Structure, growth and morphology of polyphenylene sulphide*

Part 2 *Effect of dibromobenzene**

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The crystallinity, particle size and morphology of polyphenylene sulphide synthesized from 1, 4-dibromobenzene and sodium sulphide have been investigated by X-ray diffraction and scanning electron microscopy. It was found that the crystallinity increased from 62 to 68% with an increase in reaction time. A reordering of crystalline structure with increase of reaction time was also noted. The particle size growth was slower as compared to the reaction rate and the distribution was very sharp. The results are compared with those for polyphenylene sulphide obtained from 1, 4-dichlorobenzene and sodium sulphide.

1. Introduction

Polyphenylene sulphide possesses outstanding properties of thermal stability, resistance to corrosion and processibility as a thermoplastic, but at the same time it is curable as a thermoset and shows excellent adhesion to many substrates, which make it a technologically important polymer [1–4]. This material has attracted considerable attention in recent years, even as an electrically conducting polymer [5–10]. It is well known that growth, structure and morphology play an important role in governing the various properties of the polymer. In special processes such as powder coating, free sintering and doping the size, shape and morphology of the polymer powder plays an important role in governing the various control parameters for optimum results.

There are various factors affecting particle formation during the polymerization process. Extensive studies have been made in the past on polyvinyl chloride particles obtained under various reaction conditions such as suspension, emulsion or mass polymerization and various reaction temperatures and stirring speeds [11, 12]. In our recent report [13], such studies have been described for the case of polyphenylene sulphide (PPS) synthesized from paradichlorobenzene (PDCB). It was shown there that the particle morphology is greatly influenced by the reaction conditions. During these investigations it was found that the reaction rate and/or presence of ionic species in the polymerization medium may influence the growth behaviour of PPS. The use of paradibromobenzene (PDBB) for the synthesis of PPS would lead to a variation of only the ionic species without changing other parameters such as temperature and concentration used in the case of PDCB. Hence, detailed investigations were made on the

growth behaviour of PPS obtained from the bromo-compound and the results are described in this report.

2. Experimental procedure

The polymer was synthesized on a laboratory scale in a stainless steel 600 ml reactor provided with mechanical stirrer, external heating chamber, cooling coils etc. PPS was prepared by reacting sodium sulphide (Na_2S) with non-stoichiometric (1:1.06) amount of PDBB in N-methyl pyrrolidone (NMP) at 195° C. The stirring speed was maintained at 660 rpm. Other details of the experiment and polymer recovery were the same as described earlier [14].

The PPS powder obtained was analysed for crystallinity, structure and morphology by wide-angle X-ray diffraction (WAXS) and scanning electron microscopy (SEM). A Philips PW 1730 diffractometer with CuKα target and β-Ni filter was used for WAXS and a Cambridge Model 150 was used for SEM studies. The details of estimation of crystallinity, average particle size etc. were the same as reported earlier [13, 15].

The crystallinity C_i was determined from the WAXS scans in 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. C_i was estimated from the areas under the amorphous halo (ϕ_a) and crystalline peaks (ϕ_c) using the relation [15]

