

# Morphological Studies on the Blends of Poly(butylene Terephthalate) and Bisphenol-A Polycarbonate

R. S. HALDER, MANGALA JOSHI, and A. MISRA,\* *Center for Materials Science and Technology, Indian Institute of Technology, Delhi, New Delhi-110016, India*

## Synopsis

The morphology of the blends of poly(butylene terephthalate) (PBT) and bisphenol-A polycarbonate (PC) crystallized from the melt were studied by density measurement and small angle light scattering techniques. Rate of crystallization of these blends was found to be slower with increasing amount of PC. The Avrami exponent  $n$  for the blends was calculated and related to the shape of superstructures formed.  $H_v$  and  $V_v$  scattering patterns as seen by small angle light scattering were analyzed to determine the nature, shape, and size of the superstructures. The changes in the superstructure formation with increasing amount of PC in these blends have been analyzed.

## INTRODUCTION

Poly(butylene terephthalate) (PBT) finds importance as an engineering thermoplastic because of its attractive mechanical properties, rapid crystallization rate, and good moldability. Structure and properties of this polymer have been well studied and reported in the literature.<sup>1-4</sup> It has been found that PBT has a lower glass-transition temperature, lower melting point, higher crystallization rate, and lower value of maximum attainable crystallinity compared to poly(ethylene terephthalate), the other commercial thermoplastic polyester. Although PBT is a successful engineering plastic, it has some shortcomings such as relatively low impact strength, low heat deflection temperature, low melt viscosity, and poor optical properties. Some of these can be improved by blending PBT with other suitably chosen polymers while retaining its excellent properties.

The fast crystallization rate of PBT has been advantageous in improving the crystallization rate of PET when both the polymers are copolymerized with suitable block lengths.<sup>5</sup> Crystallinity and phase behavior for blends of PBT and polyacrylates has been reported by Kimura.<sup>6</sup> Wahrmund and co-workers<sup>7</sup> studied melt blends of bisphenol A polycarbonate (PC) with PBT by DTA and dynamic mechanical behavior to determine their state of miscibility. Both techniques showed multiple glass transition temperatures indicative of incomplete miscibility in the amorphous phase. They suggested that there are amorphous phases containing both components, i.e., partial miscibility of the PBT-PC system. Crystallization behavior of PBT supported this

\*To whom correspondence should be sent.

view. Two crystallization exotherms were observed for quenched samples, which is interpreted as polyester crystallization from two separate phases, one richer in this component than the other. Birley and Chen<sup>8</sup> also conclude that PBT and PC show significant mixing in the melt but the partially mixed components phase-separate during dissolution. Partial melt miscibility of the PBT-PC system is also suggested by Hobbs and co-workers.<sup>9-11</sup> They have characterized the morphologies of melt blends of PBT-PC by studies on the transmission electron microscope (TEM) and the scanning electron microscope (SEM). SEM studies of specimens etched with diethylene triamine as well as TEM studies of specimens stained with RuO<sub>4</sub> provide convincing evidence of melt miscibility and phase separation of the two resins during crystallization of the PBT. Similar observations have also been reported by Dellimoy and co-workers.<sup>12</sup> They have also reported that blends of PC and PBT exhibited a biphasic nature and partial compatibility in the molten state. In this paper we have made a systematic study of the morphology of PBT-PC blends isothermally crystallized from the melt using the well-known characterization techniques.

## EXPERIMENTAL

### Materials

PBT under the trade name ARNITE T006 with an  $M_w = 55,000$  was obtained from Cenka Plastics Ltd. (India). Bisphenol-A polycarbonate used for this work was LEXAN ML 4403-III with an intrinsic viscosity of 0.5 DL/g was obtained from General Electric (U.S.A.).

### Sample Preparation

Blends of PBT and PC were prepared by melt mixing in a single screw extruder (Betol BM 1820) at 260°C with the amount of PC varying from 0 to 50% by weight. The blend compositions prepared are listed in Table I. The molten extrudate was quenched at room temperature in a water bath and collected as strands which were subsequently chopped into granules. Dried granules of blends as well as pure PBT were compression-molded to make 10 mil thick films on a Craver laboratory hydraulic press at 250°C with a pressure of 10,000 psi. Isothermal crystallization was carried out using these thick films from the molten state. Pieces of the molded films were pressed between two microscopic cover glasses and melted in a silicone oil bath at a

TABLE I  
Blend Compositions (wt %)

Blend no.	PBT	PC
PBT (pure)	100	0
1B	90	10
2B	80	20
3B	70	30
4B	60	40
5B	50	50

temperature of 250°C for 5 min to make a film thickness of 1 mil. The molten sandwich was then directly transferred to a separate silicone oil bath maintained at 50°C for various times of crystallization and then quenched rapidly in an ice-water mixture.

