CHAPTER 5
MORPHOLOGICAL STUDIES
5. MORPHOLOGICAL STUDIES

Most high temperature polymers are based on aromatic units. Amongst these, those based on para phenylene type such as polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polyether ether ketone (PEEK) and polyether sulfone (PES) have attracted much attention in the recent years due to their excellent thermal/chemical stability and resistance to corrosive materials. The unique feature of PPS is its thermal stability in air upto 400°C and the ability to be transformed into fine insoluble, chemical resistant coating by thermal curing process. The adhesive properties of PPS towards various metal substrates are excellent and is an extremely useful material in high temperature coatings.

It is well known that growth, structure and morphology of the polymer play an important role in governing the various properties for end use application of the processed articles. In particular, the size, shape and structure of the polymeric powders are critical factors influencing their processibility in solid state compaction and sintering processes and also the coating properties. These powder metallurgical processing techniques are used extensively for PPS coatings. The studies on growth and morphology of PPS samples polymerized under different conditions would be useful in a better understanding of its behaviour in subsequent processing steps. The crystallinity, particle size and morphology of PPS synthesized under varying conditions have been investigated by x-ray diffraction and scanning electron microscopy.
5.1 X-RAY DIFFRACTION STUDIES

The experimental details for obtaining the XRD-scans are described in Section 2.9. The polymer samples collected at different reaction times in the reference set were chosen for the investigation. The dried powder samples were used for these investigations.

Figures 58, 59 and 60 show the wide angle diffraction scans (WAXS) for PPS samples collected at 1/2 hr, 1 hr, 2 hr, 3 hr, 6 hr and 10 hr reaction product samples in that order. It is seen that the region of diffraction angle (2θ) indicated, there are four major peaks occurring at 18.8, 20.5, 25.5 and 27.4 degrees which correspond to crystalline form of PPS. There are two additional reflections seen in the WAXS of samples collected at low reaction time (1/2 hr and 1 hr). However, the intensity of these peaks decreases rapidly with increase of reaction time and for reaction times higher than 2 hr, these additional peaks are totally absent in the WAXS data.

It is well known that PPS would crystallize in orthorhombic configuration[^250] with unit cell dimensions of a = 8.67Å, b = 5.61Å and c = 10.26Å. The analysis of the WAXS data showed that most of the reflections could be assigned according to this crystalline structure. For example, the four major peaks shown in Figures 58-60 were assigned as reflections from the planes corresponding to Miller indices.
FIG. 58: XRD SCANS - 1/2 hr, 1 hr SAMPLES
FIG. 59: XRD SCANS—2 hr, 3 hr SAMPLES
Fig. 60: XRD Scans - 6 hr, 10 hr Samples
110, 110/200, 112/003 and 211 respectively. This was found to be the case for all the samples investigated, irrespective of the differences in reaction conditions such as reaction time, variation in stirring speed and dilution of the reactants.

The crystallinity, on the other hand, was dependant on the reaction time to some extent. The crystallinity was determined from the regression curve analysis\textsuperscript{251} of the diffractometer scans as per the following relation:

\[
C_i = [1 + 0.7 (\phi_a + \phi_c)]^{-1}
\]

where, \(C_i\) is the crystallinity index, \(\phi_a\) and \(\phi_c\) are the areas under the amorphous halo and crystalline peaks.

The data on the variation of \(C_i\) with reaction time, evaluated from the four prominent peaks corresponding to 110, 200, 111 and 211 reflections in the 2\(\theta\) range 10-30 degrees are illustrated in Figure 61. It is seen from the figure that as the reaction time is increased, the crystallinity decreases slightly from 74 % to a value of 68 % upto
a reaction time of 6 hours. There is no significant change in C beyond 6 hours reaction time. The low molecular weight fractions are known to have higher crystallization rate and hence crystallinity as compared to high molecular weight polymers. The PPS samples synthesized have a wide molecular weight distribution. The crystallinity values noted for low reaction times could be due to these species in the polymers isolated.