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

The particle size was estimated from SEM as follows. At any particular position of the sample, the SEM was seen on the display screen of the instrument which also had a crosshatch grid of lines. Since the particles were mostly disc-shaped, seen more clearly at lower magnifications, the radial dimensions were essentially
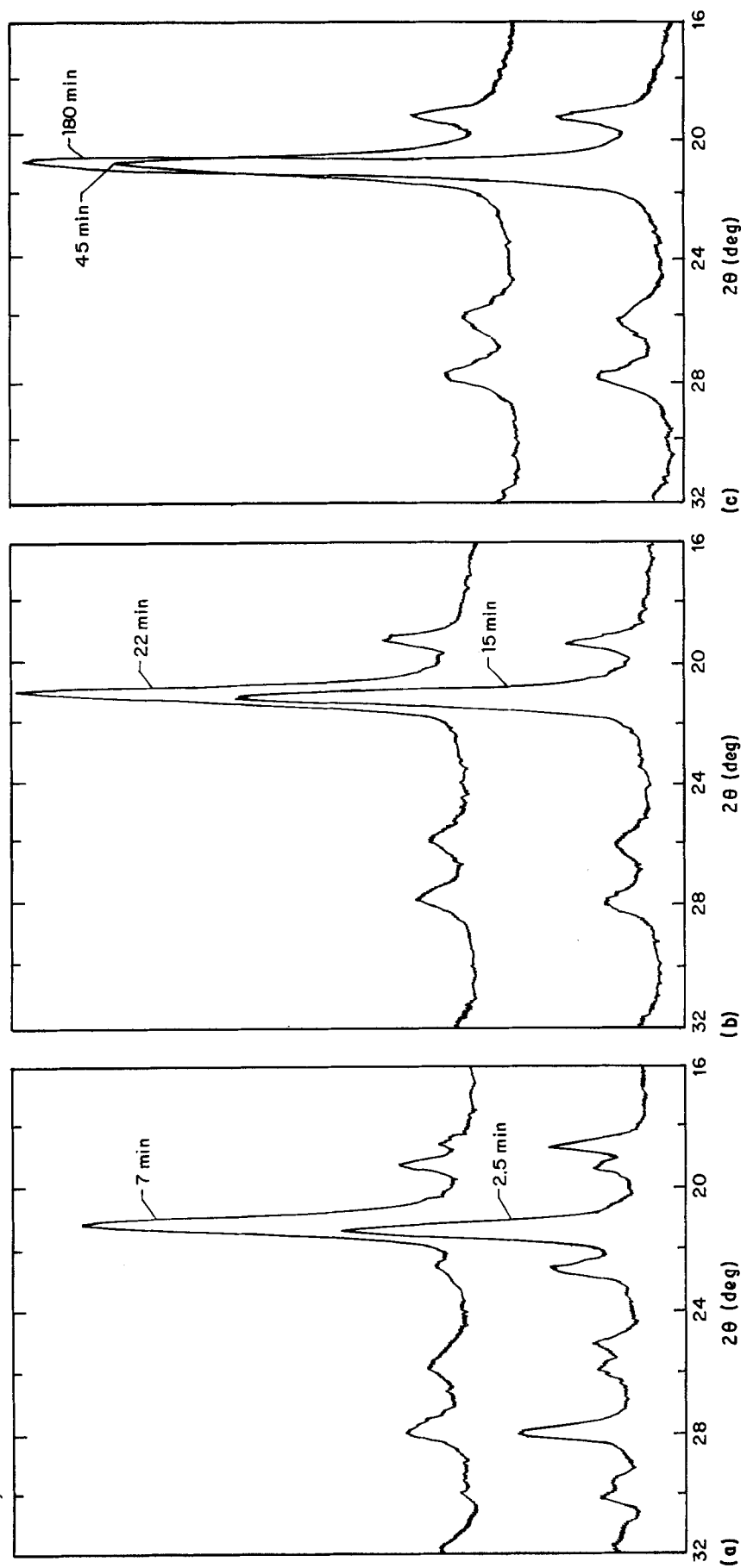
Figure 1 Wide-angle X-ray diffraction from PPS samples from PDCB at various reaction times: (a) 2.5 and 7.5 min, (b) 15 and 22 min, (c) 45 and 180 min.

measured. The total number of particles within the predetermined limits of the grid were counted and in this manner the whole sample screened (5 mm²). From this the percentage values for particles lying in various ranges of size were estimated and the weighted average evaluated.

3. Results and discussion

The PPS powder synthesized using PDBB as the reactant was similar in physical appearance to that obtained from PDCB as reported earlier. However, a few changes were noted in the X-ray diffraction and morphology which are described here.

Figs 1a, b and c show the WAXS scans for the polymer obtained after reaction times of (2.5 min, 7 min), (15 min, 22 min) and (45 min, 180 min), respectively. By comparing these curves it is seen that the intensities of reflections occurring at 2θ values of 18.6, 22.5, 25 and 28° progressively decrease, while those for the reflection at 19.2, 21 and 26° increase with increase of the reaction time (t_r). These findings suggest that there is a reordering of the crystalline structure for the polymer with the increase of reaction time t_r. These results are discussed below.