### Sample Characterization

**Density Measurements.** Densities of the blend samples were determined by applying the Archimedes principle of weight loss of a body when suspended in a liquid (ASTM D792). Xylene was used for the accurate measurement of density as it has a specific gravity of 0.86, far below the density of the test samples. A Sauter electronic balance with an accuracy of four decimal places was used for weighing purposes. The amorphous and crystalline densities of blends were determined by,

$$\frac{1}{(\rho_a)_{\text{blend}}} = \frac{X_1}{(\rho_a)_1} + \frac{X_2}{(\rho_a)_2}$$

$$\frac{1}{(\rho_c)_{\text{blend}}} = \frac{X_1}{(\rho_c)_1} + \frac{X_2}{(\rho_c)_2}$$

where  $X_1$  and  $X_2$  are the weight fractions of the components,  $(\rho_a)_1$  and  $(\rho_a)_2$  are the amorphous densities while  $(\rho_c)_1$  and  $(\rho_c)_2$  are the crystalline densities respectively of components 1 and 2. Amorphous and crystalline densities for PBT were taken as 1.282 and 1.396 g/cc, respectively.<sup>13</sup> PC was considered to be totally amorphous under the conditions used in this study<sup>14</sup> and its amorphous density was taken as 1.200 g/cc.<sup>15</sup>

**Small Angle Light Scattering (SALS).** SALS was carried out with the usual experimental setup as had been used by Stein.<sup>16</sup> Photographs of the SALS patterns were taken on flat photographic films with the required exposure time which were then scanned azimuthally along the scattering lobe on a Joyce Lobel microdensitometer. The spherulite size was calculated using the following relation<sup>12</sup>:

$$R = 1.025\lambda_0/\pi n \sin(\theta'_m/2)$$

where  $R$  is the average spherulitic radius,  $\lambda_0$  is the wavelength of light in air,  $n$  is the refractive index of the sample, and  $\theta'_m$  is the corrected scattering angle for maximum intensity, which is related to the actual scattering angle  $\theta_m$  as

$$\sin \theta'_m = \sin \theta_m/n$$

## RESULTS

### Crystallization Kinetics

The study of isothermal crystallization has been done by the method of density measurements. The increase in density has been taken as the index of crystallinity. If the density of a material after crystallization for time  $t$

becomes  $\rho_t$ , its crystallinity  $X_t$  can be given by

$$X_t = \frac{\rho_c}{\rho_t} \cdot \frac{\rho_t - \rho_a}{\rho_c - \rho_a}$$

where  $\rho_c$  and  $\rho_a$  are the crystalline and amorphous densities, respectively. In these calculations it has been assumed that under the condition of crystallization used in the study, only PBT crystallizes while PC remains completely amorphous throughout. The fraction of material crystallized at time  $t$  is called the reduced crystallinity  $\alpha$  and can be determined using the following relation:

$$\alpha = \frac{X_t}{X_\infty} = \frac{\rho_a}{\rho_t} \cdot \frac{\rho_t - \rho_a}{\rho_\infty - \rho_a}$$

where  $X_\infty$  and  $\rho_\infty$  are the crystallinity and density, respectively, after infinite time of crystallization.  $\alpha$  can be used to determine many important crystallization parameters using the Avrami equation,<sup>17,18</sup> which is given as

$$\frac{X_t}{X_\infty} = 1 - \exp(-kt^n)$$

and

$$\log[-\ln(1 - X_t/X_\infty)] = n \log t + \log k$$

where  $k$  is the crystallization rate constant associated with the rate of nucleation and  $n$  is the Avrami exponent, the value of which depends both on the primary nucleation and growth geometry of the crystalline entities. The plot of  $\log[-\ln(1 - X_t/X_\infty)]$  vs.  $\log t$  yields a straight line with slope  $n$  and intercept equal to  $\log k$ .

Plots of density as a function of crystallization time for PBT/PC blends of different compositions are shown in Figure 1. Crystallinity values were determined from density data and percent crystallinity at infinite time of crystallization for all the blends are presented in Table II. The reduced crystallinity values were obtained from density data and have been plotted as a function of time in Figure 2. From these curves the half-time of crystallization ( $t_{1/2}$ ) was determined and plotted as a function of PC concentration as shown in Figure 3. Also, the induction periods of crystallization ( $t_i$ ) were determined from the initial horizontal portion of the density curves and are plotted as a function of the concentration of PC in Figure 3. As is observed in this figure, the values of  $t_{1/2}$  and  $t_i$  increase linearly with the increasing amount of PC in the system. This clearly signifies that the incorporation of PC inhibits the crystallization rate of PBT in the blends.

Figure 4 shows the Avrami plots of PBT and its blends. The values of  $n$  and  $k$  were determined from these curves and are presented in Table II. These values describe useful information regarding the crystallization process of PBT in the blends, as mentioned earlier. The value of  $n$  for pure PBT is found to be 2.1 and this value decreases as PC level is increased in the blend. For the

