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Structure, growth and morphology of polyphenylene sulphide*

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The crystallinity, particle size and morphology of polyphenylene sulphide synthesized under various conditions have been investigated by X-ray diffraction and scanning electron microscopy. It was found that crystallinity decreased from 71 to 66% with increase of reaction time. The growth of particle size as well as total polymer mass followed a time dependence of the form $X = X_0 (1 - e^{-\alpha t})$. The particle size distribution curve was noted to be sharp centring at 3 μm for short reaction time, high speed of stirring and also for low concentration of reactants. The particle morphology showed very strong dependence on various reaction parameters. Intricate sheaf-like morphology was noted for the particles at long reaction times or low stirring speeds while oblong platelet type two-dimensional morphology was noted when a low concentration of reactants was used.

1. Introduction

Amongst the various high temperature polymers, those based on aromatic units, especially the paraphenylene type such as polyphenylene oxide (PPO), polyphenylene sulphide (PPS), polyether ether ketone (PEEK) and polyether sulphone (PES) have attracted much attention in the last few years since these possess many desirable properties such as thermal and chemical stability, resistance to corrosive chemicals etc. [1, 2]. Polyphenylene sulphide has additionally some unique features such as stability in air up to 400° C and processibility as a thermoplastic but at the same time being curable by heating to give insoluble, oxidation resistant material having excellent adhesive properties towards metals thus being extremely useful for high temperature coating applications [3, 4]. PPS has also drawn the attention of physicists and electrical engineers in as much as that it can be made conducting by doping with charge transfer agents such as arsenic pentafluroride [5–7]. It is well known that growth, structure and morphology play an important role in governing the various properties of the polymer-based articles. In particular, the size, shape and structure of polymeric powders are critical factors in coating and free sintering (powder metallurgical) techniques of processing polymers which are extensively used for PPS [8]. The particle compaction, packing and curing depend on these factors. Hence it was thought the studies on growth and morphology of the starting material itself, namely polyphenylene sulphide polymerized under different conditions, could be useful in understanding its behaviour in subsequent processing steps. The results of our investigations in this direction are reported.

2. Experimental details

Polyphenylene sulphide was synthesized on laboratory scale in a stainless steel 600 ml reactor provided with a variable speed mechanical stirrer, external heating chamber, cooling coils, etc. The polymer was prepared by reacting sodium sulphide (Na_2S) with paradichlorobenzene (PDCB) in *N*-methylpyrrolidone (NMP) at 195° C. NMP was obtained from GAF Corporation (USA) and used as such. PDCB was obtained from M/s High Purity Chemical, New Delhi (India) and its purity was determined to be greater than 99.9%. Na_2S was obtained from Poona Chemicals (India) but was recrystallized from methanolic solution prior to use. In a typical experiment, the required amount (15 g) of recrystallized Na_2S was dissolved in methanol and filtered. This solution together with 45 ml NMP was charged into the reactor and the temperature raised to 190° C. Heating was continued until the last traces of methanol/water were removed. A solution of PDCB (30 g/45 ml) was then added to the reaction mixture and temperature raised to 195° C and maintained at this value for the required period of time. The stirring speed was maintained in most experiments at 660 rpm but in some cases it was kept at 0 and 440 rpm. The dilution experiments were carried out by taking one-half or one-quarter parts of the constituents mentioned above. The reaction was stopped at any particular time by removing the heater and cooling the reactor vessel with tap water. The polymer mass was removed by flushing with methanol followed by filtering and thorough washing with water until no traces of NaCl, Na_2S, etc., remained. Complete details of the apparatus and procedure are being reported separately.

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Polymer powder obtained from the reactor at various stages was analysed for crystallinity, structure and morphology by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Philips PW1730 diffractometer with Cu$K\alpha$ target and β-nickel filter was used for X-ray diffraction studies. The microstructure and morphology were investigated by means of Cambridge Model Stereoscan 150 scanning electron microscope using powder samples placed on the mounting studs and coating them with Pd/Au alloy (vacuum deposited) for enhancement of contrast.