The crystallinity C_i was determined from the WAXS data in the same manner as for PPS synthesized from PDCB. The variation of crystallinity with reaction time for the same concentration of reactants and stirring speed is shown in Fig. 2 (curve I). It is seen that C_i increases slightly at first from 62 to 68% with

an increase in t_r up to 45 min reaction time, but with a 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 was found to decrease continuously from a high value (74%) with an increase of reaction time.

The growth of the polymer particles was studied by means of SEM, and curve II of Fig. 2 shows the increases rapidly with increase of reaction time up to a t_r of 60 min, above which the particle size increases increases rapidly with increase of reaction time upto a t_r of 60 min, above which the particle size increases slowly to attain a limiting value S_f. 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, see dotted line in Fig. 2).

Curve III in Fig. 2 shows the variation of total polymeric mass obtained as a function of reaction time, other reaction parameters being the same. In this case, too, it is seen that the polymer yield increases rapidly up to a reaction time of 45 min, above which it gradually tends to a constant value (18 g). These observations clearly indicate that the polymerization reaction proceeds at a very rapid rate in the case of PDBB, giving a large polymeric yield, but the particle growth takes place at slower rate and proceeds more or less uniformly over the reaction periods studied.

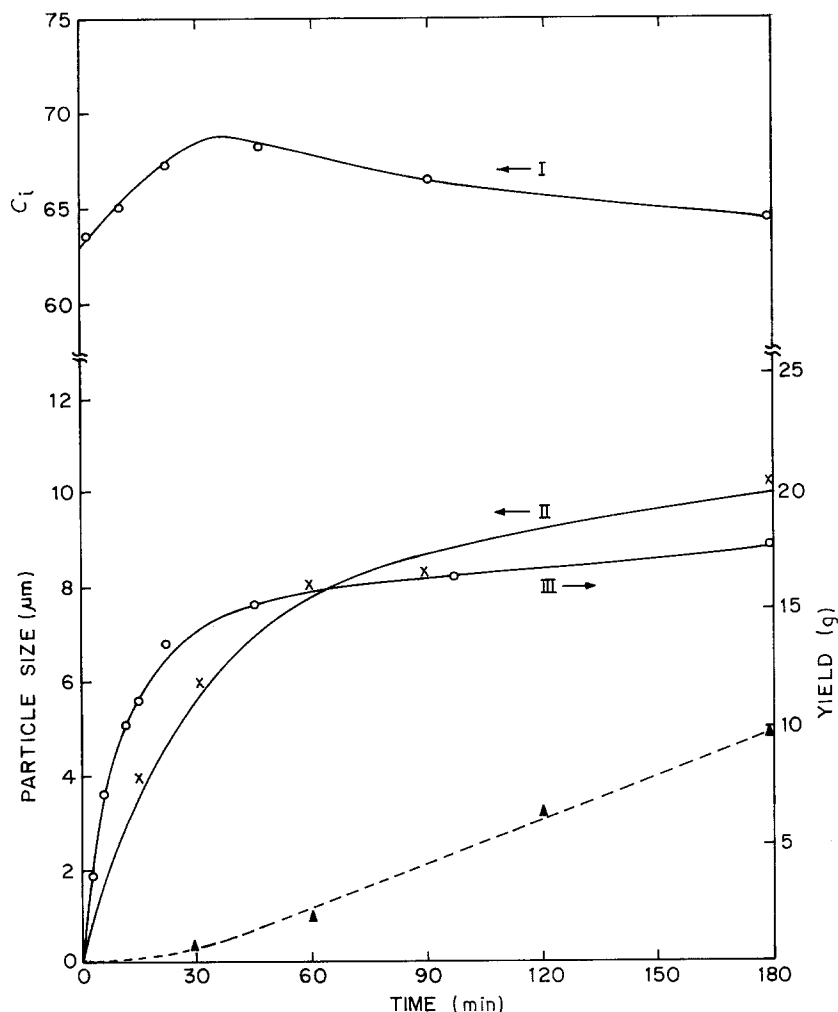In order to investigate the time dependence of the growth phenomena for both particle sizes as well as

