Study on the agglomeration of nucleating agents in amorphous and semicrystalline polymer systems

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The agglomeration of an organic nucleating agent, dibenzylidene sorbitol, in polystyrene and polycarbonate has been studied with the help of small-angle light scattering. Characteristic V_v patterns (with parallel polars) show that the intensity of the scattering increases with an increase in the level of nucleating agent. The angular distribution of the intensity has been analysed on the basis of Debye–Bueche theory and the average sizes of the agglomerated nucleant particles have been determined. The size of the agglomerated particles is then related to the effect of nucleant on the superstructure when incorporated in semicrystalline polymers such as poly(ethylene terephthalate).

(Keywords: crystallization; nucleation; nucleating agents; agglomeration; small-angle light scattering; Debye–Bueche theory)

INTRODUCTION

It is well known that certain additives, preferably known as nucleating agents[1], when added to a semicrystalline polymer significantly affect the crystallization behaviour and related morphology of the polymer. The nucleating agents provide additional nucleation sites which are responsible for a faster crystallization rate as well as the formation of small spherulites which improve the clarity of the polymer[2]. In the case of polypropylene[3] it has been shown that the incorporation of a nucleating agent improves the clarity in a film and is accompanied by a decrease in the spherulitic size. However, beyond a certain level of incorporation, the transparency of the film gets reduced with practically no further reduction in spherulite size. This study also showed that these nucleating agents tended to agglomerate, forming large particles which scatter visible light, thereby decreasing the transparency. In a previous paper[4] we have shown that dibenzylidene sorbitol (DBS), an organic nucleating agent, considerably improves the rate of crystallization of poly(ethylene terephthalate) (PET). It also reduces the spherulitic size of the polymer and consequently improves the clarity of PET films. It was also observed that the same nucleating agent, when used beyond a certain level, did not further reduce the spherulitic size but reduced the transparency of the film a little. A faint rod-like H_v pattern also appeared in the case of quenched PET film containing an excess amount (about 1%) of the nucleating agent whereas no such pattern was observed in the case of quenched PET without nucleating agent or with nucleating agent below 0.7%. The V_v scattering showed no pattern for pure PET but showed circular patterns for nucleated PET. The V_v intensity was observed to increase with an increase in DBS content.

It is on the basis of these observations[3,4] that we have developed special interest in studying the probable size of the agglomeration of nucleating agents in polymer systems. However, this would be difficult with PET since the crystal structure of PET itself would interfere, but it would be possible by using amorphous polymers which have solubility parameters similar to that of PET.

From the well known theories of small-angle light scattering[5,6] it is known that the H_v scattering (with cross polars) arises out of anisotropic fluctuations whereas the V_v scattering (with parallel polars) is due to both anisotropic and density fluctuations. Since PET is essentially a crystalline polymer it may give rise to anisotropic fluctuations due to spherulite formation, which will combine with the density fluctuations due to the presence of extraneous materials. Hence a V_v scattering pattern would be obtained from which it is very difficult to isolate the effect due to only density fluctuations that is of prime importance in this case in order to determine the size of DBS agglomerates. Therefore it was fairly logical to select some amorphous polymers such as polystyrene (PS) and polycarbonate (PC) which generally do not show any anisotropic fluctuations and hence show no H_v scattering pattern. Thus these two polymers would provide ideal systems to study the V_v scattering which in these cases only arises out of the density fluctuations due to the presence of the nucleating agents.

The solubility parameters[7] of PS and PC are also not much different from that of PET. Therefore the level of compatibility between this nucleating agent and PS or PC would be comparable to that between the nucleant and PET.

THEORETICAL BACKGROUND

It is well known that inhomogeneities of any kind in a system lead to scattering of light[8,9]. These inhomogeneities are the source for density fluctuations in the system. If a beam of polarized light is allowed to be incident on such systems the intensity and angular