3. Results and discussion

The crystal structure, crystallinity, particle size and morphology were determined for PPS polymerized under various conditions. The various results obtained in our studies are described.

3.1. Structure and growth

Polyphenylene sulphide is known to crystallize in orthorhombic configuration with unit cell dimensions of $a = 0.867$ nm, $b = 0.561$ nm and $c = 1.026$ nm. This was found to be the case in all our studies irrespective of the differences in reaction conditions such as dilution, stirring speed, time and temperature (190 to 250° C). This was determined from the XRD patterns which had peaks at the same 2θ values for all cases. Crystallinity, on the other hand, depended to some extent on the reaction time (t_r). The crystallinity was determined from regression curve analysis of the XRD pattern as described earlier [9], which gave the follwing relation

$$C_i = [1 + 1.4(\phi_a/\phi_c)]^{-1} \qquad (1)$$

where C_i is the crystallinity index, ϕ_a and ϕ_c are the areas under amorphous halo and crystallinity peaks. The 2θ range of 10 to 30° where four prominent peaks corresponding to 1 1 0, 2 0 0, 1 1 1 and 2 1 1 reflections occur, was chosen for the evaluation of C_i. Fig. 1 shows the variation of C_i together with the average particle size (as determined from SEM) and also the amount of material (M_t) obtained for PPS reacted under the same conditions of temperature (195° C), stirring speed (660 rpm) and total charge (90 g) but with increasing time (t_r). It is seen from the figure that as t_r increases the crystallinity decreases slightly from 74% to a value of 68%, up to $t_r = 6$ h, but for higher values of t_r (> 6 h) there is practically little change in C_i. The low molecular weight fractions are known to have higher crystallization rate and hence crystallinity than high molecular weight polymers. The crystallinity values noted for low reaction times could be due to these species in the polymer mass.

The average particle size was taken as the weighted mean value and is indicated in Fig. 1, curve II, for various reaction times. It is seen that the particle size which is initially small (< 1 μm) increases rapidly up to 3 h and more gradually for higher t_r tending to the asymptotic limit (S_f) of 11 μm for very large reaction times. Curve III indicates the total mass of the polymer obtained at various reaction times and it may be noted that this curve also follows more or less similar trends as the above.