Figure 2 Variation of crystallinity (curve I), average particle size (curve II) and total polymer yield (curve III).
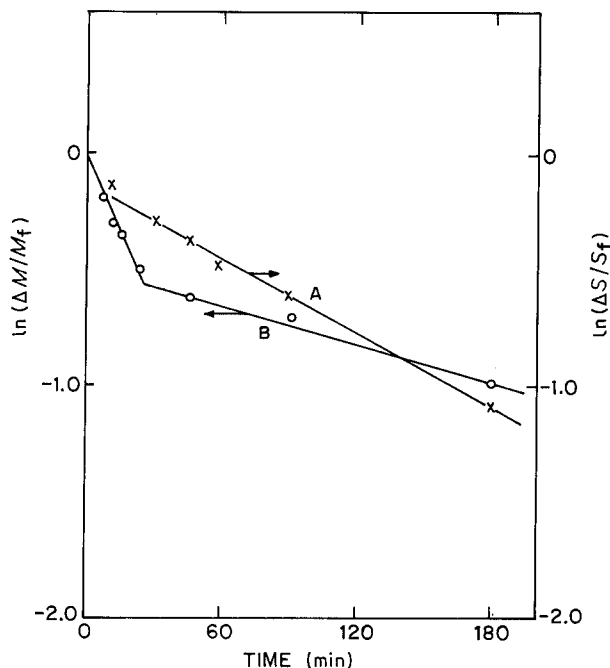
Figure 3 Plot of $(S_f - S_t)/S_f$ and $(M_f - M_t)/M_f$ against reaction time on semilog scale.

TABLE I Growth behaviour of PPS using PDBB

t_r (min)	Size, S_t (μm)	Yield, M_t (g)	N_t (cm^{-3})
15	4	9	9.8×10^{11}
30	6	14	9.7×10^{11}
60	8	15.5	4.5×10^{11}
90	8.5	16.4	4.0×10^{11}
180	10.5	17.8	3.0×10^{11}

the polymer yield, a plot was made as before of $\ln (\Delta S/S_f)$ and $\ln (\Delta M/M_f)$ against t_r on a semilog scale as shown in Fig 3, where ΔS is $(S_f - S_t)$ and ΔM is $(M_f - M_t)$, respectively. Curve A is for the particle growth while curve B 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 dependence of the particle size follows the equation

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

where α is a constant with a value of $8.8 \times 10^{-5} \sec^{-1}$. The graph for the time dependence of the yield (curve B), on the other hand, does not appear to be simple linear one. Nevertheless, one may represent the graph in terms of two straight lines having differing slopes as shown in the figure. The slope in the initial region is $3.5 \times 10^{-4} \sec^{-1}$ while that in the higher t_r region is seen to be $4.7 \times 10^{-5} \sec^{-1}$. Thus the reac-

tion appears to proceed at two distinct rates giving different yields with an increase of reaction time. The time dependence of the yield may be represented by the equation

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

with $\beta = 3.5 \times 10^{-4} \sec^{-1}$ when $t_r < t'$, and $\beta = 4.7 \times 10^{-5} \sec^{-1}$ when $t_r > t'$; t' is the delineating time (35 min) between the fast and slow processes.

