

Study on the Effect of Dibenzylidene Sorbitol as a Nucleating Agent on the Crystallization and Morphology of Poly(ethylene Terephthalate)

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Synopsis

The effect of dibenzylidene sorbitol (DBS) as a nucleating agent on the crystallization of poly(ethylene terephthalate) (PET) has been studied. It has been found that DBS, when incorporated into the polyester, at a 0.5–1.0 wt % level, significantly lowers the induction period and reduces the half-time of crystallization. Thermal studies clearly show that the addition of DBS results in decreasing the temperature of crystallization, T_{ch} , when heated from the glassy state as well as increasing the temperature of crystallization, T_{cc} , when cooled from the melt. Maximum spherulitic radius at 110°C has been determined for pure and nucleated PET. The spherulitic size has been found to decrease slightly with the increase in the level of DBS. Optical transmittance measurements reveal that PET containing 0.5–0.7 wt % of DBS gives the best clarity, and, beyond this level of DBS, the clarity decreases. This is probably due to the formation of agglomerates of DBS which in turn scatter visible light, thus making the film appear more hazy.

INTRODUCTION

The study on the nucleation of crystallization in polyesters mainly in poly(ethylene terephthalate) (PET) has been extensively carried out for the last few decades as a response to its increased industrial use.^{1–12} Although the nucleation process may be either homogeneous or heterogeneous, the former is practically never achieved in polymer crystallization¹³; yet heterogeneous nucleation generally implies that the crystallization is carried out in the presence of some deliberately added foreign substance. Such substances are better known as nucleating agents, the influence of which on the polymer crystallization is then evaluated. Although considerable number of studies has been reported on the crystallization of PET, there is still a lack of sufficient information to understand the nature and mechanism of crystallization in nucleated PET.¹⁴ This becomes specially significant since the addition of nucleating agents to PET enhances the rate of crystallization considerably and thus makes it suitable for injection molding applications. It is well known that unmodified PET due to its slow rate of crystallization can only be used

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for fiber spinning and not for molding. The heterogeneous nucleation in PET has been studied mainly in the presence of certain inorganic and organometallic nucleating agents which are generally salts of inorganic or organic acids³⁻⁵ with a very high melting point. Recently a few organic nucleating agents have been developed,¹⁵ which generally melt along with the polymer while being processed. Very little work has been published so far on this type of nucleating agent used in crystalline polymers like PET. The present work aims at the evaluation of such an organic nucleating agent specially for PET.

EXPERIMENTAL

Materials

Pure amorphous PET with an intrinsic viscosity of 1.18 in 1:1 phenol-tetrachloroethane at 25°C, corresponding to $M_n = 37,000$ was supplied by Cenka Plastics, India. Dibenzylidene sorbitol (DBS) was supplied by Milliken Research Corp., Spartanburg, SC.

Mixing of the Nucleating Agent with PET

Pure PET and DBS at several preselected levels (0.3, 0.5, 0.7, 1, and 2 wt %) were first mixed at room temperature in a closed glass vessel by shaking it slowly but continuously. In this method a layer of DBS was coated over the granules of PET. These coated granules of PET as well as those of pure PET were dried in a vacuum oven at 100°C for 72 h. These dried granules were then fed separately into the Brabender twin screw extruder (DSK/42/5) and extruded in the temperature range of 270–275°C. The extruded strands were readily cooled in ice-cold water. The strands were then cut into small pieces and stored in a dessicator after drying under vacuum for 72 h.

Sample Preparation

(a) For Thermal Analysis. Dried pellets of pure and DBS mixed PET were compression-molded at 275°C and under 4000 psi followed by rapid quenching in ice-water mixture to make amorphous PET films. These films were dried as before under vacuum prior to all characterization.

(b) For Density Measurements. The small pieces of compression molded, amorphous films were sandwiched between two microscopic cover glasses. These films were then crystallized isothermally in a silicone oil bath kept at temperature of $110 \pm 1^\circ\text{C}$. The samples were taken out at different time intervals and readily quenched by dipping into cold carbon tetrachloride at 0°C.

(c) For Studies by Small Angle Light Scattering (SALS) and Optical Transmittance Measurement. The compression-molded films were further made into thinner films by melting in a silicone oil bath kept at 270°C and rapidly quenched into cold carbon tetrachloride at 0°C. These films were then isothermally crystallized from the glassy state at 110°C for 5–6 h to give fully crystallized films.

Techniques of Characterization

Differential Scanning Calorimetry (DSC)

For thermal analysis of the samples, Mettler FP 800 thermosystem was used. The compression-molded films were used separately. First the sample was heated from room temperature to 275°C at the rate of 10°C/min, kept at this temperature for 5 min, and subsequently cooled at the same rate. All the transition temperatures were correlated properly.¹⁶

Density Measurements

The densities of crystallized samples were determined in density gradient column using the mixture of xylene and carbon tetrachloride liquids. The temperature was maintained at $25 \pm 1^\circ\text{C}$. The increase in density was taken as the index of crystallinity. If d_t and d_a are the densities of a sample after crystallization for time t and for a time much longer than the half-time of crystallization, respectively, then the volume fraction crystallinity in these two cases would be X_t and X_a , respectively, and are given by

$$X_t = \frac{d_t - d_a}{d_c - d_a} \quad (1)$$

and

$$X_a = \frac{d_a - d_a}{d_c - d_a} \quad (2)$$

where d_c and d_a are the densities of fully crystalline and purely amorphous samples, respectively. The reduced volume crystallinity (α) would, then be obtained by dividing Eq. (1) by Eq. (2), which is as follows:

$$\alpha = \frac{X_t}{X_a} = \frac{d_t - d_a}{d_a - d_a}$$

Small Angle Light Scattering (SALS)

The photographic light scattering apparatus used to record scattering pattern was previously described.¹⁷ The H_v light scattering patterns were recorded on NP22 ORWO plan film and scanned by a Joyce and Loebel microdensitometer. The H_v scattering pattern designates the directions of the polarizer and the analyzer with one in horizontal and other in vertical position.