Fig. 2 shows the actual distribution of particle size

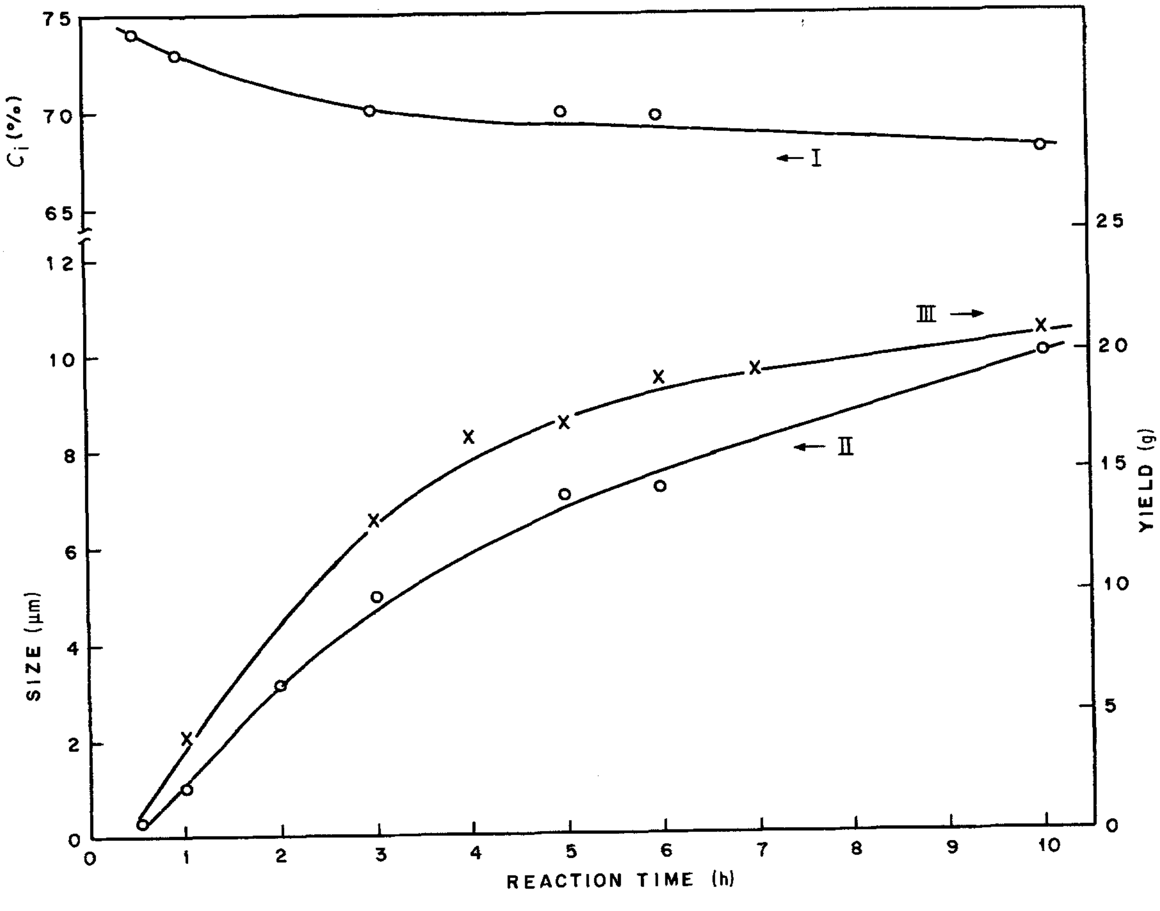

Figure 1 Variation of crystallinity (I), average particle size (II) and total polymer yield (III) with reaction time for PPS synthesized at 195° C, 660 rpm and 45 g total charge.

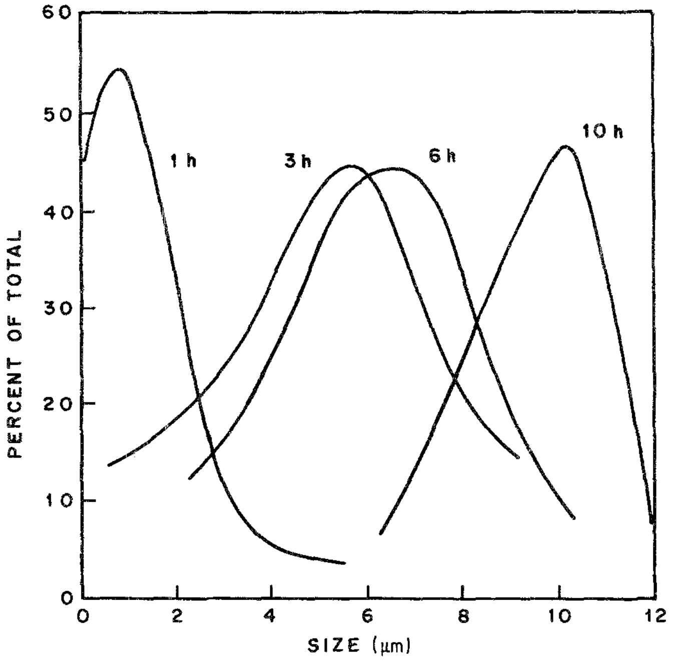

Figure 2 Particle size distribution in the PPS polymer for various reaction times.

obtained in the mass of polymer taken out of the reactor at reaction times of 1, 3, 6 and 10 h. In the early stages of the reaction, the distribution curve is sharp and shows a maximum at about 1 μm particle size. As t_r is increased the distribution curve becomes increasingly broader and also the maximum peak value shifts towards the higher particle size region. At very large times ($t_r > 6$ h), however, the curve again tends to become sharp centring at about 11 μm although it is asymmetric in the higher particle size region indicative of an upper limit of the size that can be built up under the present reaction conditions.