5.2 SCANNING ELECTRON MICROSCOPE STUDIES

The particle size distribution and average particle size were evaluated using a scanning electron microscope. The instrumental details are described in Section 2.10. Counts were taken for the existing particles of various sizes in the electron beam scanned area (0.5 mm²) and the spot was shifted to various locations of the sample. Percentage average values for each size was then determined from these. The average particle size was taken as the weighted mean value. The data on the average particle size growth variation with reaction time are presented in Table 28. The data in particle size-polymer yield and reaction time are shown in Figure 62. It is seen that the particle size, which is initially less than a micron, increases rapidly upto 3 hours and more gradually for higher reaction times, tending to the asymptotic limit of 11 microns for very large reaction time. The polymer yield data also follows a similar trend.

Figure 63 shows the actual distribution of particle size obtained after polymer isolation at different reaction times. In the early stages of the reaction, the distribution curve is sharp and shows a maximum at about 1 micron particle size. As the reaction time is increased, the
<table>
<thead>
<tr>
<th>Reaction time, ( t_\text{hrs} )</th>
<th>Average particle size, ( S_\text{t} ) microns</th>
<th>Yield, ( Y_\text{t} ) gms</th>
<th>Total number of particles, ( N_\text{t} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.59</td>
<td>( 8.13 \times 10^{11} )</td>
</tr>
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<td>3.0</td>
<td>6.2</td>
<td>( 3.95 \times 10^{10} )</td>
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<td>10.0</td>
<td>20.9</td>
<td>( 3.6 \times 10^{9} )</td>
</tr>
</tbody>
</table>
FIG. 62: PARTICLE SIZE - YIELD - REACTION TIME DATA
FIG. 63: PARTICLE SIZE DISTRIBUTION - REACTION TIME DATA
distribution curve becomes increasingly broader and the maximum peak value shifts towards higher particle size region. Figure 71 shows the typical SEM of particles obtained at \( t_r \) of 6 hours. It is seen that there are a large number of particles with varying sizes ranging from 3 to 10 microns. At reaction times beyond 6 hours, however, the curve again tends to become sharp centering about 11 microns though it is asymmetric in the higher particle region indicative of upper limit of the size can be achieved under the reaction conditions investigated.

In order to investigate the exact time dependance of the growth phenomena, a plot of \( \log (S_t - S_f) \) with reaction time was made where \( S_t \) is the saturation limit of the particle size and \( S_f \), the average particle size at time \( t \). The data are shown in Figure 64. It could be seen that the plot is a linear one with a negative slope suggesting that the growth equation is of the type,

\[
S_t = S_f (1 - e^{-\alpha t})
\]

where, the slope \( \alpha \) has a value of \( 2.6 \times 10^{-5} \)/sec. Figure 64 also shows the plot of \( \log (m_t - m_t^*) \) with reaction time where \( m_t \) and \( m_t^* \) represent the mass of polymer obtained at asymptotic limit (reaction time \( \infty \)) and reaction time \( t \) respectively. This graph interestingly is also a linear one with a slope of \( 3.8 \times 10^{-5} \)/sec. The build up of the total mass also follows a similar time dependance as shown below.

\[
m_t = m_f (1 - e^{-\alpha t})
\]

where, \( \alpha \) has a value \( 3.8 \times 10^{-5} \)/sec.

It thus seems that the build up of the polymer mass is accompanied by growth of the original particles rather than reaction of new number
FIG. 64: PLOT OF $S_f - S_t / S_f$ AND $M_f - M_t / M_f$
VERSUS REACTION TIME
of particles. This may be further confirmed by estimating the total number of particles in polymer mass obtained at different reaction times. The total number of particles can be estimated by calculating the mass of the particle from average particle size giving volume and crystallinity giving effective density (crystalline + amorphous) and dividing the total mass by it. These calculations are summarized in Table 28. The total number of particles are found to decrease with increase in reaction time.

Figures 65, 66 and 67 show the scanning electron microscopes of PPS obtained under identical reaction conditions but at different reaction times of 1, 3 and 10 hours respectively. It could be noted that the particles at reaction time of 1 hour are small, well defined and having (crystalline-like) sharp boundaries indicative of high crystallinity. As the reaction time is increased, the particles not only grow in size but also develop complex structure as seen from Figures 67 and 68. It may be noted from these figures that as the reaction proceeds, the polymer mass develops on top of the existing particles from all directions giving rise to generally spherical shape but containing 'sheaf-like' structure (opened cabbage analogy). The most interesting feature of these observations is that the sheaf-like structure continues to grow even at large reaction times.

