophenoxide would also help, in deducing the effect of halide centre at the para position. Reactions with PDCB and PDBB indicate that the reaction rates might be comparable. This system would also confirm whether the rate of the reaction is uniform or bimodal.

(4) Molecular weight build up by using a comonomer like dichloro diphenyl sulfone can be studied to prepare copolymers that could be used directly for various end applications. PPS synthesized with PDCB and sodium sulfide requires molecular weight enhancement for molding grade applications.

(5) Addition of reagents like pyridine to the reactants, that would increase the electron density around the halogen atom that is to
be eliminated could be explored. This step would assist the escape of the halogen as an ion from the aromatic nucleus.

(6) ESR studies to evaluate conclusively whether the mechanism is SNAr or has free radical characteristics as recently reported.

(7) Systematic evaluation of molecular weight build up and molecular weight distribution as a function of reaction time for the system PDCB-sodium sulfide.