In order to investigate the exact time dependence of the growth phenomena, a plot of $\log(S_f - S_t)$ against t_r was made where S_f is the saturation limit of the particle size and S_t the average particle size at time t. Fig. 3 shows such a plot of PPS and it is seen that the graph is a linear one with a negative slope suggesting that the growth equation is of the type

$$S_t = S_f(1 - e^{-\alpha t}) \qquad (2)$$

where α is the slope $= 2.6 \times 10^{-5}\,\text{sec}^{-1}$.

Fig. 3 also shows (curve II) the plot of $\log(M_f - M_t)$ against t_r where M_f and M_t are mass of

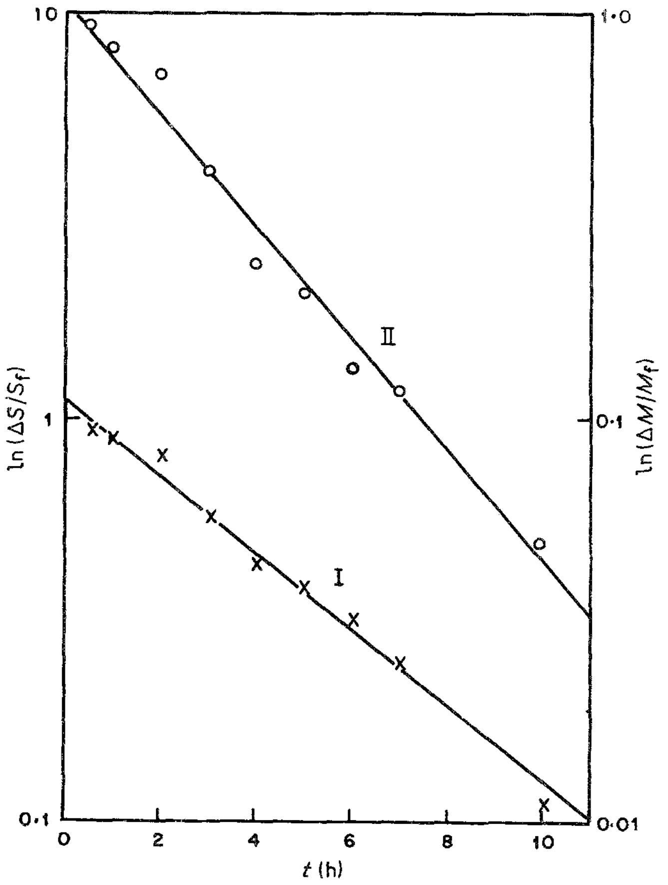

Figure 3 Plot of $(S_f - S_t)/S_f$ (I) and $(M_f - M_t)/M_f$ (II) against the reaction time (t_r) on a semi-log scale.