Optical Transmittance

The films prepared for the above studies were characterized by Unicam SP series 2 spectrophotometer for determining the clarity of the films.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC)

DSC results on pure and nucleated PET have been shown in Figures 1–3. Figure 1 shows the DSC scans of pure as well as nucleated PET. The incorporation of DBS into the polymer clearly shows the expediting effect on the crystallization kinetics of PET. The temperature of crystallization (T_{ch}) when heated from glassy state is reduced to 118–119°C for PET containing DBS in the range of 0.5–1% while that of pure PET is 131°C. This decrease in the crystallization temperature can be taken as an indication of increase in the rate of crystallization.¹² Similarly the temperature of crystallization from the melt (T_{cc}) is significantly increased to 220–222°C in the case of PET containing nucleating agent, DBS, in the range of (0.5–2%) compared to 210°C for pure PET which can also be taken as the increase in crystallization rate.^{18,19} Figures 2 and 3 show the variation of T_{ch} and T_{cc} , respectively, with the level of nucleating agent. From Figure 2 it can be clearly seen that the effect is maximum at the level of 0.5–1%. After this (1%) there is a slight decrease in the rate of crystallization which is manifested by a slight increase in T_{ch} to 121°C in the case of PET containing 2 wt % DBS. The slight decrease in the overall rate of crystallization as evidenced by the increase in T_{ch} is not very clearly understood at this stage. One plausible reason may be that the addition of excess amount of nucleating agent beyond a certain level does not necessarily increase the number of nucleation sites proportionately. However, due to over congestion of the present crystalline entities, the subsequent growth of the spherulites is hindered due to increased chances of impingement. On the other hand, there is not much difference in the value of T_{cc} in the case of PET containing DBS in the range of 0.5–2%, as observed in the Figure 3. Therefore, at the lower range of temperature the restriction of growth is slightly more prominent because of the high viscosity of the medium, since, in addition to the enhanced possibilities of mutual impingement, the mobility of the molecules are much more hindered.

Density Results

The density vs. log (time of crystallization) plots are given in Figure 4. The sigmoidal part of these curves represents the primary crystallization, i.e., nucleation and growth of the crystalline entities, the development of which is ultimately stopped by mutual impingement. The increase in density after this becomes too small to be detected by this experiment. The reduced volume fraction crystallinity (α) vs. log (time of crystallization) plots for all compositions are given in Figure 5. Figures 4 and 5 both show that the rate of crystallization is significantly affected by the use of DBS in PET. Here it is found that the induction period (T_i) represented by the initial, almost horizontal part of the crystallization curves, get more and more reduced with increasing amount of DBS. In the case of pure PET no appreciable change in density was observed until 10 min, whereas, for PET nucleated by DBS, the crystallization started much earlier (T_i is about 2 min). Furthermore, PET containing 0.5–1% DBS attained more than 50% of crystallinity before crystallization starts for pure PET. PET containing 2% DBS has been found to

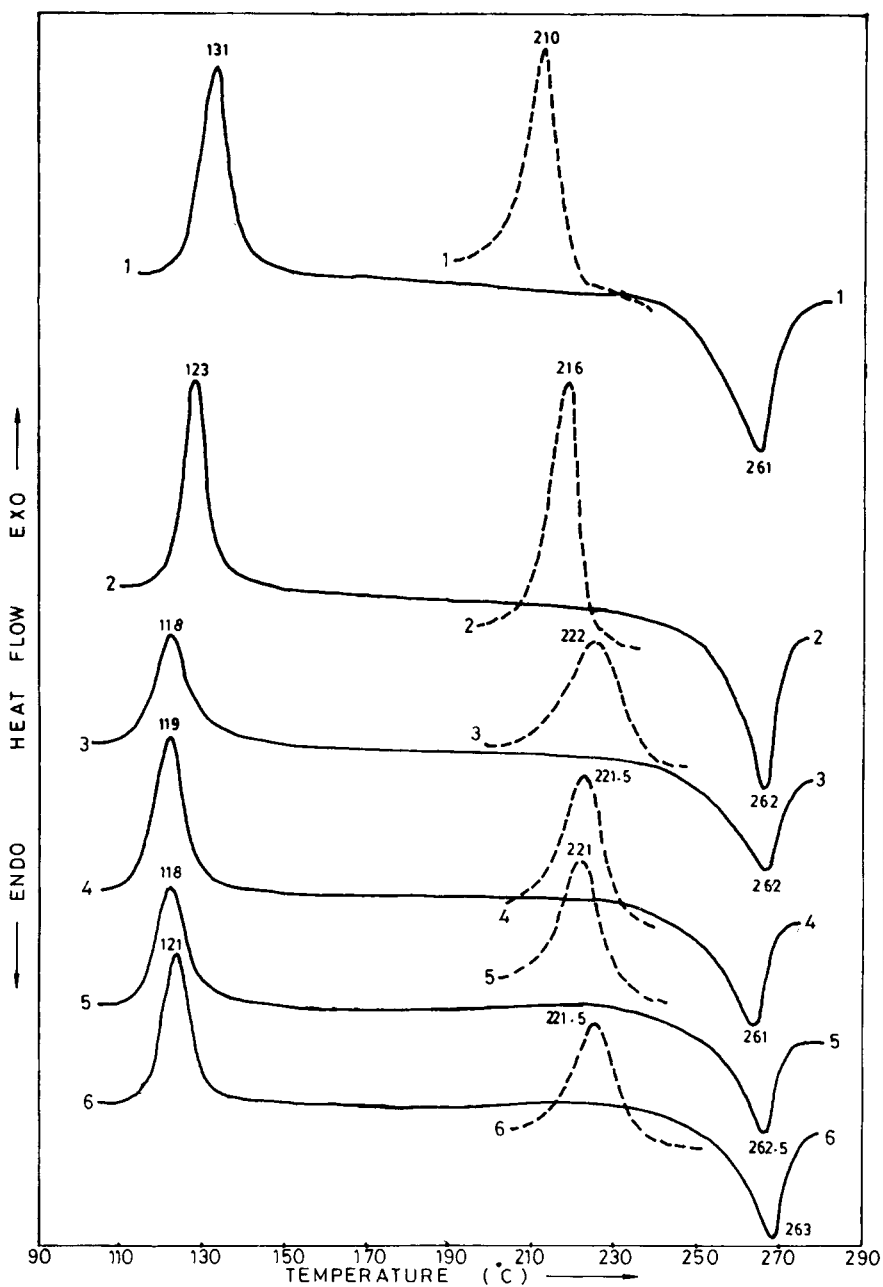


Fig. 1. DSC scans of pure and nucleated PET: (1) pure PET; (2) PET + 0.3 wt % DBS; (3) PET + 0.5 wt % DBS; (4) PET + 0.7 wt % DBS; (5) PET + 1.0 wt % DBS; (6) PET + 2.0 wt % DBS.