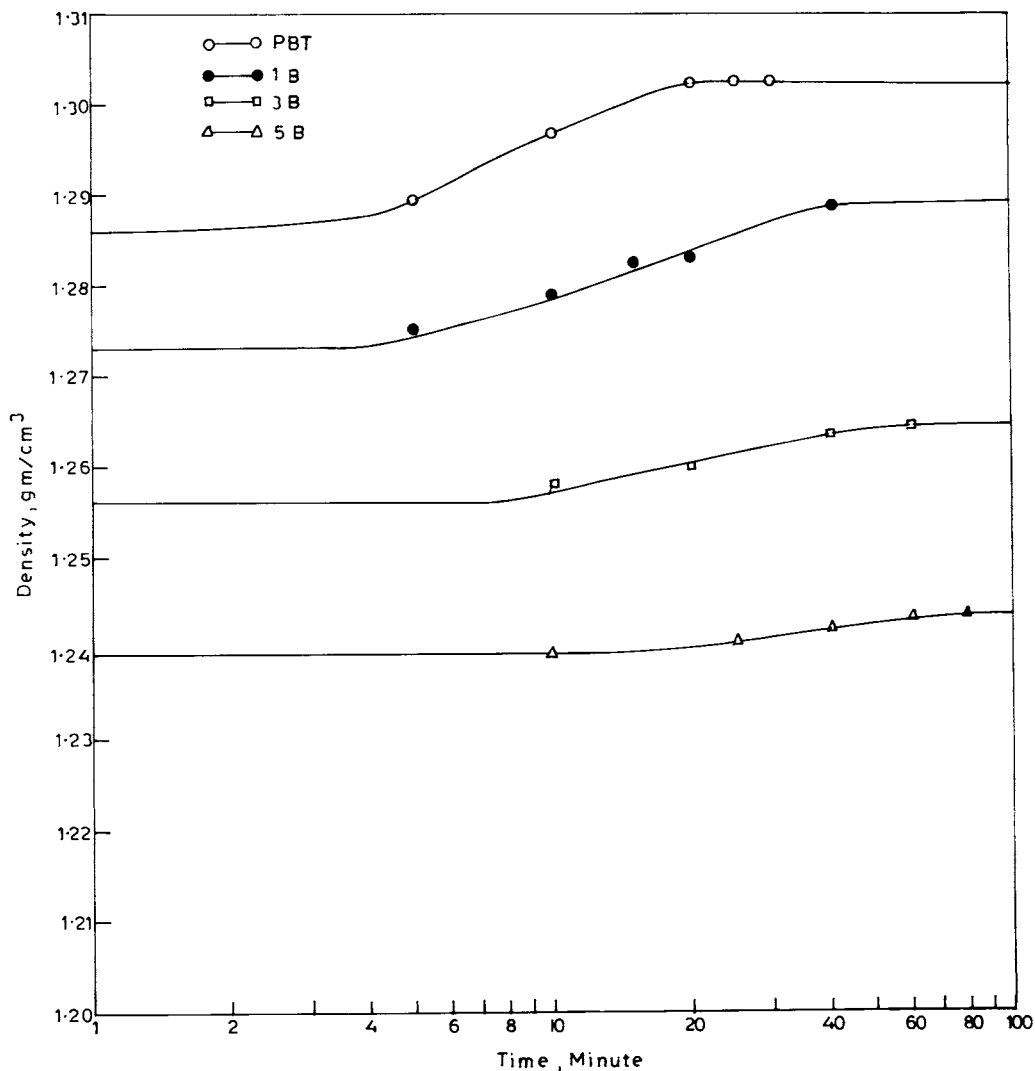


Fig. 1. Variation of density with the time of isothermal crystallization for PBT and the blends of PBT/PC (1B-PBT/PC: 90/10, 3B-PBT/PC: 70/30, 5B-PBT/PC: 50/50).

TABLE II  
Parameters of PBT Crystallization from Its Blends with PC

Composition	$X$ (%)	$n$	$k$
PBT (PC 0%)	19.7	2.10	$8.06 \times 10^{-3}$
1B (PC 10%)	16.9	1.66	$10.13 \times 10^{-3}$
3B (PC 30%)	12.4	1.51	$7.11 \times 10^{-3}$
5B (PC 50%)	8.9	1.43	$5.27 \times 10^{-3}$

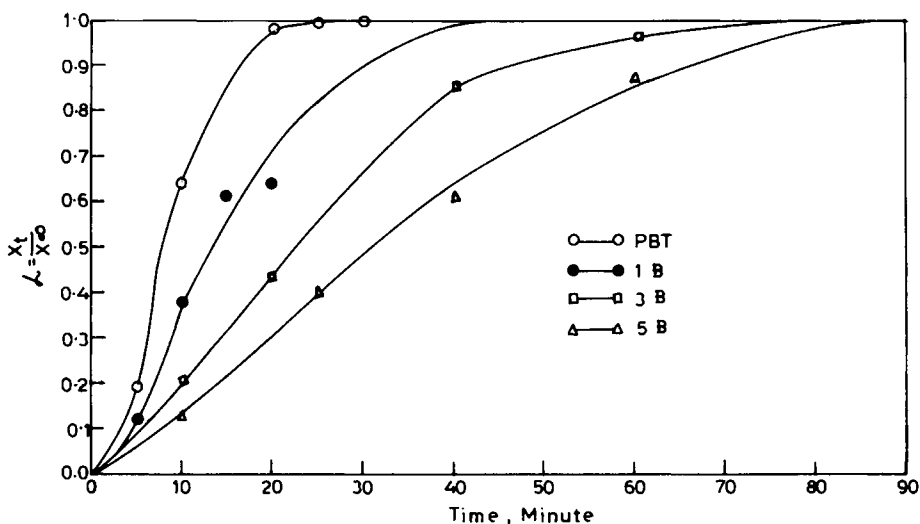


Fig. 2. Variation of reduced crystallinity ( $\alpha$ ) with the time of isothermal crystallization for PBT and the blends of PBT/PC (1B-PBT/PC: 90/10, 3B-PBT/PC: 70/30, 5B-PBT/PC: 50/50).