The growth behaviour of the polymer amongst the various possibilities, under a given set of reaction conditions, depends upon the nucleation and termination rates, the type of polymerization reaction (condensation, addition etc.) and the phase of the monomers (solid, liquid or vapour). For example, if the nucleation rate remains steady for a given time period but the termination rate is high, then one would expect the polymer mass to contain small particles with sharp distribution curve.
SEM OF PPS PARTICLES 1 hr, 3 hr, AND 10 hr
FIG. 68: PARTICLE SIZE DISTRIBUTION FOR VARIOUS STIRRING SPEEDS.
The rate of growth of the polymer mass depends upon the reaction kinetics or the type of reaction such as whether the type is condensation or addition. The crystallinity, orientation etc. depend upon the form of the monomers used, as for example in the solid phase one can expect high crystallinity and even epitaxy to develop. Extensive studies on the particle formation for polyvinyl chloride have revealed that the particle size and shape not only depend upon the mode of reaction such as suspension, emulsion or bulk polymerization but also the process variables like the reaction temperature, stirring speed, suspension medium etc. However, such studies have not been reported for other polymers. In particular, no data are available on PPS. Nevertheless, one may well understand that the various parameters are bound to play an important role in the type of polymer particles produced.

As already indicated in Section 3.1, sodium sulfide is not completely soluble in the solvent used for the reaction. The state of sodium sulfide at the reaction temperature in NMP, is as tiny particles of less than 1 micron floating in the medium representing a suspension system in a solution of the other reactant PDCB. As the polycondensation reaction progresses, the growth takes place mainly on the solid-liquid interface with the solid particles acting as nuclei, the concentration of which is very high in the initial stages but drops at the latter stages of the reaction. However, it was noted that the total number of particles decreased with an increase in reaction time, indicating the possibility of considerable amount of coalescence taking place internally. This process seems to be present at the microscopic level rather than macroscopic one since the particle morphology did not give any indications of agglomerate formation.
5.3 EFFECT OF STIRRING SPEED ON POLYMER MORPHOLOGY

The polymer samples collected at the same reaction time of 6 hours but with different stirring speeds of 0, 400 and 660 RPM were analysed for their morphology. The particle size distribution is shown in Figure 68 for samples obtained at varying stirring speeds represented by curve nos. I, II and III. A comparison of these curves indicates that as the stirring speed is increased, the average particle size decreases and the distribution becomes progressively sharp. This seems to suggest that the coalescence process which has been outlined earlier is greatly affected by the agitation created in the medium. However, since the polymerization processes are also dependant on the stirring speeds, their correlation is not a simple one.

Figures 69, 70 and 71 show the scanning electron micrographs on the particles obtained in the polymer samples at 0, 400 and 660 rpm respectively. It is seen that large amount of polymer can build up as a single particle (> 12 microns) with very complex internal structure, as revealed in Figure 70, at low stirring speeds (small amount of internal convectional currents exist in the case where no mechanical stirring was used). With the increase in stirring speed, the particles seem to develop more and more sheaf-like structure. There was practically no change in the crystallinity (~ 66 percent) with increase in stirring speed suggesting that crystallization rates were quite high. On the other hand, the particles obtained at high speeds (660 rpm), seem to have less porosity.