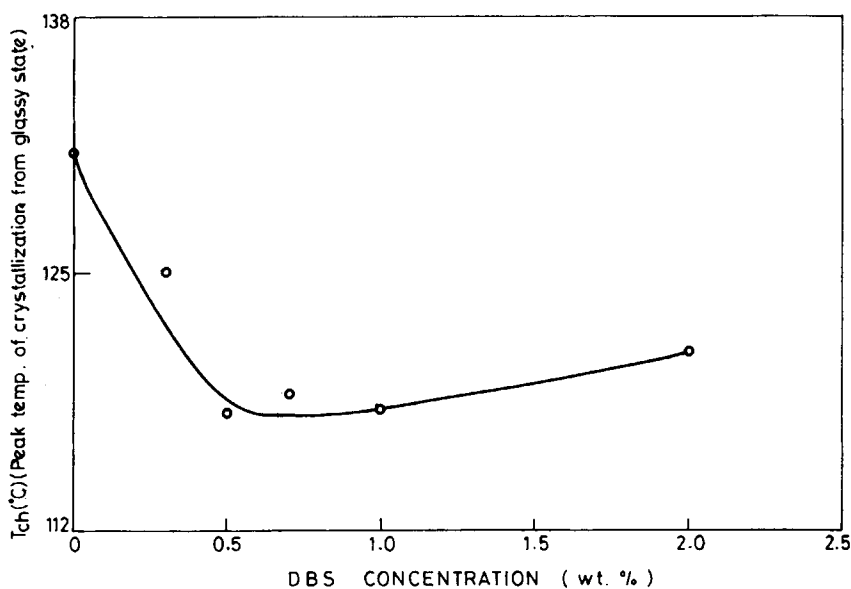


Fig. 2. Plot of T_{ch} as a function of the concentration of the nucleating agent.

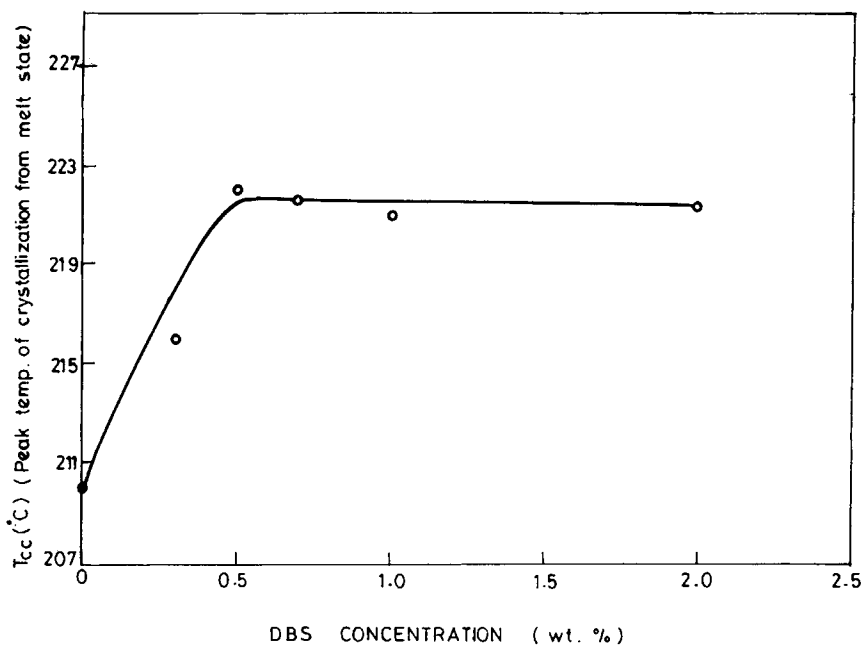


Fig. 3. Plot of T_{cc} as a function of the concentration of the nucleating agent.

start crystallizing almost as early as PET with 0.5–1% of DBS, but proceeds a little slower after the initial period.

Figure 6 shows the plot of $\log[-\ln(1 - \alpha)]$ against $\log t$ according to the well-known Avrami equation (3): $\log[-\ln(1 - \alpha)] = \log k + n \log t$,⁴ from which the crystallization rate constant K , the Avrami exponent n , and the half-time of crystallization $t_{1/2}$, are determined. The values of K , n , and $t_{1/2}$

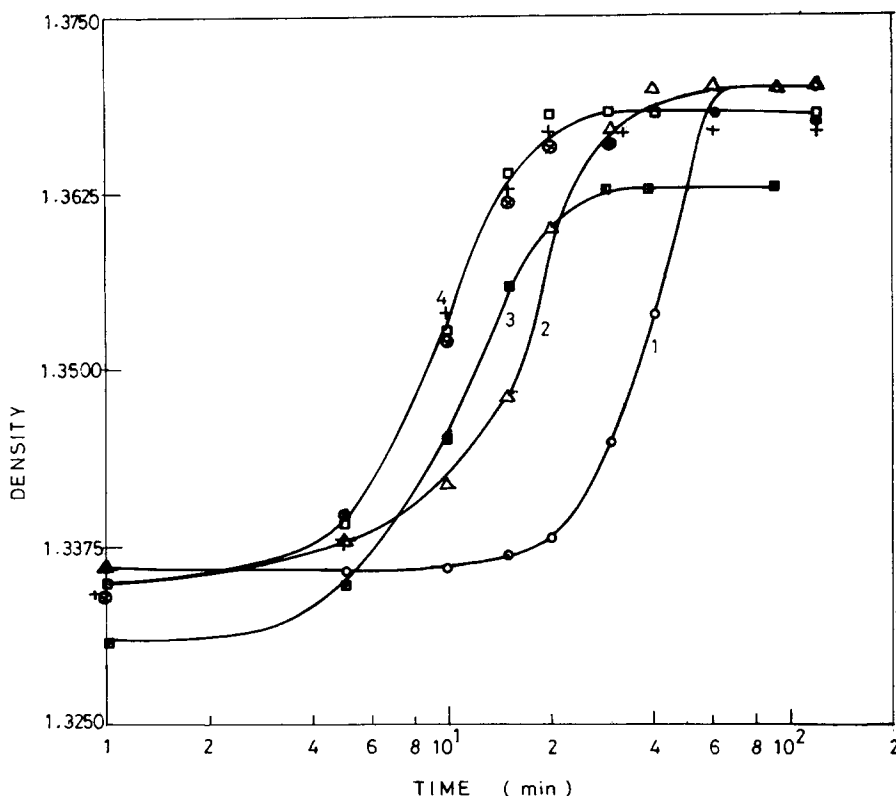


Fig. 4. Plot of density as a function of log (time of crystallization): (1) pure PET; (2) PET + 0.3 wt % DBS; (3) PET + 2.0 wt % DBS; (4) PET + (0.5, 0.7, 1.0) wt % DBS.