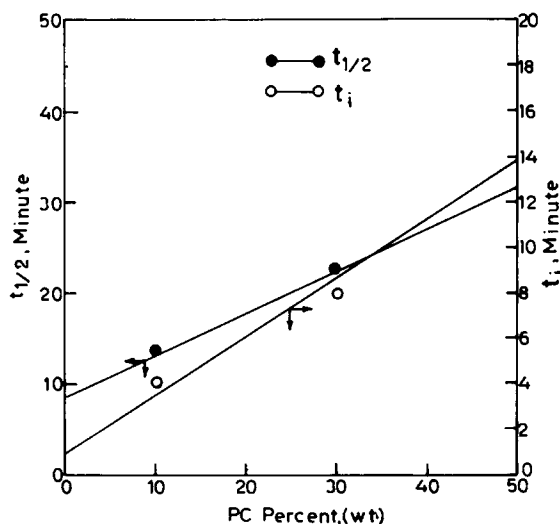


Fig. 3. Half-time of crystallization ( $t_{1/2}$ ) and the induction period of crystallization ( $t_i$ ) as a function of PC composition for the blends of PBT/PC.

minimum percentage of PC the value of  $n$  decreases to 1.6 and for the maximum level of PC it goes down to as low as 1.4. On the other hand, the values of  $k$  for PBT and its blends are of the same order. This signifies that the rate of nucleation of PBT remains unhampered when PC is incorporated into it.

### Morphological Observations

The superstructure formed during the isothermal crystallization of the PBT/PC blends was examined by SALS technique. The  $H_v$  scattering pattern

obtained from pure PBT samples crystallized at 50°C for different times from its melt are shown in Figure 5. In all the cases the patterns are of the four-leaf-clover type with the lobes along the polar directions (0°–90° pattern) and referred to as unusual patterns. They also exhibit a maximum intensity in each of the lobes, which is a characteristic of spherulitic scattering. The size of the patterns is found to decrease with an increase in the time of crystallization, which refers to an increase in the size of spherulites formed with time. The spherulitic radius was calculated to be about 4.0 μm for 30 min of crystallization after which no change in the size of the pattern was observed. Blends with 10% and 20% PC show similar behavior except that the rate of final superstructure build up is slower.

Figure 6 shows the  $H_v$  patterns of blends 3B (PBT/PC = 70/30) crystallized for different times. Unlike pure PBT, the usual type patterns where the

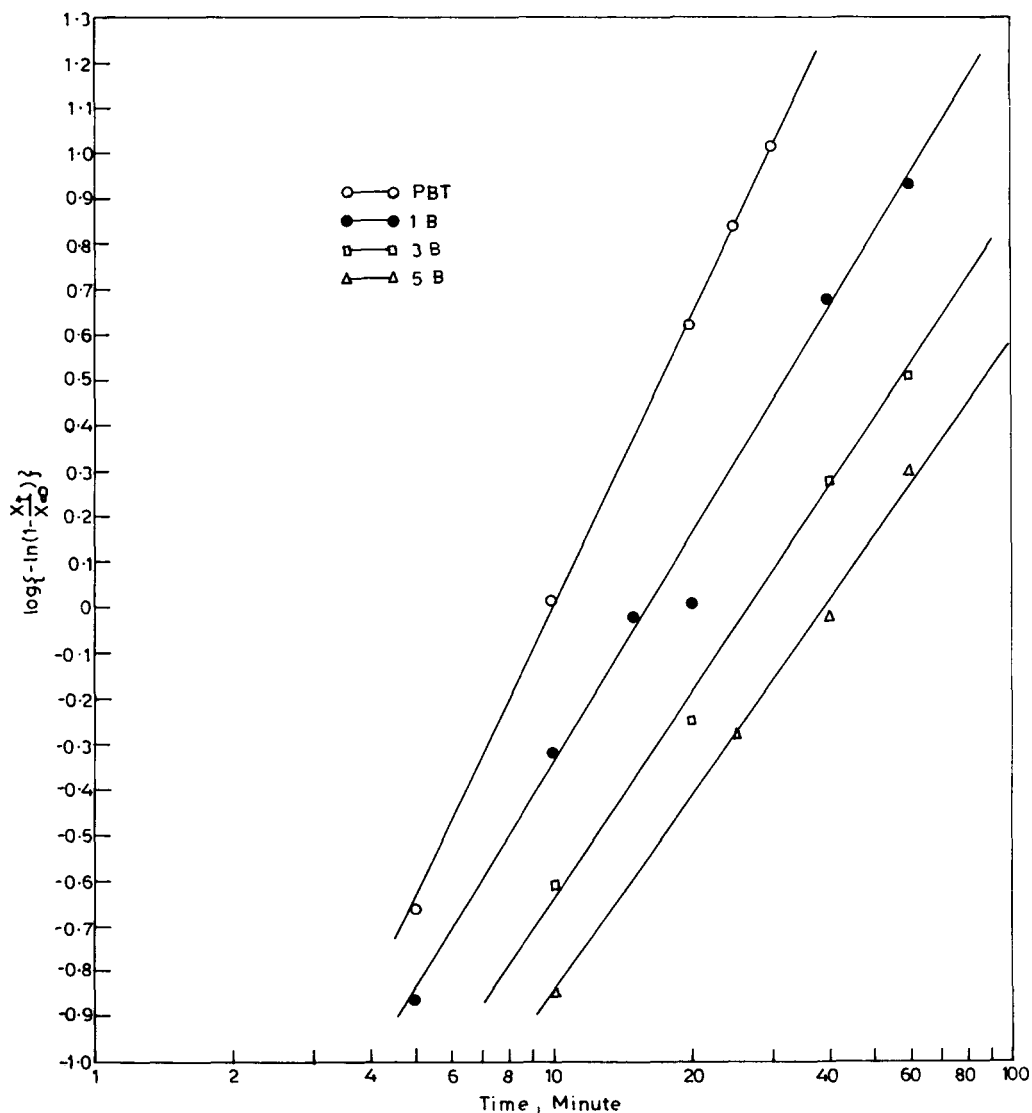


Fig. 4. Avrami plots of  $\log[-\ln(1 - X_c/X_\infty)]$  vs.  $\log t$  for PBT and the blends of PBT/PC (1B-PBT/PC: 90/10, 3B-PBT/PC: 70/30, 5B-PBT/PC: 50/50).