The particle size distribution for PPS synthesized from PDBB for various reaction times is shown in Fig 4. Curves I, II and III correspond to reaction times of 15, 30 and 180 min, respectively. It is seen that the distribution of particle size is quite sharp in all three cases, namely the initial, intermediate and final stages of the reaction ($t_r > 50$ min). The peak position, however, is seen to shift to higher value of the particle size with increase of t_r. In the case of PPS synthesized from PDCB [13] the particle size distribution was sharp at small reaction times as well as very large t_r (> 10 h), while for the intermediate stages (3 to 6 h) the particle size distribution was a broad one. In the present case it has already been shown that the reaction is a rapid one (maximum yield obtained in 45 min) as compared to the PDCB case (more than 6 h). Since the particle size distribution is also sharp, it appears that either the termination rate is fast or the number of nucleating centres is large. It may be noted that the particles continue to grow even at large reaction times at which the yield is almost at maximum level. Hence the former possibility of a fast termination rate is unlikely.
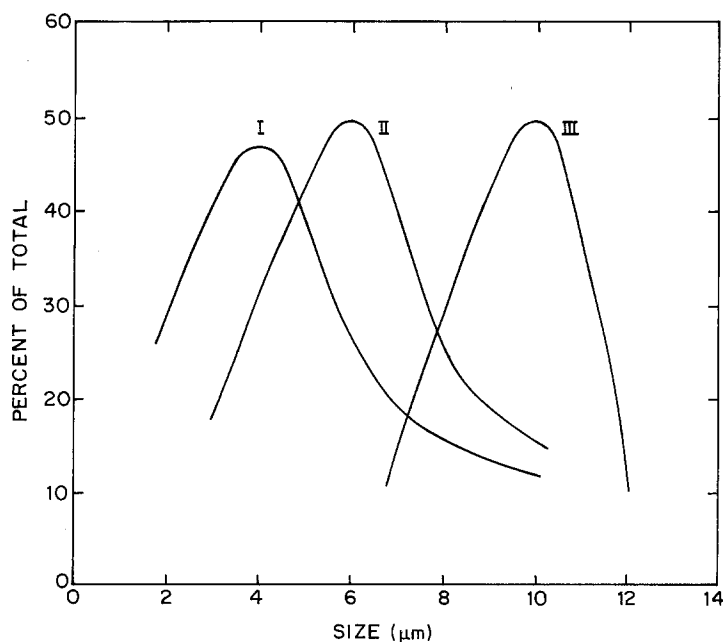
On the other hand, the second possibility of large

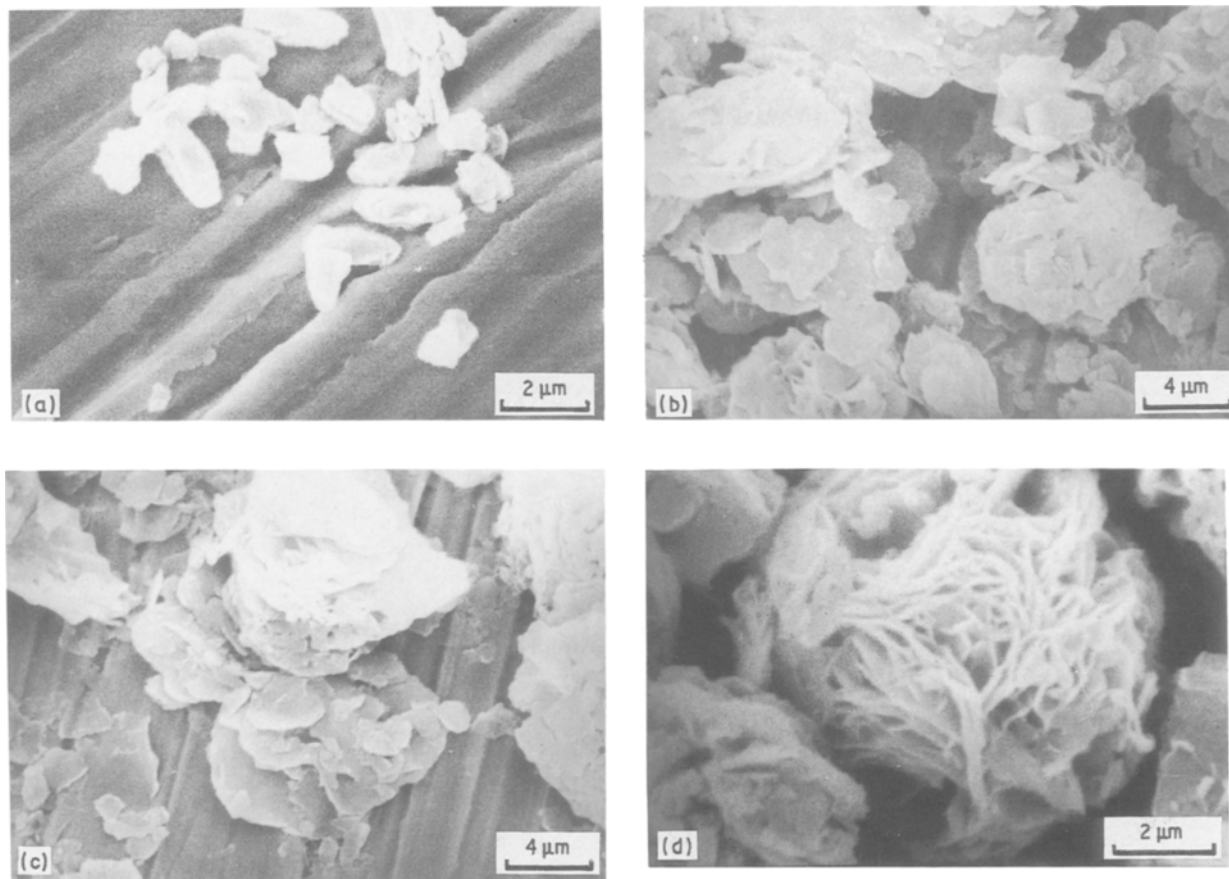*Figure 4* The particle size distribution in PPS synthesized from PDBB.