5.4 EFFECT OF DILUTION ON POLYMER MORPHOLOGY

In this set of experiments, the reaction time was set at 6 hours, but the concentration of the reactants were varied, keeping the stoichiometric
SEM OF PPS PARTICLES WITH DIFFERING STIRRING SPEEDS
and reaction parameters identical. Some remarkable changes were noted in the morphology of PPS samples taken for analysis. Figures 73, 74 and 75 show the particle morphology, as revealed by SEM, when the initial concentration was decreased from 100 to 50 and 25 percent respectively representing a dilution factor of 1, 2 and 4. In the normal case (dilution factor 1), the particles have more or less spherical boundaries but with internal sheaf-like structure, those for diluted reactants have an entirely different morphology and particle size. In the case where the dilution factor is 4 (Figure 75), the particle growth is very much restricted and their shape is oblong platelet like giving almost two dimensional appearance. It is interesting to note that this morphology is entirely different from that observed at low reaction time. This suggests that the neighbouring nuclei have a strong influence on the growth pattern of the polymer in the particular state. Further, the shape of the particles obtained under dilute conditions is almost two dimensional one while that for high concentrations of the reactants is a three dimensional one. The particle size distribution is also extremely sharp in the former case than in the latter, suggesting that the termination of the particle growth i.e. the upper limit of the size \( S_T \) is mainly set by concentration of the reactants rather than other parameters.
SEM OF PPS PARTICLES WITH INCREASING DILUTION
5.5 CHARACTERIZATION OF STRUCTURE, CRYSTALLINITY AND MORPHOLOGY OF PPS FROM PDBB

The PPS polymer synthesized using PDBB as the reactant in place of PDCB was characterized for structure, crystallinity and morphology by means of x-ray diffraction and scanning electron microscopy in the same way as described earlier.

Figures 76 to 78 show the WAXS scan for the polymer obtained after the reaction time of 2.1/2, 7, 22, 45 and 180 minutes respectively. By comparing these curves, it is seen that the intensities of reflections occurring at 2θ 18.6, 22.5, 25 and 28 degrees progressively decrease while those for the reflections at 19.2, 21 and 26 degrees increase with the increase in the reaction time (t_r). These findings suggest that there is a reordering of the crystalline structure for the polymer with the increase in reaction time. These results are discussed later in the chapter.

The crystallinity (C_j) was determined from the WAXS data in the same manner as for PPS synthesized from PDCB. The variation of crystallinity with the reaction time for the same concentration of reactants and stirring speed is shown in Figure 79 (curve I). It is seen that C_j increases slightly first from 62 percent to 68 percent with increase of t_r upto 45 minutes but with the further increase of reaction time, the crystallinity decreases gradually. This is in contrast to the findings in the case of PPS synthesized from PDCB where the crystallinity from the high value (74 percent) was found to decrease continuously with the increase of reaction time.

The growth of the particles was studied by means of SEM as before and curve II of Figure 79 shows increase of average particle size as a function of reaction time. It is seen that the particle size (S_I) increases
FIG. 76: XRD SCANS - 2.5 min, 7 min SAMPLES
FIG. 77: XRD SCANS - 15 min, 22 min SAMPLES
FIG. 78: XRD SCANS - 45 min, 180 min SAMPLES
rapidly with increase of reaction time up to a $t_r$ of 60 minutes above which the particle size increases slowly to obtain a limiting value ($S_\infty$). This behaviour is very similar to that noted for PPS synthesized from PDCB only with a difference that the time scales in the present case are very small (minutes) as compared to the former case (hours). Curve III in Figure 79 shows the variation of total polymeric mass obtained as a function of reaction time, other reaction parameters being maintained the same. In this case too, it is seen that the polymer yield ($M^e$) increases rapidly with increase in $t_r$ up to a reaction time of 45 minutes above which it gradually tends to a constant value (18 grams). These observations clearly indicate the polymerization reaction proceeds at a very rapid rate in the case of PDBB giving a large polymeric yield. However, the particle growth takes place at a slower rate and proceeds more or less uniformly over the reaction period studied.

In order to study the time dependance of the growth phenomena for both particle size as well as polymer yield, a plot was made as before of $\ln(\Delta S/\Delta S^0)$ and $\ln(\Delta M/\Delta M^0)$ versus $t_r$ on a semilog scale as shown in Figure 80. $\Delta S$ and $\Delta M$ are defined as,

$$\Delta S = (S_f - S_t)$$

and

$$\Delta M = M_f - M_t$$

respectively.