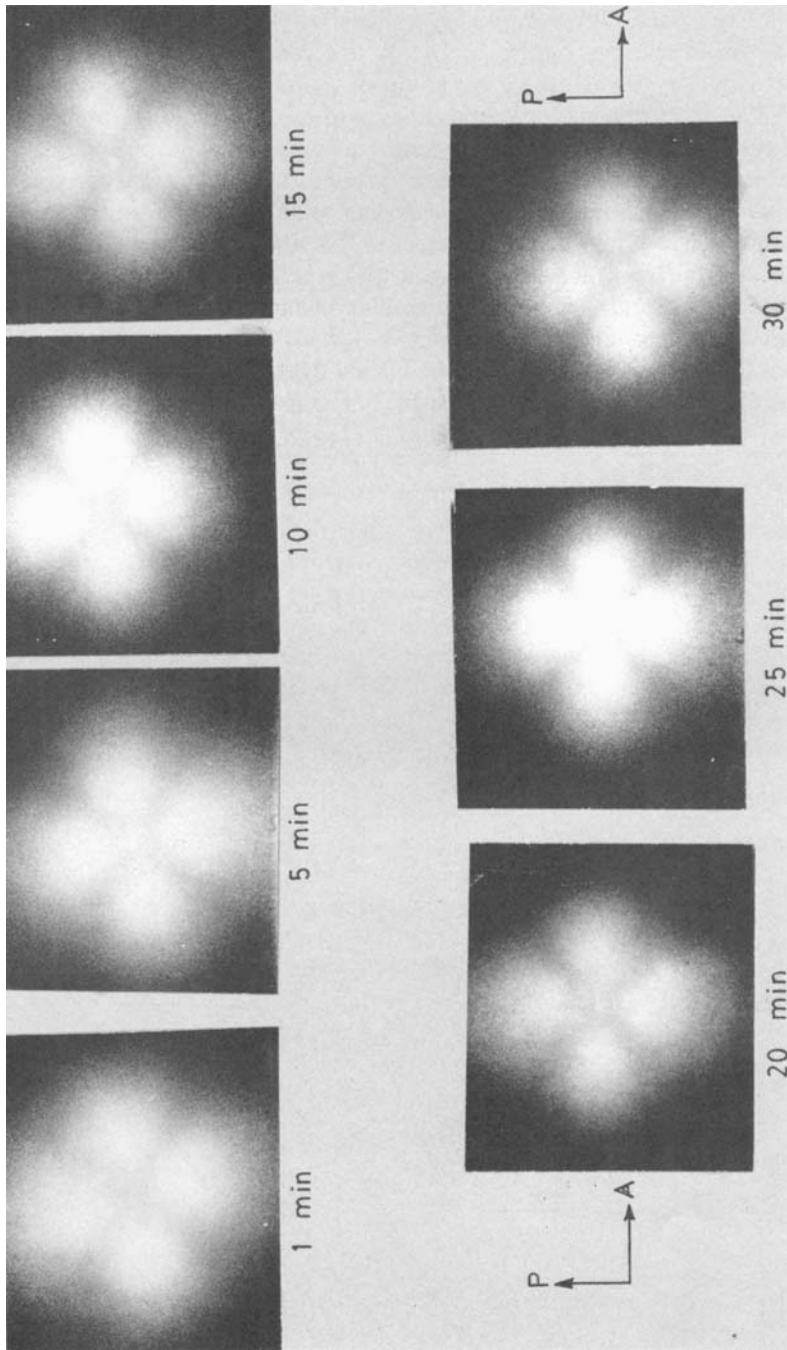


Fig. 5.  $H_v$  scattering patterns for PBT crystallized at 50°C for different times.