for the various samples are listed in Table I. The plot of $t_{1/2}$ as a function of concentration of DBS has been shown in Figure 7. This figure shows that DBS acts as a good nucleating agent for PET in the level of (0.5–1%) where the minimum $t_{1/2}$ is 9.7 min while the corresponding $t_{1/2}$ for pure PET is 39 min. When DBS is added at a higher level of about 2%, the slight increase in $t_{1/2}$ (10.4) clearly indicates small reduction in the overall rate of crystallization as has been observed in the other figures including the DSC isotherms. This also supports the fact that when DBS is used beyond a certain level, the growth rate of the spherulites is restricted with ensuring reduction in the overall rate of crystallization. Such reduction in the overall rate of crystallization when the nucleating agents are used above a certain level has been reported for other nucleating agents also.^{4, 11}

The values of Avrami exponent n can signify, as mentioned earlier, the mechanism of crystallization.^{1,20} The value of n for pure PET is 3.5 whereas with DBS it becomes 2.1–2.5. Although the fractional values of n make the proposition of well-defined mechanism of crystallization somewhat difficult, it can be qualitatively described as the overlapping of several growth processes.²⁰ The value of about 3.5 of n for pure PET indicates 3-dimensional spherulitic growth rate. Furthermore, the value of about 3.5 for n is still indicative of heterogeneity in the process because the theoretical value of n should be 4 for 3-dimensional growth for homogeneous nucleation. This can be attributed to

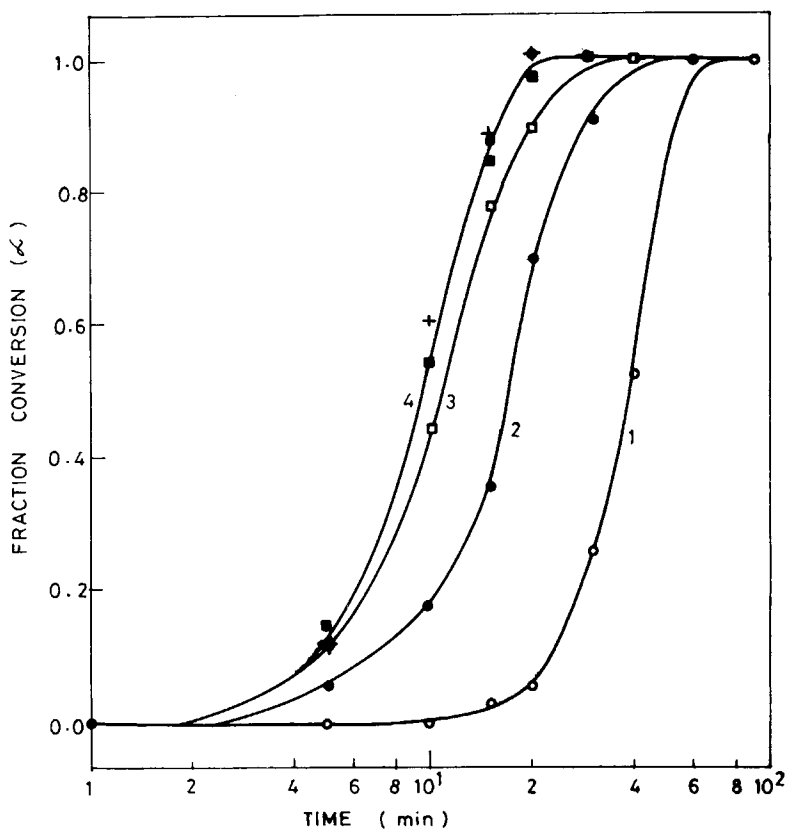


Fig. 5. Plot of volume fraction crystallinity as a function of long (time of crystallization): (1) pure PET; (2) PET + 0.3 wt % DBS; (3) PET + 2.0 wt % DBS; (4) PET + (0.5, 0.7, 1.0) wt % DBS.

the fact that pure homogeneity in nucleation is a rare possibility. The growth nature is essentially 3-dimensional, spherulitic with sporadicity or heterogeneity.

As we increase the heterogeneity of the system by deliberate addition of the nucleating agents, the value of n comes down to 2.5 for PET containing 0.5–1% of DBS with convincing indication of heterogeneity as well as the possibility of 2-dimensional growth. This further reduces to a value of 2.2 for PET containing 2% of DBS. These values indicate a combination of spherulitic and sheaflike superstructure with different time dependency of the nucleation in different samples. The value of 2.2 indicates the major contribution from sheaflike growth with instantaneous nucleation or rodlike with sporadic nucleation. However, combination of more than one process may be a possibility in all the cases. In the following sections study on the morphology by small angle light scattering would shed some light on this behavior.