Curve I is for the particle size growth while curve II is for the polymer yield. It is seen that the graph for the particle size growth is a linear one with a single slope suggesting that the time dependance for the particle size follows the equation,

$$S_t = S_f (1 - e^{-\alpha t})$$
FIG. 79: VARIATION OF CRYSTALLINITY (I), AVERAGE PARTICLE SIZE (II) AND TOTAL POLYMER YIELD (III) FOR PPS SYNTHESIZED FROM PDBB
FIG. 80: PLOT OF \( \frac{(S_f - S_t)}{S_f} \) AND \( \frac{(M_f - M_t)}{M_f} \) AGAINST REACTION TIME ON SEMILOG SCALE - PPS FROM PDBB
where $\mathcal{A}$ is constant with a value of $8.8 \times 10^{-5}$ $\text{sec}^{-1}$.

The graph for the time dependence of the yield (curve II) on the other hand, does not appear to be a simple linear one. However, one may represent the graph in terms of two straight lines having different slopes as shown in the Figure 80. The slope in the initial region is estimated to be $3.5 \times 10^{-4}$ $\text{sec}^{-1}$ while that in the high $t_r$ region is seen to be $4.7 \times 10^{-5}$ $\text{sec}^{-1}$. Thus the reaction is seen to proceed at two distinct rates giving different yields with increase in reaction time. The time dependence of the yield nevertheless can be represented by the equation,

$$M_t = M_f (1 - e^{-\beta t})$$

with $\beta = 3.5 \times 10^{-4}$ $\text{sec}^{-1}$ for $t_r < t'$

and $\beta = 4.7 \times 10^{-5}$ $\text{sec}^{-1}$ for $t' > t'$

where $t'$ is the delineating time (35 minutes) between the fast and slow processes.

The particle size distribution for PPS synthesized PDBB for various reaction times is shown in Figure 81. Curves I, II and III correspond to reaction time of 15, 30 and 180 minutes respectively. It is seen that the distribution of particles is quite sharp in all cases - namely the initial, intermediate and the final stages of the reaction (large $t_r$). The peak position however is seen to shift to higher values of particle size with increase in reaction time. Figure(81a) shows the typical SEM of PPS particles obtained at a reaction time of 30 min. and it is clearly seen that most of the particles have similar shape and size indicative of very sharp particle size distribution. In the case of PPS synthesized from PDCB (page 186), it was found that the particle size distribution was sharp at small reaction
FIG.81(a)

SEM OF PPS FROM PDBB
FIG. 81: PARTICLE SIZE DISTRIBUTION IN PPS SYNTHESIZED FROM PDBB
times as well as for very large $t_r$ while for the intermediate stages (3-6 hours), the particle size distribution was a broad one. In the present case, it has already been shown that the reaction is faster by an order of magnitude (see Chapter 3) and hence the growth is expected to be much faster than in the case of PPS synthesized from PDCB. However, since the particle size distribution is also sharp, it appears that either the termination rate is fast or the number of nucleating centers is large. Since the particles continue to grow even at large reaction times at which the maximum yield of polymer is obtained, the former possibility seems to be unlikely. On the other hand, the second possibility of large number of nucleating centers with high growth rate can give not only sharp distribution in particle size but also large number of particles in the total polymer mass. This has been confirmed during the SEM studies on the morphology of these particles.

Figure 82 shows the morphology of the PPS particles obtained at various reaction times. The photographs (a), (b) and (c) are for reaction times of 15, 30 and 180 minutes respectively. It can be clearly seen that the particles in all cases have more or less similar morphology consisting of flat, round disc shaped platelets with practically no variation in their shape but only in size. Further these morphological features were observed even for very large reaction times. By comparing these figures with Figures 65-68, it is seen that there is a remarkable change in morphology by the use of PDBB for the synthesis of PPS. While in the former case (PPS synthesized from PDCB) very intricate morphology of lettuce type, sheaf like or even pealed onion type was noted, that in the later case it was more or less uniform disc type. It is interesting to note that morphological features observed in the present case are somewhat similar
FIG. 82(a)

FIG. 82(b)

FIG. 82(c)

SEM OF PPS FROM PDBB
to those seen in very dilute conditions of PPS synthesized from PDCB. (Figure 73-74), wherein the particles were also platelet shaped. However, the particle size noted there was very much smaller ($<2 \mu m$) than in the present case.