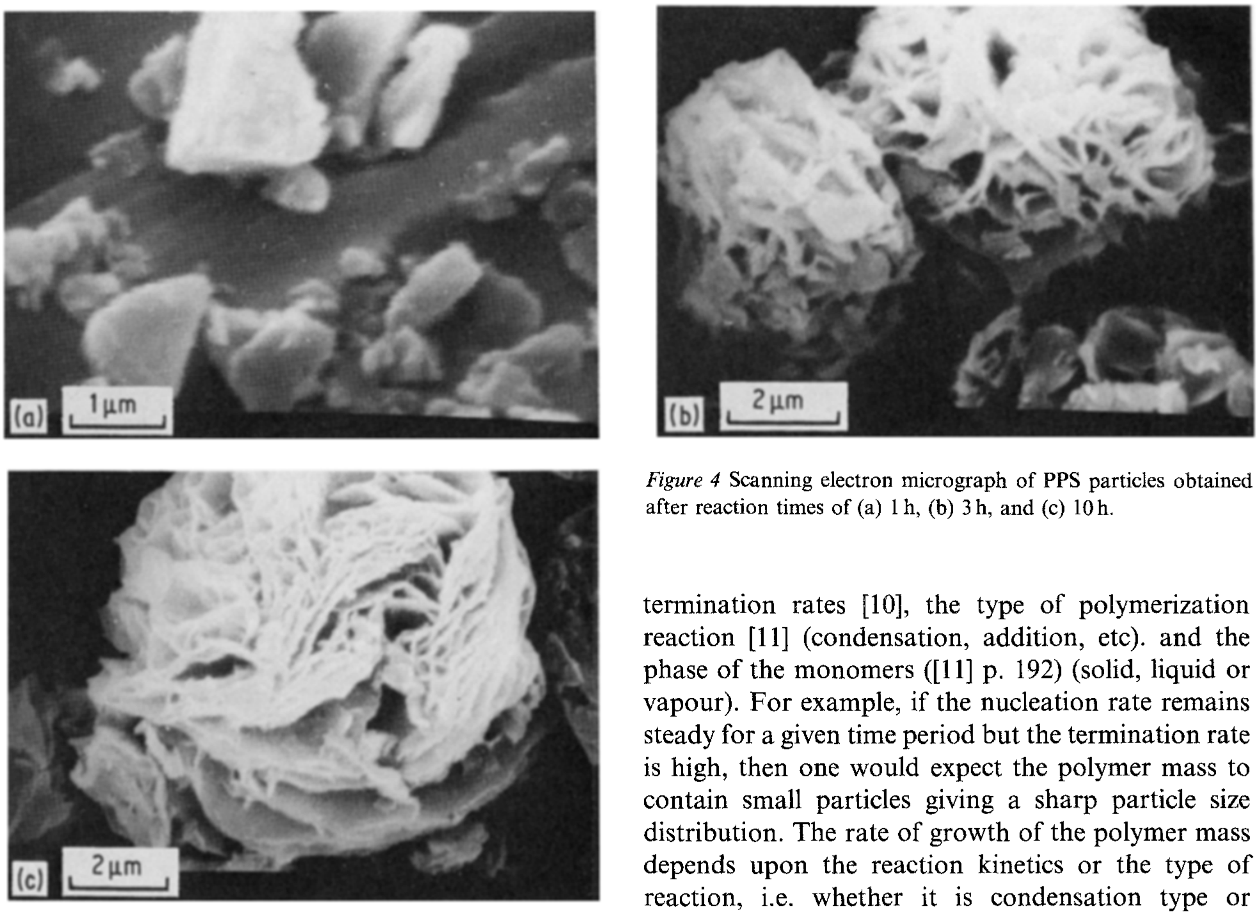

Figure 4 Scanning electron micrograph of PPS particles obtained after reaction times of (a) 1 h, (b) 3 h, and (c) 10 h.

polymer obtained at asymptotic limit (t_r) and $t_r = t$, respectively. It is interesting to see that this graph also is a linear one with a slope of $3.8 \times 10^{-5}\,\text{sec}^{-1}$. Thus the build up of the total mass also follows a similar time dependence, i.e.

$$M_t = M_f(1 - e^{-\alpha t}) \qquad (3)$$

where α is now $3.8 \times 10^{-5}\,\text{sec}^{-1}$.

It thus seems that the build up of the polymer mass is accompanied by growth of the original particles rather than creation of a number of new particles. This may be further confirmed by estimating the total number of particles (N_t) in the polymer mass obtained at each reaction time.

Figs. 4a, b and c show the scanning electron micrographs of the PPS particles obtained under the same reaction conditions but at different times, namely 1, 3 and 10 h, respectively. It is seen that the particles at $t_r = 1$ h are small, well defined and having (crystalline) sharp boundaries indicative of high crystallinity. As t_r increases, the particles not only grow in size but also develop a complex structure as seen from Figs. 4b and c. 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 a generally spherical shape but containing a "sheaf-like" structure ("lettuce"-like). The most interesting feature of these observations is that the sheaf-like structure continues to grow even at large reaction times.

Amongst the various possibilities, the growth behaviour of a polymer, under a given set of reaction conditions, would depend upon the nucleation and termination rates [10], the type of polymerization reaction [11] (condensation, addition, etc). and the phase of the monomers ([11] p. 192) (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 giving a sharp particle size distribution. The rate of growth of the polymer mass depends upon the reaction kinetics or the type of reaction, i.e. whether it is condensation type or addition type.