With regard to mechanism of nucleation, it is feasible that DBS can act as nucleating agent both in the molten and resolidified state. However, in the present case it has been assumed that DBS mainly nucleates in resolidified state as has already been reported by Stein and co-workers,¹⁵ especially in case

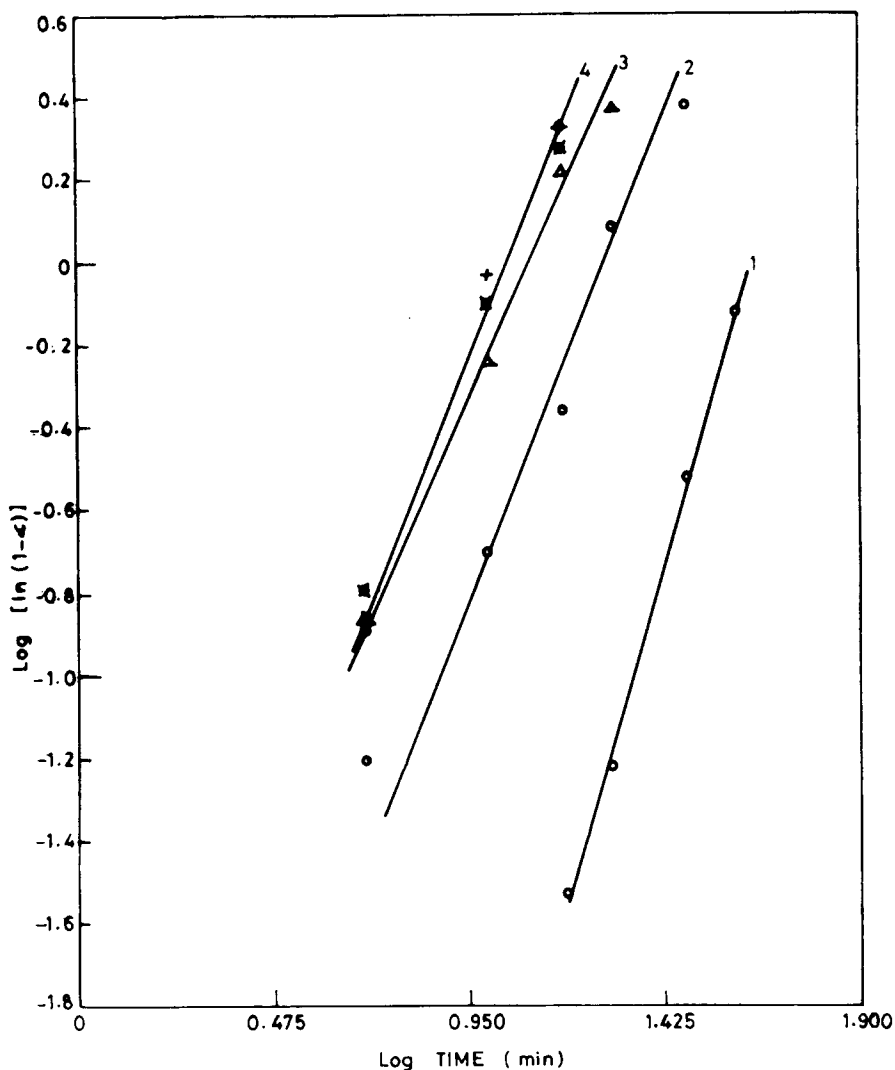


Fig. 6. Avrami plots for pure and nucleated PET: (1) pure PET; (2) PET + 0.3 wt % DBS; (3) PET + 2.0 wt % DBS; (4) PET + (0.5, 0.7, 1.0) wt % DBS.

TABLE I
Crystallization Parameters for Pure and Nucleated PET Crystallized at 110°C
from Glassy State

Sample	% volume crystallinity at the limiting time	Half-time of crystallization $t_{1/2}$ (min)	Rate constant K (min) ⁻ⁿ	Avrami exponent (n)
Pure PET	28.60	38.74	2.10×10^{-6}	3.47
PET + 0.3% DBS	29.00	15.68	5.10×10^{-4}	2.60
PET + 0.5% DBS	28.10	9.70	2.06×10^{-3}	2.56
PET + 0.7% DBS	28.20	9.70	2.06×10^{-3}	2.56
PET + 1% DBS	29.48	9.70	2.06×10^{-3}	2.56
PET + 2% DBS	28.39	10.42	3.99×10^{-3}	2.20

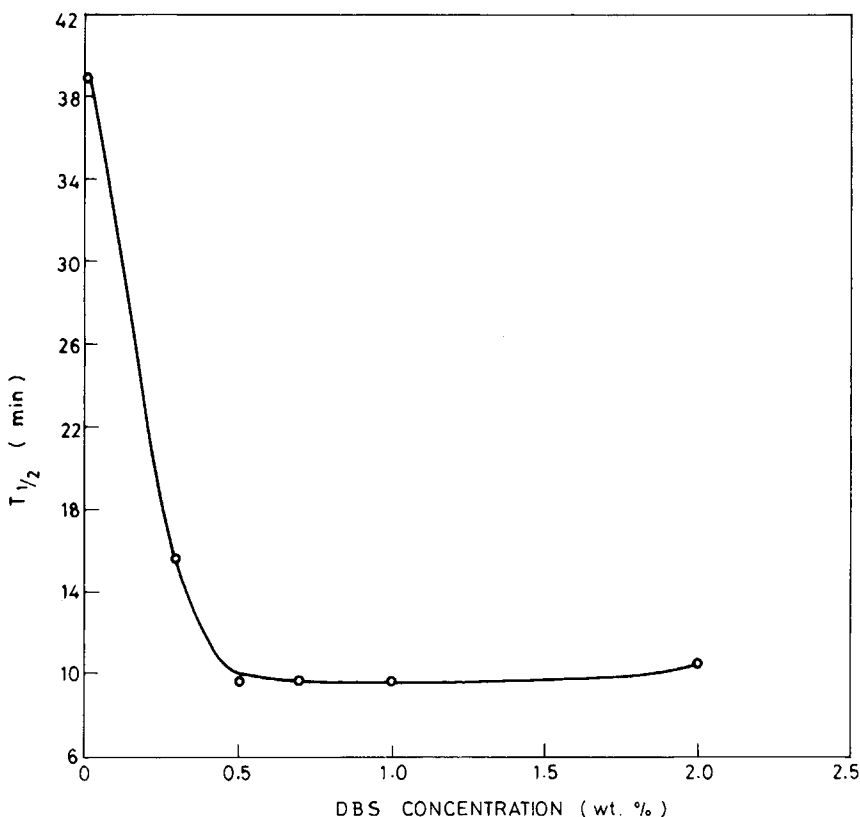


Fig. 7. Plot of half-time of crystallization ($t_{1/2}$) as a function of the concentration of the nucleating agent.