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distribution of the scattered light would depend on the fluctuations in density and/or refractive index of the system. Besides the amplitude of these fluctuations, there is another important factor, which may be called the correlation distance. It can be considered as a length which is a measure of the grain size in the medium. This consideration can be expressed mathematically by the introduction of a new term known as the correlation function, $\gamma(r)$, given by the following equation[8]:

$$\gamma(r)\langle\eta^2\rangle_{\text{ave}} = \langle\eta_1\eta_2\rangle_{\text{ave}}$$

where η_1 and η_2 are the local fluctuations in refractive index from some average value at points 1 and 2 a distance r apart and $\langle\eta^2\rangle_{\text{ave}}$ is the average value of η^2. Now if r is equal to zero, then $\langle\eta^2\rangle = \langle\eta_1\eta_2\rangle$ which leads to $\gamma(r) = 1$. When the value of r is very large, then η_1 and η_2 would vary quite independently of each other so that the product $\langle\eta_1\eta_2\rangle = 0$, which gives $\gamma(r) = 0$. It is found that the value of $\gamma(r)$ changes from 0, when r is very large, to 1.0, when $r = 0$. For simplicity $\gamma(r)$ can be described by the Debye–Bueche model to be an exponential function[8]. In the case where $\gamma(r)$ is an exponential function, the inverse square root of the scattering intensity would be a linear function of the square of the scattering angle. The slope of this straight line would provide information about the size of the agglomeration. The size of the agglomeration can be determined by the equation[8,9]:

$$a = \frac{\lambda}{2\pi n}\left(\frac{\text{slope}}{\text{intercept}}\right)^{1/2}$$

where λ is the wavelength of visible light (6328 Å) and n is the average refractive index of the medium (1.59 for both PS and PC).

When one component is very dilutely dispersed into another component, the correlation distance a can be taken as a measure of the size of the first component. However, when a concentrated dispersion is considered, the correlation distance in that case can best be interpreted in terms of the transverse lengths given by Porod and Kratky[10]:

$$l_1 = a/\phi_2$$

$$l_2 = a/\phi_1$$

where l_1 and l_2 are the average lengths of random chords passing through the two phases with volume fractions ϕ_1 and ϕ_2 respectively. Our present study also involves the determination of nucleation density on the basis of these transverse lengths.

EXPERIMENTAL

Polystyrene with an intrinsic viscosity of 0.62 dl g^{-1} in toluene at 25°C corresponding to $M_w = 170000$ was obtained from Polychem India, and polycarbonate with an intrinsic viscosity of 0.51 in chloroform at 25°C corresponding to $M_w = 26000$ was obtained from the Plastics Division of General Electric Company (USA). The nucleating agent, dibenzylidene sorbitol (DBS), was obtained from Milliken Chemical Co., Spartunburg, USA under the tradename Millad 3905.

DBS was mixed with polystyrene and polycarbonate by using the method of solvent blending. DBS in required amount (0.75, 1.5, 2 and 3 parts per 100 parts of the polymer) was dissolved in *o*-chlorophenol along with the polymer. The mixture was refluxed continuously for 1 to 2 hours to get a clear solution. These solutions were then spread slowly and uniformly over mercury and quickly evaporated to give thin films. Films of pure polystyrene and polycarbonate were also prepared under similar conditions for proper comparison.

The films were cut into small pieces and placed between two microscope coverglasses. These sandwiched films were melted in a silicone oil bath for 5 min at 200°C and 270°C for polystyrene and polycarbonate respectively and then rapidly cooled in an ice/water mixture. These films were characterized by small-angle light scattering (SALS); circularly symmetric V_v scattering patterns were obtained for all the films and these patterns were recorded on NP22 Orwo plan films and scanned by a Joyce & Loebel microdensitometer.

RESULTS AND DISCUSSION

The characteristic V_v patterns for polystyrene and polycarbonate samples are shown in the *Figures 1* and *2* respectively. Here both the polymers are essentially amorphous; though polycarbonate is a semicrystalline polymer, it crystallizes with difficulty under certain conditions[7]. It can, therefore, be assumed here that the gradual increase in the size and intensity of the patterns is mainly due to the density fluctuations of the nucleant DBS only. The fluctuations increase with increase in the level of the nucleant. It may be noted that no H_v pattern was observed for any of the samples. The scattered intensity due to DBS has been obtained by subtracting the background intensity (I_{pp}) of a pure polymer sample from the intensity of polymer containing DBS (I_{np}). This can be termed a corrected intensity. This corrected intensity ($I_{\text{np}} - I_{\text{pp}}$) has been considered as the scattered intensity due to DBS only. The inverse square root of this effective intensity has been plotted as a function of θ^2. These plots of $I^{-1/2}$ as a function of θ^2 for polystyrene and polycarbonate containing different amounts of DBS have been shown in *Figures 3* and *4* respectively. It is observed that at low levels (0.75%) the slope of the line is very small, indicative of considerably lower extent of scattering. The slope of the line gradually increases with increase in the level of DBS.