The crystallinity, orientation etc. depend upon the form of monomers used, as for example in the solid phase on can expect high crystallinity and even epitaxy to develop. Extensive studies on the particle formation for polyvinyl chloride have revealed [12–15] that the particle size and shape not only depend upon the mode of reaction, i.e. suspension, emulsion or mass polymerization, but also the process variables such as reaction temperature, stirring speed, suspension medium, etc. However, such studies have not been made for other polymers, in particular PPS. Nevertheless, one may well understand that these various parameters are bound to play an important role in the type of polymer particles produced.

Now, considering the various steps followed in the synthesis of PPS in the present case, it is quite possible that tiny microparticles of Na_2S (being not completely soluble in NMP) get suspended in the solution of PDCB (soluble in NMP) before the reaction starts. This possibility has been confirmed by us in a separate experiment where small amounts of methanolic solution of Na_2S were poured into NMP and heated to 195° C and observed in the hot stage of an optical microscope. Particles less than 1 μm in size were seen to be floating. Now as the polymerization reaction progresses, the growth takes place mainly at the solid–liquid interface with the solid particles acting as nueclei, the concentration of which is very high in the initial stages but drops at the later stages of the reaction. However, since the total number of particles is also seen to decrease, with increase of t_r, there seems to be considerable amount of coalescence taking place internally. This process seems to be present at the microscopic level rather than macroscopic one since

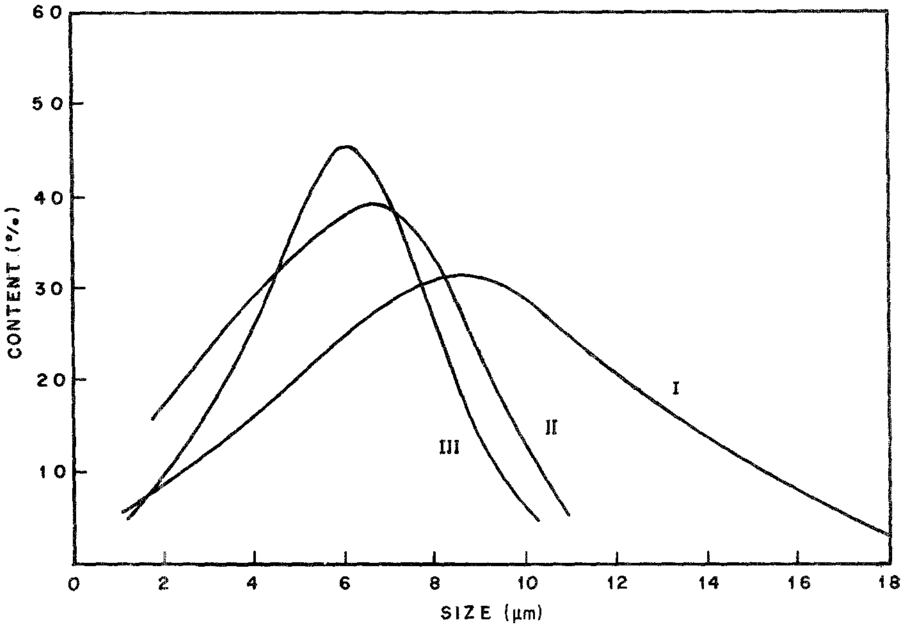

Figure 5 Particle size distribution curves for PPS synthesized at various stirring speeds. Curves I, II and III correspond to stirring speeds of 0, 400 and 660 rpm, respectively.

the particle morphology did not give any indications of agglomerate formation.

3.2. Effect of stirring on size and morphology

A set of reactions were carried out at different stirring speeds of 0, 400 and 660 rpm, while maintaining other conditions such as temperature, concentration, etc. the same and the product taken out after same time t_r (6 h). Fig. 5 shows the particle size distribution curves obtained for various stirring speeds of 0, 400 and 660 rpm corresponding to curves I, II and III, respectively. It is clear by comparison of these curves, 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 above, is greatly affected by the agitation created in the medium. However, since the polymerization processes are also dependent on the stirring speeds, this correlation is not a simple one.