Figure 5 The morphology of the PPS polymer as revealed by scanning electron micrographs at various reaction times. PDBB: (a) 15 min, (b) 30 min, (c) 180 min. PDCB: (d) 180 min.

nucleating centres with a high growth rate can give a sharp distribution in particle size as well as an increase in the total number of particles in the polymer mass. This was confirmed by us by estimating the total number of particles from the knowledge of particle size, density, shape (cylindrical disc shape) and yield. Table I shows the various values of these parameters for different reaction times, from which it is clear that the total number of particles N_t decreases slightly with an increase of reaction time but remains within the same order of magnitude. In comparison to PPS synthesized from PDCB this decrease is negligible, since in the former case the decrease of N_t was more than two orders of magnitude (8×10^{11} to 3×10^9).

Figure 5 shows the morphology of the PPS particles obtained at various reaction times. Figs 5a, b and c are for reaction times of 15, 30 and 180 min respectively. It can be clearly seen that the particles in all cases have a more or less similar morphology consisting of flat, round, disc-shaped platelets with practically no variation in their shape but only in size. These morphological features were observed even for very large reaction times. The typical morphology found for PPS synthesized from PDCB under similar conditions is shown in Fig. 5d. By comparing these figures it is seen that there is a remarkable change in morphology by the use of PDBB for the synthesis of PPS.

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, and clustering or coalescence of the polymer molecules/particles. Amongst these various factors, the dominating ones for the present studies seem to be related to the rate of reaction and the presence of ionic species. In the early stages of the reaction ($t_r < 5$ min), the rate being high, one would expect a large number of end-groups to be present in the polymer. 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 [16–18] which would give rise to additional peaks in the WAXS data, and these have indeed been observed by us.

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 an increase in crystallinity and sharp diffraction peaks corresponding to the orthorhombic-type crystal described earlier [13]. With a further increase of reaction time there would be a corresponding increase of molecular weight, and the same processes which lead to the decrease of crystallinity mentioned earlier would operate [13]. Thus, one finds a slight increase of C_i initially followed by a decrease in its value with an increase of t_r.

In addition to the polymerization process, the growth of the PPS particles also depends upon nuclea-

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tion, termination and coalescence. Since the total number of particles as well as their morphology remains more or less the same it is quite likely that there are a large number of nucleating centres, and the polymer mass builds up by nucleation of fresh particles rather than the growth and coalescence of already nucleated ones with an increase of reaction time. These observations, together with the well-defined boundaries of the PPS particles noted in the SEM photographs, reveal the important role of the ionic species and the types of propagating group for polymerization in governing the final morphology of the PPS.

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