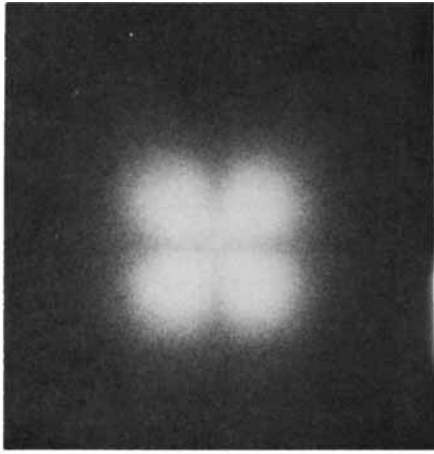
of polypropylene. Moreover, the crystallization of PET has been studied mainly from the glassy state and at a temperature as low as 110°C , which is far below the melting point of DBS (225°C), and hence it is essentially a case of nucleation by resolidified DBS. At present, further work to identify the mechanism of nucleation of DBS is under consideration mainly to ascertain whether DBS can also nucleate PET in the molten condition as in the case of liquid-induced crystallization of PET.

Small Angle Light Scattering (SALS)

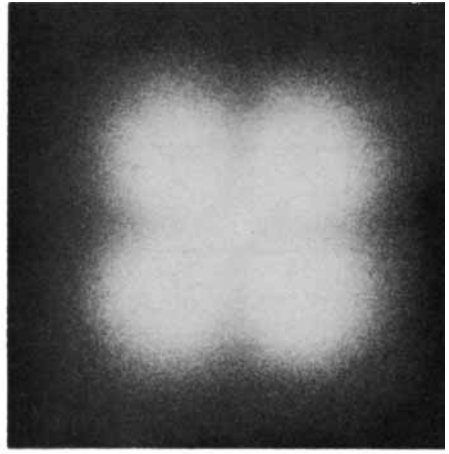
The H_v scattering patterns of pure and nucleated PET have been shown in Figures 8(a)–8(f). The samples have been crystallized at 110°C for 6 h to achieve the limiting crystallinity and maximum spherulitic growth at this particular temperature. In all cases except in Figure 8(f), where the pattern is sheaflike, the spherulitic radii have been calculated using Stein's equation¹⁷:

$$R = 1.025\lambda / \sin(\theta_m/2)\pi$$

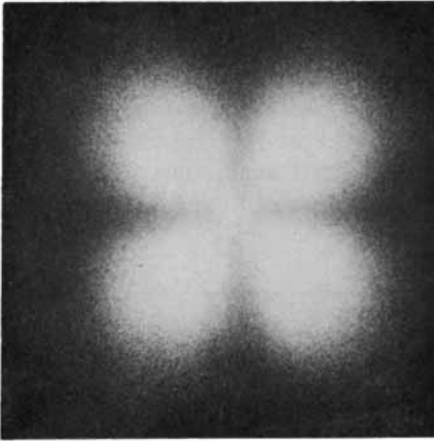
where $\lambda = 6328 \text{ \AA}$ and θ_m is the angle of maximum intensity measured at an azimuthal angle of 45° . Figures 8(a)–(e) are distinctly spherulitic with a



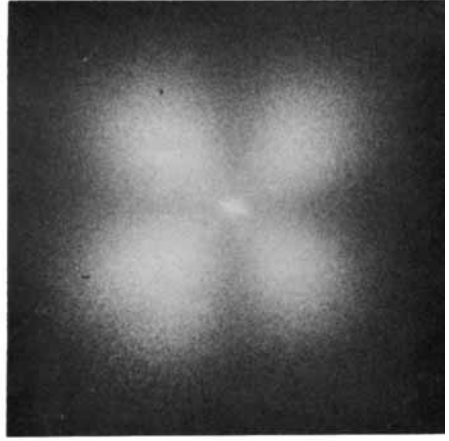
(a) Pure PET



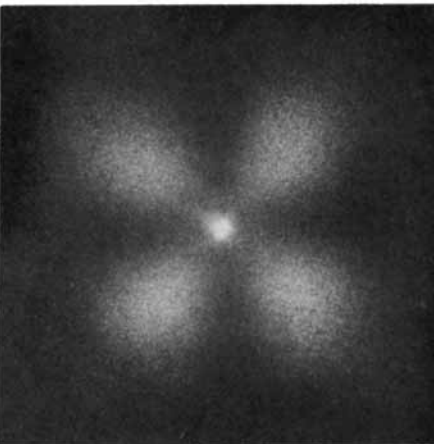
(b) PET + 0.3% DBS



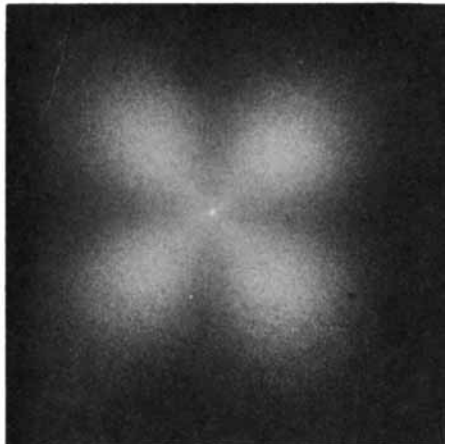
(c) PET + 0.5% DBS



(d) PET + 0.7% DBS



(e) PET + 1% DBS



(f) PET + 2% DBS

Fig. 8. H_v scattering patterns of pure and nucleated PET.

TABLE II
Ultimate Spherulitic Radius and Nucleation Density for Pure and Nucleated PET Crystallized at 110°C from Glassy State

Sample	Maximum spherulite radius R_{\max} (μm)	Nucleation density $N \times 10^{-18}$ (m^{-3})
Pure PET	1.59	0.059
PET + 0.3% DBS	0.95	0.275
PET + 0.5% DBS	0.93	0.296
PET + 0.7% DBS	0.89	0.340
PET + 1% DBS	0.85	0.390
PET + 2% DBS	Sheaflike	—

gradual increase in the size of the pattern, which implies that the smaller spherulites are formed with increase in the level of DBS. The values of the Avrami exponent obtained from the density data can be matched with the SALS pictures at this stage. The value of 3.5, for pure PET, clearly indicates and is verified by the spherulitic structure which is 3-dimensional and develops mainly out of instantaneous nucleation. Figures 8(b)–(e) cannot be directly correlated with the fractional values obtained for n from density data given in Table I and can be due to the combination of 3- and 2-dimensional