For the polycarbonate system, similar observations were seen. Taking the ratio[3,8] of the slope and intercept of these lines, the value of a has been determined according to Debye–Bueche analysis using the relationship given earlier.

The values of a and l_1, the agglomerate size for polystyrene and polycarbonate, were calculated and these values are listed in *Table 1*. It is observed that the average size of the agglomerates gradually increases with increase in the level of DBS. The plot of agglomerate size (l_1) as a function of DBS concentration has been shown in *Figure 5*. Both polystyrene and polycarbonate behave in the same manner. In *Figure 5*, it has been shown that the slope of the line for polycarbonate is the same as that for polystyrene. With higher level of DBS, the size of the agglomeration in polycarbonate is slightly higher than that in polystyrene. This is also evidenced through the V_v pattern with higher intensity in *Figure 2*. This can be attributed to two reasons: (a) the slightly higher solubility parameter (9.5) for polycarbonate compared to polystyrene (9.2), which makes the difference from that of DBS (theoretically about 9) slightly higher; and (b) probably a slight amount of anisotropic fluctuation also takes place in polycarbonate in the presence of the

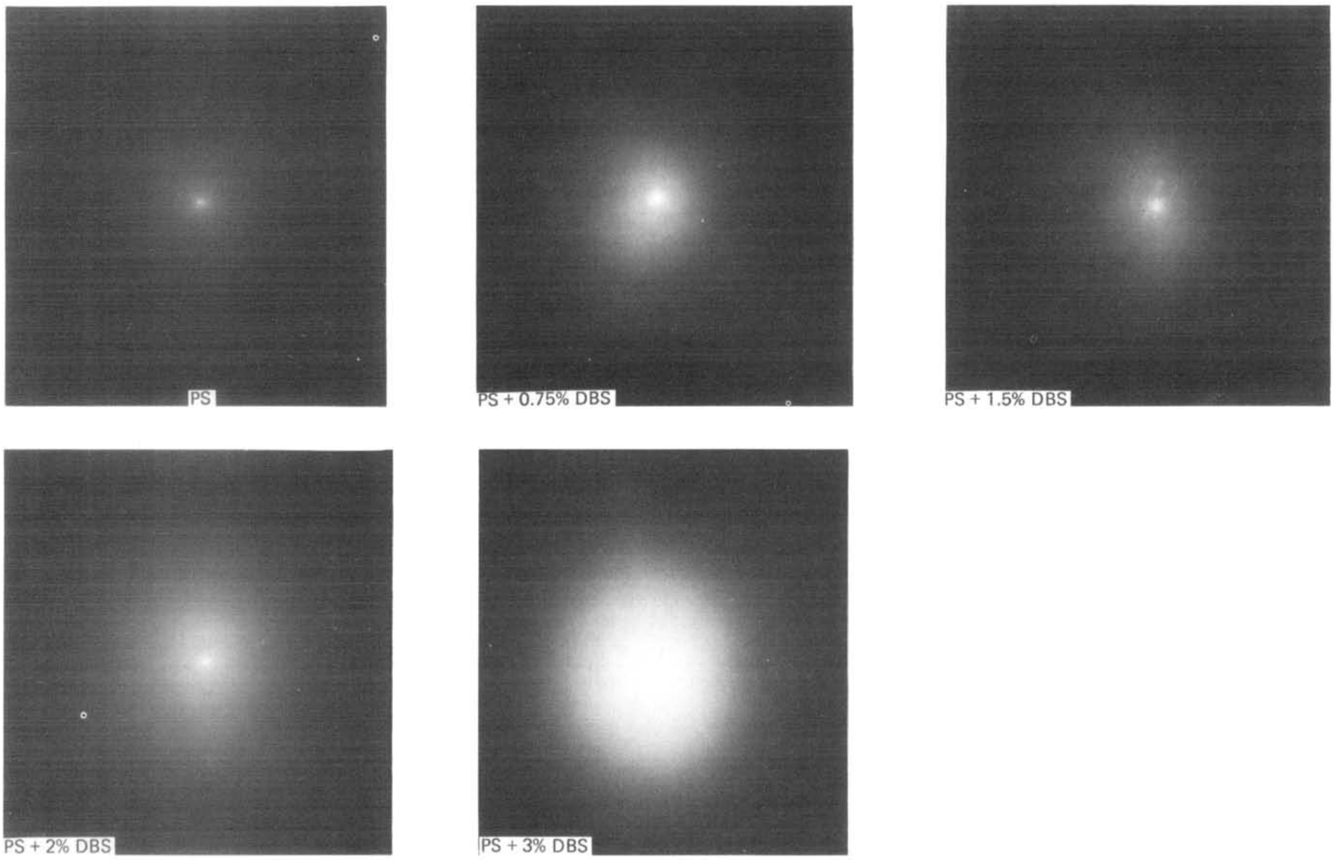

Figure 1 V_v scattering patterns for polystyrene samples

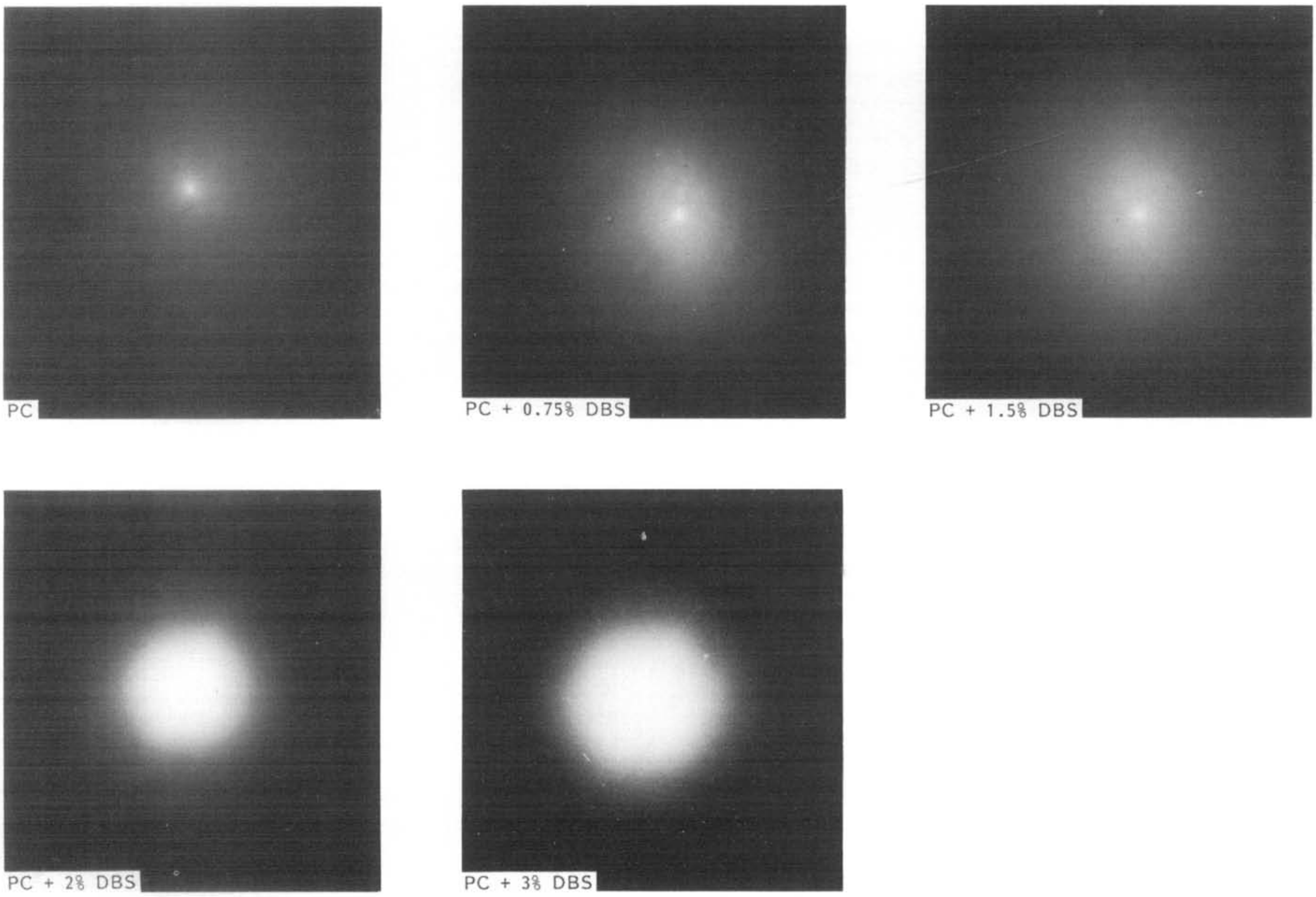

Figure 2 V_v scattering patterns for polycarbonate samples

nucleating agent. This higher intensity leads to higher size of agglomeration. In the case of polypropylene[3], a similar variation of agglomeration size with nucleant level was noticed.

The nucleation density due to the nucleating agents forming agglomerates can be determined on the basis of the transverse length (l_1) which will be given by:

$$N=\frac{\text{specific volume of nucleant}}{\frac{4}{3}\pi l_1^3}$$