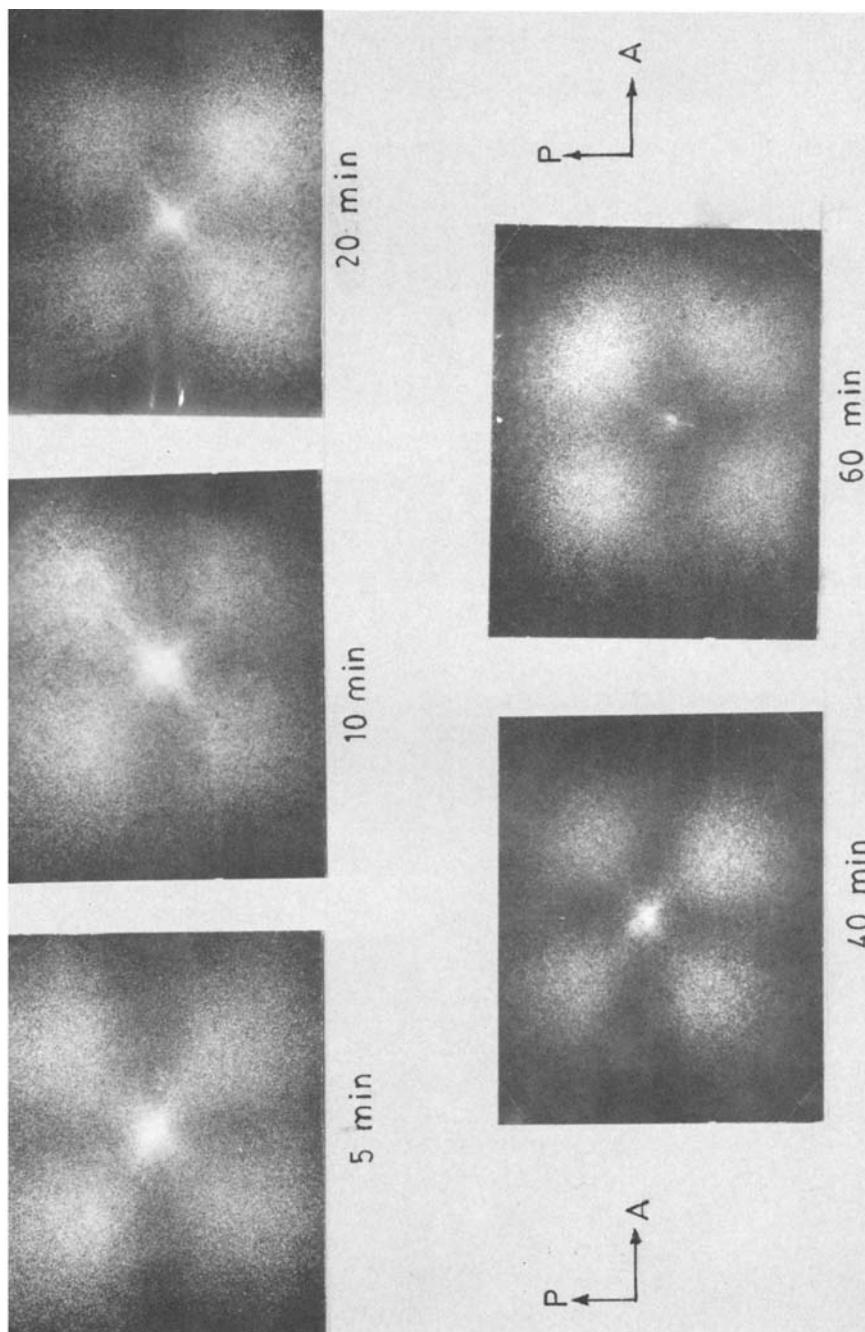


Fig. 6.  $H_v$  scattering patterns for PBT/PC blends 3B (70/30) crystallized at 50°C for different times.

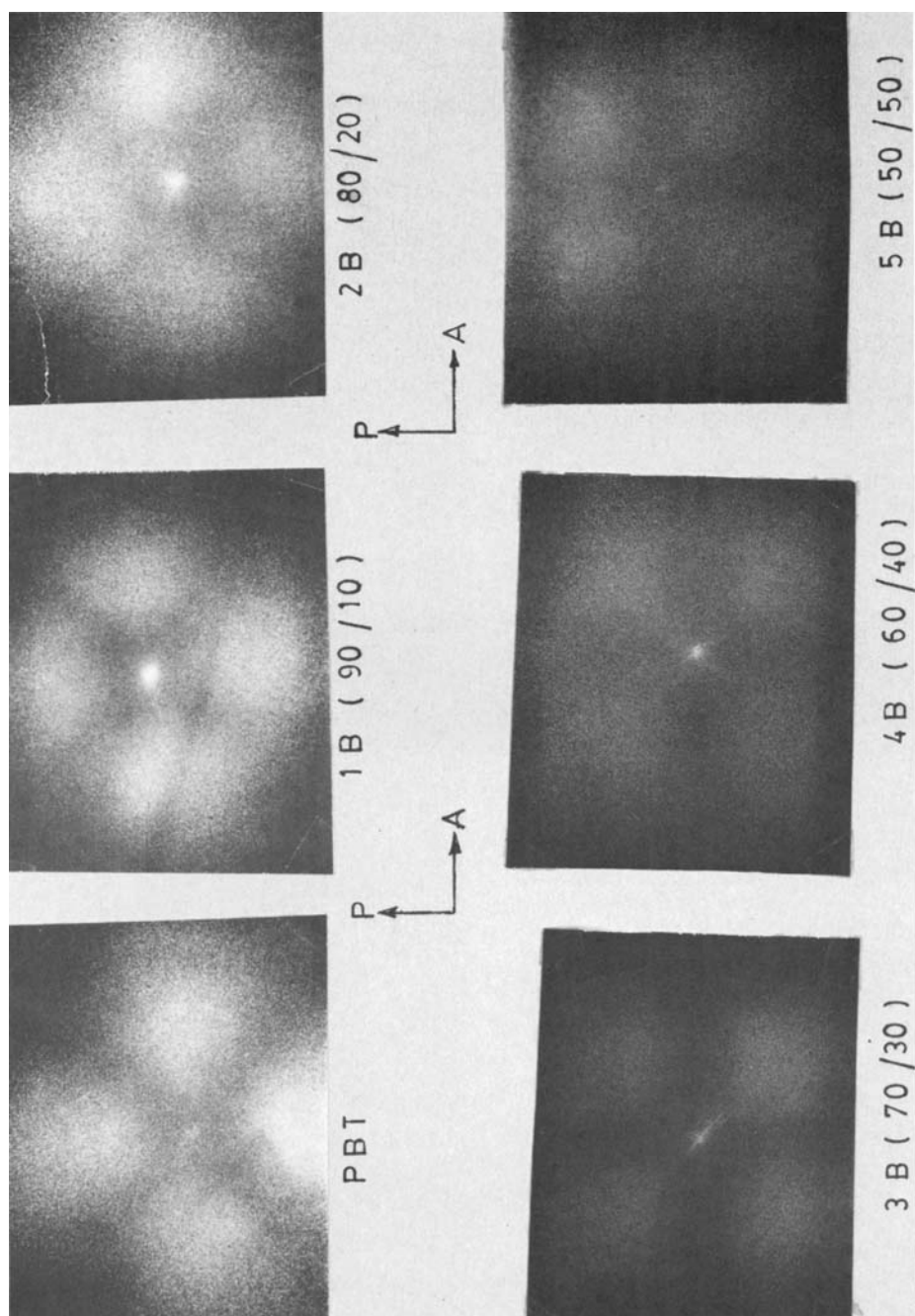


Fig. 7.  $H_c$  scattering patterns for PBT/PC blends of differing composition crystallized at 50°C for infinite time.