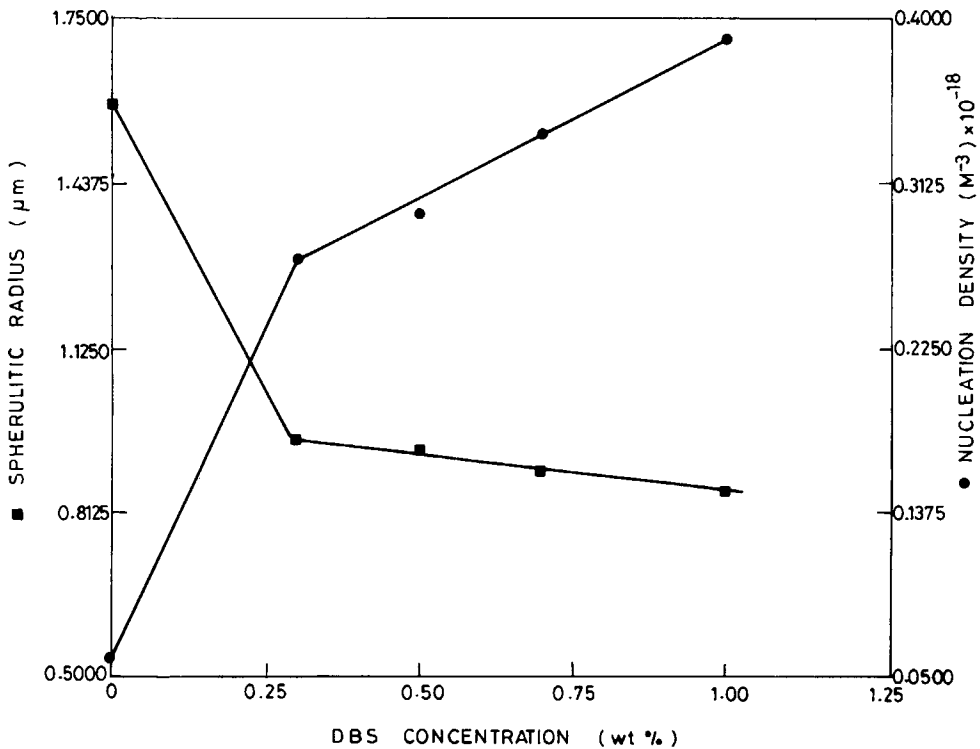


Fig. 9. Plots of spherulitic radius and nucleation density as function of the concentration of the nucleating agent.

growth. Figure 8(f) clearly shows a sheaflike scattering pattern for PET containing 2 wt % DBS, which is in good agreement with the value of 2.2 for n . The introduction of heterogeneity makes the system more complex, and combination of more than one growth process cannot be altogether ruled out.

The ultimate spherulitic radii calculated using Stein's equation for all the samples are given in Table II. The spherulitic radius for pure PET is about 1.5 μm , whereas for the nucleated samples the radii are in the range of 0.8–0.9 μm . Above 1% of DBS there is no appreciable decrease in the spherulite size. The nucleation density has been calculated using the equation of Keizer²¹:

$$(4/3) \pi R_{\max}^3 = 1/N$$

where N is the number of nuclei per unit volume. The nucleation densities are given in Table II. Figure 9 shows the nucleation density as well as the spherulitic radius as functions of DBS concentration which shows that the addition of more than 1% of DBS does not have further effect on the size of the spherulites. The change in spherulitic size and hence in the nucleation density is very sharp in going from pure PET to PET containing 0.3 wt % DBS. After that, this change is remarkably less. This confirms that, with the addition of the nucleating agent, DBS, the nucleation sites do not increase proportionately.

The H_V scattering patterns of quenched PET with and without nucleating agent, DBS, have been shown in Figure 10. PET and PET containing 0.3–0.5 wt % DBS do not show any characteristic pattern. PET containing 0.7–2 wt % DBS shows distinct rodlike superstructures with increasing intensity with the level of DBS in the system. DBS is itself a crystalline material. So the scattering may be either due to the DBS particles or due to the rapid formation of PET superstructure. So at this stage it can be assumed that the excess of DBS has formed agglomerates which both scatter the visible light as well as restrict the growth of spherulites. To determine the average size of agglomerates, an amorphous polymer matrix is essential. Though quenched PET did not produce any characteristic H_V pattern, still there may be some small superstructures formed when nucleating agents are used. So these superstructures will overlap with the scattering, if any, due to the nucleating agents. Some amorphous polymers, e.g., polystyrene, polycarbonate, etc., having no anisotropy of their own, can be used to determine the agglomeration size using corresponding V_V pattern and its analysis.¹⁵ In a follow-up study, it has been conclusively shown that DBS forms agglomerates and is being reported in a separate paper.²² Stein and co-workers have also shown the formation of agglomerates of DBS when used with polypropylene.¹⁵

Studies on Light Transmission

The effect of nucleating agent on the clarity of a polymer film is also of considerable importance. As has been mentioned earlier, the addition of nucleating agent expedites the process of crystallization by providing more nucleation sites to the crystallizing phase, which results in the formation of smaller spherulites and giving better clarity of the film. The light transmission of quenched films and crystallized films are shown in Figure 11. The trans-