Figure 6 shows the variation of nucleation density as a function of concentration of DBS. The corresponding data as shown in *Table 1* and *Figure 6* for nucleation densities clearly show that the presence of the nucleating agent provides nucleation sites which are fairly constant in the range 0.75–1.5 wt%. Beyond this, the number of nucleating particles falls sharply. This clearly points out that all the nucleating agent particles do not act as acutal 'nucleating' sites but remain ineffective. They may form agglomerates. In our earlier work on PET[4], we have shown the same trend in nucleation density. Though the actual numerical values for the nucleation density are slightly different, the trends are similar. The difference in the magnitude of the nucleation density may be attributed to the difference in the two approaches to determining

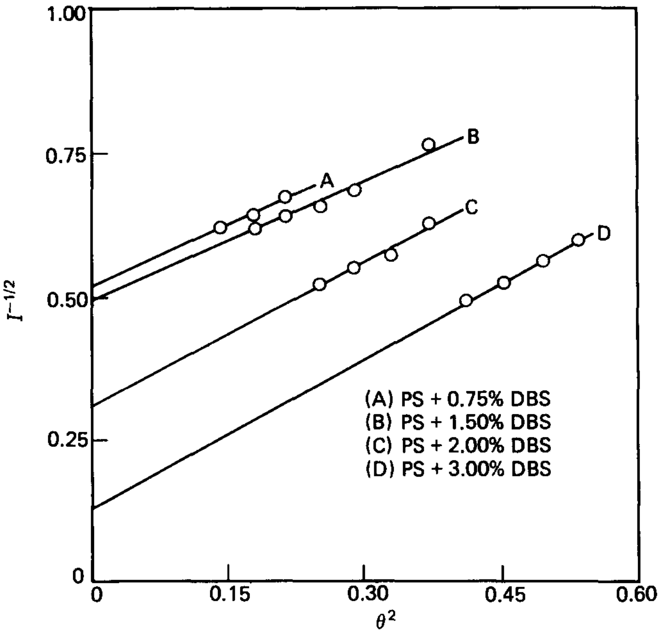

Figure 3 Plot of (intensity)$^{-1/2}$ as a function of θ^2 for polystyrene samples

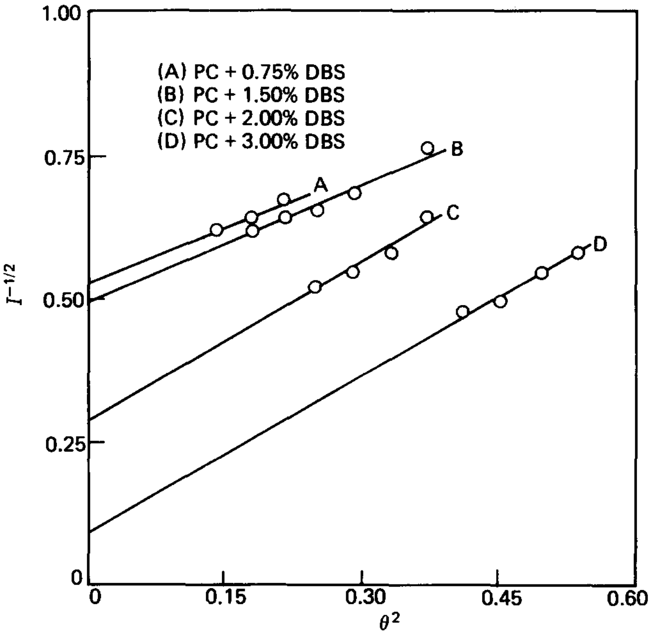

Figure 4 Plot of (intensity)$^{-1/2}$ as a function of θ^2 for polycarbonate samples