Now, the growth and morphology of the polymer depend upon the nucleation and termination rate, type of polymerization, kinetics of reaction, the phase of the monomer and also on factors such as the presence of ionic impurities, aggregation, clustering or coalescence of polymer molecules/particles etc. Amongst these various factors, the dominating ones for the present studies seem to be related to the rate of reaction and presence of ionic species. Since these parameters are essentially varied by using PDBB instead of PDCB for the PPS synthesis. In the early stages ($t_r < 15$ min.) of the reaction with PDBB, the rate being high, one would expect a large number of end groups to be present. These end groups would have to be incorporated in the subsequent growth of crystals. In order to accommodate such groups, the polymer crystal lattice would be distorted/modified. Such a modified lattice would give rise to additional peaks in the WAXS data which indeed have been observed by us (see Figure 76). As the polymerization reaction proceeds and the molecular weight builds up, the defects in the crystalline structure gradually reduce and more perfect crystals are available giving rise to increase in crystallinity and sharp diffraction peaks corresponding to the single orthorhombic type crystal structure of PPS described earlier (page 180). With further increase of reaction time, there would be corresponding increase of molecular weight and same processes which lead to the decrease of crystallinity as mentioned earlier would operate. Thus one finds the increase in $C_i$ up to a reaction time of 35 minutes but a decrease in $C_i$ for higher reaction times.
The time dependence of growth of polymer particle was found to be essentially similar to that for PPS synthesized from PDCB excepting for the fact that the constant $\alpha$ had much higher value (four times) in the present case. On the other hand, increase of the polymer yield with reaction time showed two regions; one where the rate was very high having an order of magnitude higher than the PDCB case and the second region where the rate was comparable to that of the PDCB case. These findings correlate well with the reaction kinetics for the polymerization process of PPS synthesized from PDBB (see Chapter 3). It has been shown in that chapter, that the polymerization reaction with PDBB follows a two step process with rate constants of $3.21 \times 10^{-4} \text{ m}^{-1} \text{s}^{-1}$ and $3.87 \times 10^{-5} \text{ m}^{-1} \text{s}^{-1}$ for two regions. By comparing these values with that the values of the constant $B$ in the two regions, it is seen that there is a good correlation between these values.

In addition to the polymerization process, the growth of the PPS particle also depends upon the termination rate as well as coalescence and other such phenomena. It was seen earlier that there was a considerable amount of coalescence taking place in the particle growth of PPS synthesized from PDCB. This was evidenced by the fall in the total number of particles with the increase of reaction time. In the present case the total number of particles ($M_t$) in the polymer mass was estimated by taking into account the disc shaped morphology (cylinder shape) with known dimensions (from SEM), density of the polymer and yield for each reaction time. Table 29 shows the various values of $M_t$, $S_t$ and $M_t$ for the various reaction time $t_r$. It can be seen from the table that the total number of particles decreases slightly with increase of reaction time but still remains within the same order of magnitude. It is interesting
<table>
<thead>
<tr>
<th>$t_r$ (min)</th>
<th>Size $S_t$ (m)</th>
<th>Yield $M_t$ (gms)</th>
<th>Total No. of particles $N_t$</th>
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<tr>
<td>15</td>
<td>4</td>
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</tr>
<tr>
<td>180</td>
<td>10.5</td>
<td>17.8</td>
<td>$3.0 \times 10^9$</td>
</tr>
</tbody>
</table>

**TABLE 29**

GROWTH BEHAVIOR OF PPS FROM PDBB
to note here that for PPS synthesized from PDCB on the other hand $N_t$ decreased considerably (for same $t$), much more than an order of magnitude (see Table 28). This clearly suggests that in the present case the polymer mass builds up by continuous nucleation of fresh particles and their growth as the reaction time is increased rather than the growth of the already nucleated particles as observed for PPS synthesized from PDCB. These observations together with the sharp well defined boundaries of the PPS particles noted in the SEM photographs reveal the important role played by the ionic species and the type of the group in governing the morphology of PPS.