TABLE III  
Morphological Parameters of PBT Blends

Blend	Composition PBT : PC	Nature of super structure	Type of ultimate super structure	Spherulitic radius ( $\mu\text{m}$ )	$I(V_v)/I(H_v)$
PBT	100 : 0	Unusual	Spherulites	4.0	2.1
1B	90 : 10	Unusual	Spherulites	2.5	2.4
2B	80 : 20	Unusual	Spherulites	2.3	2.9
3B	70 : 30	Usual	Spherulites	2.1	3.3
4B	60 : 40	Usual	Disc/Plate	—	3.4
5B	50 : 50	Usual	Disc/Plate	—	3.4

lobes are at  $45^\circ$  to the polar directions are obtained. Initially the patterns are sheaflike corresponding to a 2-dimensional plate or disc type growth.<sup>16</sup> After a long time of crystallization, the patterns change to clover type, which corresponds to a 3-dimensional growth. The radius of the final spherulites formed was calculated to be  $2.1 \mu\text{m}$ . Blends with 40 and 50% PC show a similar behavior except that the total time required for forming stable patterns, which do not change with time, increases with increasing level of PC.

Figure 7 shows the  $H_v$  patterns of PBT and all of its blends crystallized for infinite time to attain a stable superstructure formation. All the  $H_v$  patterns are of unusual type ( $0^\circ$ – $90^\circ$  pattern), where the scattering lobes are along the polars for PC concentrations less than 30%. On the other hand, blends containing 30% or higher PC show the usual patterns where the scattering lobes are at  $45^\circ$  to the polar directions.

Intensities of  $V_v$  patterns were compared with the corresponding  $H_v$  patterns from  $I$  vs.  $\theta$  plots and  $I(V_v)/I(H_v)$  values obtained were calculated and are shown in Table III. It has been found that the ratio gradually increases with the concentration of PC in the blends. The higher  $V_v$  intensity in all the blends suggests that the spherulitic superstructure is non-volume-filling in the presence of PC. Furthermore, the extent of volume filling by the superstructures decreases with an increase of PC concentration in the blends. This further suggests that PC is not taking part in the crystallization process and in its amorphous state it exists in the interspherulitic spaces. A similar observation has also been reported by Hobbs and co-workers.<sup>9</sup> They are of the view that incorporation of PC in the interlamellar regions of PBT spherulites has a significant effect on the deformation behavior of the blends of these two polymers. Thus with increasing amount of PC, a combination of the increase in density fluctuation and decrease of anisotropy results in higher value of  $I(V_v)$  over  $I(H_v)$ .

## DISCUSSION

It has been observed that the incorporation of PC hinders the rate of crystallization of PBT and the hindrance increases with increasing percentage of PC in the system. Hobbs<sup>9</sup> examined the melt compounded blends of PBT and PC and found that PBT forms the continuous phase and PC is found as a dispersed phase. As the concentration of PC increases, the dispersed phase

becomes more highly interconnected, forming an interpenetrating network. This complicated interpenetration of the two polymers which develops during phase separation may be causing hindrance in the growth of PBT lamellae. This can be attributed to the melt miscibility effect between PBT and PC as well as the dilution effect to the crystallizable component, PBT by the presence of the noncrystallizable PC. Miscibility of the polyester and polycarbonate phases in the melt state leads to an increase in the  $T_g$  of the resulting blends (over that of PBT), which decreases the crystallization rate and the level of crystallinity of PBT noticeably. Robeson and Furtek<sup>19</sup> also observed that the level of crystallinity of PBT was depressed as the concentration of phenoxy was increased in the blends of PBT and polyhydroxy ether of bisphenol-A. This was explained on the basis of dilution effect as well as the increase in  $T_g$  over that for PBT which would depress the crystallization rate. Similar behavior has also been reported for the blends of polyvinyl chloride and poly(*E*-caprolactam).<sup>20,21</sup>

The value of the Avrami exponent have been found to be fractional for various blends as well as pure PBT. Contribution of different growth processes may therefore be considered for PBT and PBT/PC blends. Pure PBT claims mostly polyhedral (spherulitic) growth. The theoretical predicted Avrami exponent value is 3 for spherulitic growth. The observed value for PBT ( $n = 2.1$ ) is lower and can be attributed to a high nucleation density as suggested by Morgan and co-workers.<sup>22</sup> The growth geometry for the blends ( $n = 1.4-1.6$ ), on the other hand, is mostly 2-dimensional (platelike or dislike), assuming the possibility of a large number of nucleation. It is well known that the nucleation density increases as the temperature of crystallization is decreased. In this work, the crystallization temperature was sufficiently low (50°C) and at this temperature nucleation density is believed to be high. So there would still be a sufficiently large number of nucleation sites in spite of its decrease due to the dilution caused by the addition of PC.