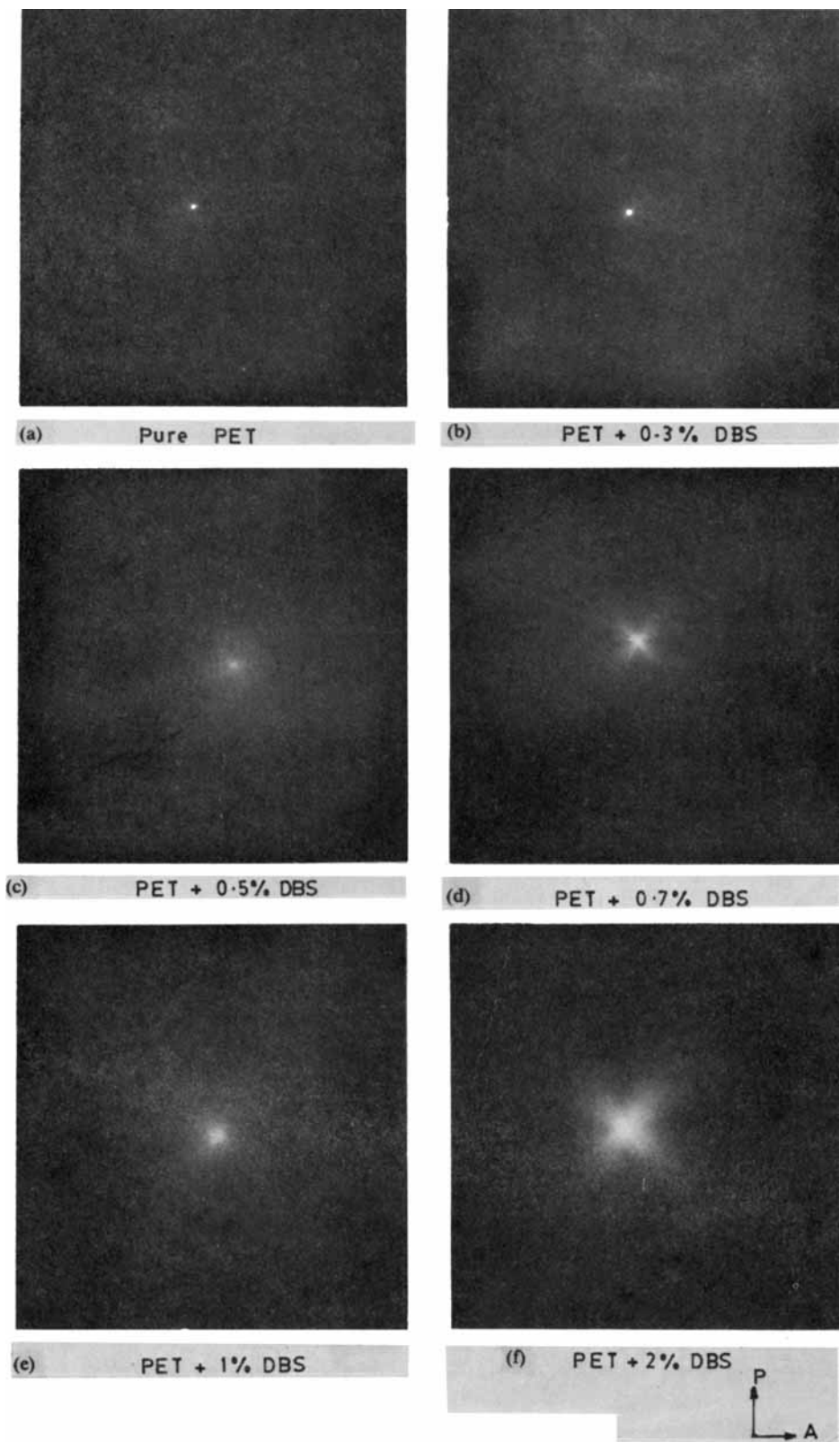


Fig. 10. H_v scattering patterns for quenched pure and nucleated PET.

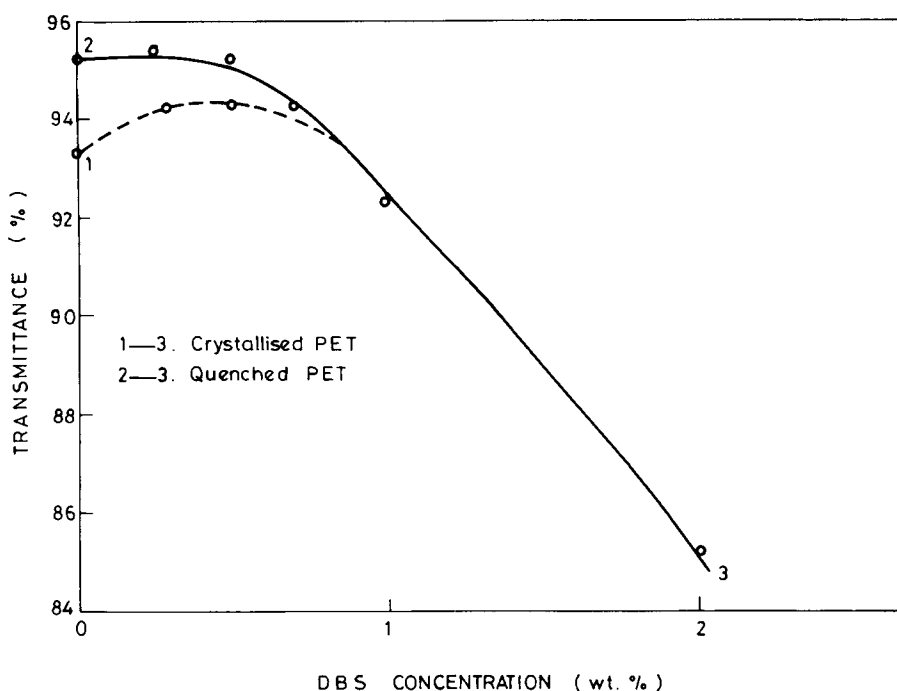


Fig. 11. Plot of % transmittance as a function of the concentration of the nucleating agent.

parency of the quenched nucleated PET films containing DBS up to 0.5% was almost the same as that of pure PET. With higher level, i.e., at 1%, the transparency of the quenched film is considerably lowered while at 2% the transparency is still lower and this transition from 1–2% is remarkable.

The crystallization from the glassy state reduces the transparency of the films. The presence of nucleating agent in PET reduces the spherulite's size thereby increasing the transparency of the film. For the crystallized films PET containing 0.5–0.7% nucleating agent show maximum transparency. Figure 11 shows the variation of transparency of the crystallized film as a function of concentration of DBS. Moreover, it is also important to see that the change in transparency due to crystallization process is significant in case of pure PET and PET containing nucleating agent up to the level 0.7%. After this, the change is not significant probably because of the scattering from DBS agglomerates, the size of which possibly outplays the contribution of the spherulites formation.

CONCLUSIONS

Based on the thermal and crystallization kinetics studies on poly(ethylene terephthalate) containing dibenzylidene sorbitol it has been clearly shown that DBS acts as a good nucleating agent for increasing the crystallization rate of PET. Morphological study reveals that this nucleating agent reduces the spherulitic size due to an increase in nucleation sites and increases the transparency due to the smaller spherulite size. However, when used beyond a

certain level, DBS tends to agglomerate, thereby decreasing the effectiveness of the nucleating agent as evidenced through the increase in $t_{1/2}$ and decrease in transparency and no appreciable change in nucleation density.

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