Summary

To summarize, the structure, growth and morphology of PPS samples synthesized under various conditions were investigated by using x-ray diffraction and scanning electron microscopic techniques. The studies revealed that although the crystal structure remained the same, there is a slight variation in the crystallinity. The crystallinity was found to decrease from 71 percent to 66 percent with increase in reaction time. The growth of the particle size as well as the total polymer mass formed (yield in gms) follow the dependance represented
by an equation of the form,

\[ X_t = X_o (1 - e^{-\alpha t}) \]

where, \( X_t \) represents the particle size or polymer mass at time 't' and \( X_o \) represents the value of these parameters at very large reaction times \( (t_r > 10 \text{ hours}) \). On the other hand, the total number of particles decreases with increase in reaction time.

The particle size distribution has been found to be dependant on the reaction time, stirring speed and the concentration of reactants in the feed. The distribution curve was noted to be sharp and centering at small particle size for short time, high speed and low concentration of the reactants. This was also the case for very large reaction times when the upper limit of the particle size was reacted, but there was asymmetry in the curve.

The particle size morphology showed a very strong dependance on various reaction parameters. In the initial stages, the particles have sharp well defined shapes reminescent of crystalline materials but with increase of reaction time these develop into complex morphologies with sheaf-like structure. This is found to be true even for the polymers grown at different stirring speeds. In fact, the most intricate morphology was noticed in the PPS grown at very low rpm. The dilution of the reactants in the feed cause the particles to decrease in size and also to develop an oblong platelet type two dimensional morphology.

These results have been explained on the basis of the formation of nuclei for the growth of polymer and their subsequent growth and also to some extent coalescence with the neighbouring ones. Sodium sulfide
seems to give rise to the initial nucleating centres and the polymer growth phenomena are not yet well understood due to the complexities of the morphological features.

PPS as obtained from the reaction, is usually heat treated in air (oxygen atmosphere) below the melting point of the polymer for various end applications. It is also treated with vapour of AsF₅ for producing conducting grade compounds. In these processes, the diffusion of gases into the polymer will be of great importance in deciding not only the various parameters such as temperature, partial pressure, time etc. used during the process, but also the ultimate properties that can be obtained after such treatment. On the other hand, in powder processing steps of PPS such as free sintering or coating, where powder compaction behaviour is involved, the particle size and shape will play an important role. Thus, it could be concluded that the control of the reaction time, stirring speed and the concentration of the reactants are essential to produce a proper polymer mass suitable for specific applications.

The results obtained above are consistent with the data obtained in the kinetic studies and thermal characterization. The change in rate observed after 3 hours of reaction, the optimum thermal properties attained after 3 hours of reaction time and the steady increase in viscosity upto 6 hours are consistent with the particle size growth upto 6 hours reaction time. It was also noted that optimum properties are obtained with a reaction time of 6 hours using the reference set conditions. The other notable observation that the dilution of the reactants has an important bearing on the PPS formed, rather than the change in stirring speeds, is clearly brought out in the morphological studies.
In the case of PPS synthesized using PDBB, it was noted that there was a reordering of crystalline structure with increase in reaction time. An initial increase in crystallinity from 62 to 68 percent upto a reaction time of 45 minutes is followed by a decrease in crystallinity with further increase in reaction time.

The particle size attained a limiting value after a reaction time of 60 minutes similar to PPS from PDCB except that the reaction times are very small. The particle size growth was linear following the equation:

\[ S_t = S_i (1 - e^{-\alpha t}) \], where \( \alpha = 8.8 \times 10^{-3} \, \text{s}^{-1} \)

The distribution of particles was very sharp. SEM photographs show the morphology to be consisting of flat round disc shaped platelets while PPS synthesized from PDCB had intricate morphology like lattice type, sheaf like or pealed onion type. Other notable difference observed was that the total number of particles remained of the same order while that in the case of PPS from PDCB, there was a decrease in increasing reaction time by an order of magnitude.

The time dependance on yield followed an equation of the form,

\[ M_t = M_i (1 - e^{-\beta t}) \]

where \( \beta = 3.5 \times 10^{-4} \, \text{s}^{-1} \) upto 35 minutes

and \( \beta = 4.7 \times 10^{-5} \, \text{s}^{-1} \) beyond 35 minutes

The time dependance on yield exhibited two regions as a function of reaction. This was noticed in the kinetics also where two regions with different rates were observed.