The 0°–90° pattern is characteristic of spherulites whose optic axis lies at an angle of 45° to the spherulitic radius. On the other hand, patterns with the scattering lobes at 45° to the direction of polars arise from spherulites whose optic axis is either along or perpendicular to the spherulitic radius. Thus, the change in the SALS patterns from the unusual to the usual type at 30% and more PC concentration have been attributed to the orientation of the optic axis at 45° to the spherulitic radius to the classical tangential or radial orientation in the usual spherulites.

Roche and co-workers<sup>23</sup> reported that in the case of PBT, the formation of unusual spherulite is the fundamental structural feature. Misra and Stein<sup>13</sup> reported that PBT shows unusual spherulites between 0°C and 180°C and usual spherulites at 200°C. They suggested that the usual spherulites are more stable than the unusual ones and form at a slower rate of crystallization. The unit cell structure obtained for crystals associated with both types of spherulites are identical and the reason for differences in the type of spherulite must be related to either their different surface energies or different crystal thickness. Density results have shown that increasing the amount of PC hinders the crystallization process of PBT. The formation of usual spherulites at higher concentration of PC, therefore, suggests that the usual spherulites must be forming at a slower rate. Thus it can be concluded that PC affects the

crystallization kinetics of PBT, leading to the formation of more stable spherulites of the usual type when it is present in sufficient quantities in the blend.

The shape of the superstructure in the blends has been found to change with the increasing percentage of PC. The 3-dimensional spherulitic nature of the superstructure in PBT has been changed to 2-dimensional plate- or disc-type structures in the blends containing higher percentages of PC. This result is in agreement with that inferred from the Avrami exponent. It has also been found that with the incorporation of PC the radii of PBT spherulites decreases, which may be due to the retardation of the growth of PBT crystals in the presence of PC. This view has also been supported by the optical microscopic studies of PBT-PC blends done by Hobbs and coworkers<sup>9</sup>. They suggest that PC produced a significant change in the gross morphology or crystallinity of the PBT phase. Their studies also provide strong evidence for a decrease in spherulite size as well as spherulites becoming less well defined as the PC concentration increases in the blend.

### CONCLUSIONS

1. PBT and PC from semicompatible blends and the presence of PC effects the crystallization behavior and crystalline morphology of PBT.
2. Crystallization of PBT is largely hindered by the presence of PC in their blends and the rate of crystallization is found to decrease with increasing level of PC.
3. The Avrami exponent for PBT ( $n = 2$ ) decreases to 1.4 for the blend containing 50% PC, indicating that the growth geometry loses its 3-dimensional nature.
4. Blends containing a lower percentage of PC (less than 30%) show the unusual SALS pattern, while the usual patterns are exhibited by the blends containing higher percentage of PC (30% and above). PC affects the crystallization kinetics of PBT, leading to the formation of the more stable usual type of spherulites when it is present in sufficient quantity. The extent of volume filling by the superstructures decreases as the concentration of PC increases in the blends.

### References

1. M. Gilbert and F. J. Hybart, *Polymer*, **13**, 327 (1972).
2. M. Gilbert and F. J. Hybart, *Polymer*, **15**, 408 (1974).
3. A. M. Josy, G. Nemiz, A. Donillard, and G. Valet, *Makromol. Chem.*, **176**, 479 (1975).
4. U. Alter and A. Bonart, *Colloid Polym. Sci.*, **254**, 348 (1976).
5. S. N. Garg and A. Misra, *Makromol Chem. Rapid Commun.*, **2**, 271 (1981).
6. M. Kimura, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 367 (1983).
7. D. C. Wahrmund, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **22**, 85 (1979).
8. A. W. Birley and Chen X in Yue, *Br. Polym. J.*, **77**, 16(2), (1984).
9. S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, *J. Mater. Sci.*, **23**(4), 1219 (1988).
10. S. Y. Hobbs, M. E. J. Dekkers, and V. H. Watkins, *J. Mater. Sci.*, **23**(4), 1225 (1988).
11. M. E. J. Dekkers and S. Y. Hobbs, *Polym. Eng. Sci.*, **27**, 1164 (1987).
12. D. Dellimoy, C. Bailley, and L. A. Devaux, *Polym. Eng. Sci.*, **28**(2), 104 (1988).
13. A. Misra and R. S. Stein, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 327 (1980).
14. W. A. Smith, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **26**, 4233 (1981).
15. J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1978.

16. R. S. Stein, in *Structure and Properties of Polymer Films*, R. W. Lenz and R. S. Stein, Eds., Plenum, New York, 1973.
17. M. Avrami, *J. Chem. Phys.*, **8**, 2123 (1940).
18. C. C. Lin, *Polym. Eng. Sci.*, **23**(3), 113 (1983).
19. L. M. Robeson and A. B. Furtek, *J. Appl. Polym. Sci.*, **23**, 645 (1979).
20. L. M. Robeson, *J. Appl. Polym. Sci.*, **17**, 3607 (1973).
21. C. Ong, Ph.D. thesis, University of Massachusetts, 1974.
22. A. Keller, G. R. Lester, and L. B. Morgan, *Phil. Trans. Roy. Soc. Lond.*, **A247**, 1 (1954).
23. E. J. Roche, R. S. Stein, and E. L. Thomas, *J. Polym. Sci. Polym. Phys., Ed.*, **18**, 1145 (1980).

Received March 22, 1989

Accepted April 3, 1989