Figs. 6a and b show the scanning electron micrographs obtained in the polymer synthesized at low stirring rates, i.e. 0 and 400 rpm, respectively. It is seen that a large amount of polymer can build up as a single particle ($> 12 \mu m$) with very complex internal structure, as revealed in (a). At low stirring speeds, some amount of internal convection currents exist even with no external stirring. With the increase of stirring speed, the particles seem to develop more and more into a sheaf-like structure. There was practically no change in the crystallinity (66%) with increase of stirring speed suggesting that crystallization rates were quite high. On the other hand, the particles obtained at high speeds (cf. Fig. 4) seem to have less porosity.

3.3. Effect of dilution on morphology

Some remarkable changes were noted in the morphology of PPS particles when the initial concentration of reactants (total change in the reactor) was varied. Figs. 7a and b show the particle morphology as revealed by SEM when the initial concentration was decreased from 100% to 50% and 25% respectively. The reaction conditions and t_r were otherwise the same in all cases. Whereas in the normal case (cf. Figs 4b and c) the particles have more or less spherical boundaries but with internal sheaf-like structure, those obtained with diluted reactants have a small oblong platelet-like shape giving almost a two-dimensional appearance. It is interesting to note that this morphology is entirely different from that

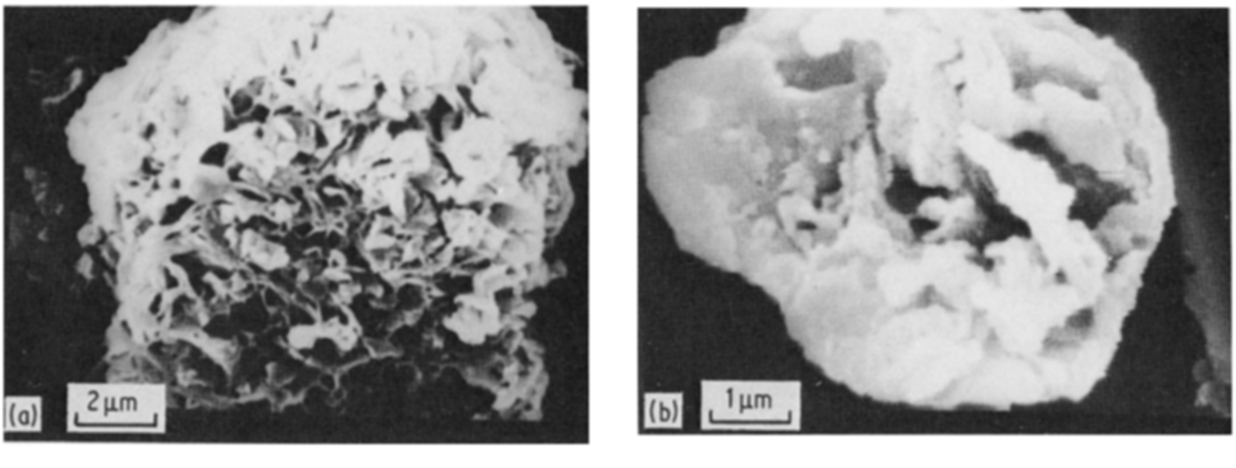

Figure 6 Scanning electron micrographs of PPS particles obtained at different stirring speeds, (a) 0, and (b) 400 rpm.