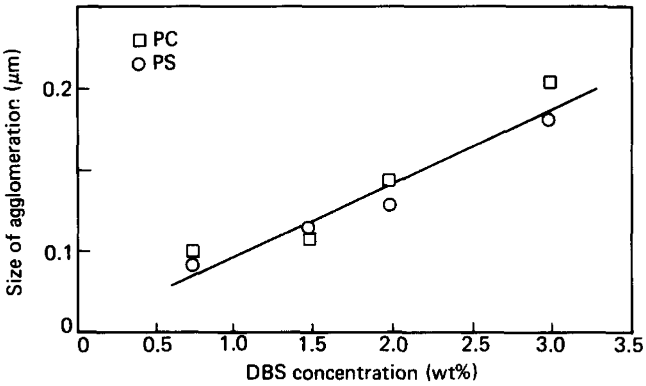

Figure 5 Plot of agglomeration size as a function of weight per cent of DBS added

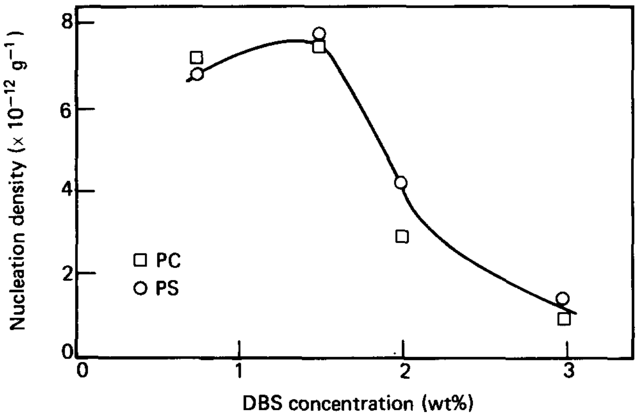

Figure 6 Plot of nucleation density as a function of weight per cent of DBS added

Table 1 Agglomerate size and nucleation density of DBS mixed with polystyrene and polycarbonate

DBS	Polystyrene				Polycarbonate			
(wt%)	ϕ_2	a	l_1	N (10^{-12} g^{-1})	ϕ_2	a	l_1	N (10^{-12} g^{-1})
0.75	0.992	0.062	0.062	6.83	0.991	0.062	0.062	6.83
1.5	0.985	0.075	0.076	7.71	0.983	0.075	0.075	7.55
2.0	0.980	0.100	0.102	4.22	0.977	0.113	0.113	2.93
3.0	0.970	0.160	0.170	1.40	0.966	0.19	0.190	0.92

these values. The former one was calculated by determining the spherulitic size on the basis of a model approach[11] and considering that each nucleation site formed a spherulite. On the other hand, in the present case the nucleation density has been determined on the basis of agglomeration size. The agglomeration size has been calculated from the angular distribution of V_v scattering intensity. This determination is based on the theory of correlation function proposed by Debye and Bueche. Irrespective of the approach used, the inference is basically the same. Therefore this agglomeration may be the cause of slight reduction in the overall crystallization of PET as mentioned earlier. This also clarifies the reason of less transparency in PET containing higher levels of DBS. Although polycarbonate has been used here as an amorphous matrix to provide a good background which only produced density fluctuations in the presence of foreign materials, this polymer was also observed to form well defined spherulites when treated under special conditions. The formation of spherulites has been observed to be much faster in the presence of DBS, which will be reported in another paper[12].

CONCLUSIONS

When DBS is mixed with polystyrene and polycarbonate, it forms agglomerates within the polymer system. The size of the agglomerates as calculated by small-angle light scattering showed that increasing the level of DBS linearly enhances the size of the agglomeration. In the case of polycarbonate, the size is a little larger. Because of this agglomeration, the films of both PS and PC become slightly turbid. The nucleation density of the nucleant has been determined on the basis of the size of agglomeration, which shows that there is a fairly constant nucleation density in the range of 0.75–1.5 wt% DBS. Beyond that, the nucleation density decreases sharply.

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