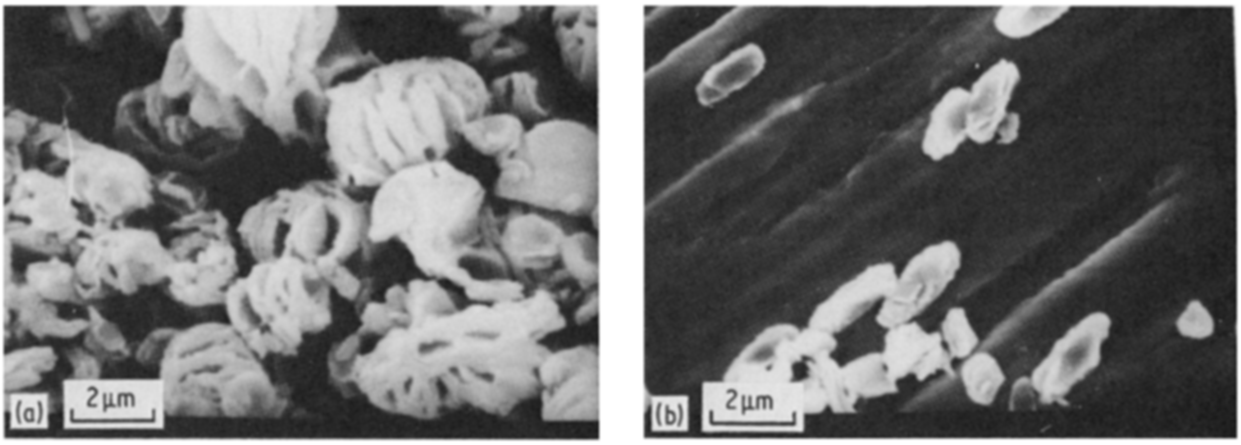

Figure 7 Change in the morphological features with increasing dilution of the reactants: (a) 50% and (b) 25% of total charge. Other conditions same as in Fig. 1.

observed for low reaction times (cf. Fig. 4a). This suggests that the neighbouring nuclei have a strong influence on the growth pattern of the polymer particulate state. Furthermore, the particle size distribution is extremely sharp for diluted reactions suggesting that the termination of the particle growth, i.e. the upper limit of the size (S_f), is mainly set by the concentration of the reactants rather than other parameters.

4. Conclusions

The above studies show that the growth and morphology of the particulate polyphenylene sulphide are highly dependent on the various reaction conditions such as stirring speed, concentration of reactant mixture, reaction time, etc. The ultimate size, shape and distribution of particles are decided by these factors. The various results could be explained on the basis of formation of nuclei for growth of the polymer and during their subsequent growth, coalescence of the neighbouring ones to give rise to intricate morphology. Na_2S particles seem to act as the initial nucleating centres and the polymer growth takes place at the solid–liquid interface. However, the various phenomena involved in the polymerization and crystallization during the synthesis are not yet fully understood and some work on the various thermodynamic aspects/kinetics may be necessary for this.

It is interesting to note that PPS polymer is usually heat treated in air (oxygen atmosphere) below the melting point for producing the coating grade material [16]. It is also treated with vapours of AsF_5 for producing a conducting grade compound. In these processes, the diffusion of gases into the polymer will play an important role and hence the porosity of the particles 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 the powder processing steps of PPS, such as free sintering or coating where powder compaction behaviour is involved, the particle size and shape play an important role. Thus from the present investigations it appears that one may have to control the reaction time, speed of stirring and also concentration of the reactants in order to produce an appropriate polymer mass suitable for specific application.

TABLE I Growth behaviour of polyphenylene sulphide

Reaction time, t_r (h)	Average particle size, S_t (µm)	Yield, Y_t (g)	Total no. of particles, N_t
0.5	0.5	0.59	8.13×10^{11}
1.0	1.1	4.33	7.46×10^{11}
2.0	3.0	6.2	3.95×10^{10}
3.0	4.75	13.2	2.1×10^{10}
4.0	6.0	16.63	1.32×10^{10}
5.0	6.8	17.25	9.4×10^{9}
6.0	7.5	19.05	7.7×10^{9}
7.0	8.2	19.3	6.0×10^{9}
10.0	10.0	20.9	3.6×10^{9}

It may be mentioned here that peculiar morphological features such as fibrilar, rod-like or globular structures have been observed in poly paraphenylene [17] which is a polymer related to PPS in as much as both have an orthorhombic type of crystal structure with slight differences in *a* and *b*-axes (*c*-axis being much larger in the case of PPS) and contain the paraphenylene moities.

The present studies suggest that PPS has more of a lamellar (sheaf-like) morphology than a fibrillar one. Although the crystal structures may be similar, the morphology can be different since it depends on the growth behaviour, the type of active nuclei present, crystallization rate, and hydrodynamic conditions, etc. However, the exact role of the various species present during the polymerization in governing the morphology is not known. Work is in progress in this direction and will be reported in the near future.

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