

# Activity of Substrates in the Catalyzed Nucleation of Poly(ethylene terephthalate) Melts

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Received 21 February 1996; accepted 20 June 1996

**ABSTRACT:** The activity,  $\Phi$ , of AgBr, AgI, PbF<sub>2</sub>, Ag<sub>2</sub>S, LiF, and CaF<sub>2</sub> in the catalyzed nucleation of poly(ethylene terephthalate) (PET) melts was determined using a nonisothermal differential scanning calorimetry (DSC) technique. A comparison with existing experimental data was made. It is established that the higher the melting temperature of the substrate the lower its activity as a crystallization core in the heterogeneous nucleation of PET. The lateral surface energy,  $\sigma$ , the end surface energy,  $\sigma_e$ , the adhesion energy,  $\beta$ , and the difference between the surface energies at the substrate/melt,  $\sigma_{sf}$ , substrate/deposit,  $\sigma^*$ , and the total energy of misfit dislocations,  $E_d$  [i.e.,  $\sigma_{sf} - (\sigma^* - E_d)$ ] were calculated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 349–353, 1997

**Key words:** nucleating activity; poly(ethylene terephthalate)

## INTRODUCTION

A number of methods for determining the kinetic constants of overall crystallization from nonisothermal experiments have been suggested in the literature.<sup>1,2</sup> Recently, we developed a formalism<sup>3</sup> for calculating the activity of substrates in the catalyzed nucleation of polymer melts using data from cooling DSC runs.

In the present investigation, an attempt was made to give an experimental proof for the method advanced in ref. 3 by studying the crystallization of poly(ethylene terephthalate) (PET) melts induced by inorganic substrates (AgBr, AgI, PbF<sub>2</sub>, Ag<sub>2</sub>S, LiF, CaF<sub>2</sub>). Experimental data existing in the literature were also considered.

To determine the lateral surface energy,  $\sigma$ , and the end surface energy,  $\sigma_e$ , of PET crystals, two

types of experiments were performed—under crystallization conditions guaranteeing sporadic or athermal nucleation, respectively. Knowing the values of the activity,  $\Phi$ , and the lateral surface energy,  $\sigma$ , the adhesion energy,  $\beta$ , was calculated.

The data on the activity of AgBr, AgI, PbF<sub>2</sub>, Ag<sub>2</sub>S, LiF, and CaF<sub>2</sub> in PET were treated in the framework of a formalism developed by Dobrev and Gutzow.<sup>4</sup> This formalism allows one to assess the relative contribution of the two main factors determining the nucleating activity, i.e., the natural misfit and the bonding energy across the substrate/overgrowing crystal interface. It turns out that in the induced crystallization of PET misfit effects are considerable.

## THEORETICAL BACKGROUND

Dobrev et al.<sup>3</sup> developed a method for determining the nucleating activity of substrates by ana-

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lyzing nonisothermal kinetics of overall crystallization at small undercoolings. According to this approach,<sup>3</sup> the cooling rate,  $q$ , and the undercooling,  $\Delta T_p$ , at which the crystallization curve reaches its maximum, are connected as follows:

$$\log q = \text{const} - \frac{B}{2.3\Delta T_p^2} \quad (1a)$$

where

$$B = \frac{16\pi\sigma^2\sigma_e V_m^2}{3k\Delta S_m^2 T_m n} \quad (2a)$$

In the above equations,  $\Delta T_p = T_m - T_p$ ,  $T_m$  and  $T_p$  being the melting temperature and the temperature corresponding to the peak of the crystallization curve, respectively;  $k$  is the Boltzmann constant;  $V_m$ , the molar volume of the crystallizing substance;  $\Delta S_m$ , the entropy of melting;  $\sigma$ , the lateral surface energy;  $\sigma_e$ , the end surface energy; and  $n$ , the corresponding Kolmogorov–Avrami exponent.

In the heterogeneous case, eq. (1a) takes the form

$$\log q = \text{const} - \frac{B^*}{2.3\Delta T_p^2} \quad (1b)$$

where

$$B^* = B\Phi \quad (2b)$$

The function  $\Phi$  can be used as a measure for the nucleating activity of a foreign substrate. For absolutely inert particles,  $\Phi$  is unity, and for very active substrates,  $\Phi$  is practically zero.

It is seen that the dependence of  $\log q$  on  $1/\Delta T_p^2$  is linear, the slope being equal to  $B/2.3$  or  $B^*/2.3$  for the homogeneous and heterogeneous cases, respectively. The ratio of the two slopes gives the value of  $\Phi$  [see eq. (2b)].

If crystallization takes place under athermal conditions, i.e., only growth of predetermined nuclei is observed, then

$$\log q = \text{const}_1 - \frac{B_a}{2.3\Delta T_p} \quad (1c)$$

The factor  $B_a$  (the index “ $a$ ” stands for the athermal case) has the form

$$B_a = \frac{4b_c\sigma\sigma_e V_m}{k\Delta S_m T_m} \quad (2c)$$

Here,  $b_c$  is the lattice cell parameter of the crystallizing substance. It is seen that by combining eq. (1a) and eq. (1c) the values of  $\sigma$  and  $\sigma_e$  can be determined. This problem was considered by Dobrev et al.<sup>5</sup>

The nucleating activity,  $\Phi$ , can be defined in a general way through the adhesion energy,  $\beta$ , as<sup>4</sup>

$$\Phi = 1 - \frac{\beta}{2\sigma} \quad (3)$$

For  $\beta = 2\sigma$  (i.e., for nucleation on its own substrate),  $\Phi = 0$ ; for  $\beta = 0$  (i.e., for homogeneous nucleation),  $\Phi = 1$ ; and for  $\beta > 2\sigma$ , the three-dimensional nucleus degenerates to a two-dimensional nucleus.

The adhesion energy,  $\beta$ , can be expressed as<sup>4</sup>

$$\beta = \sigma + \sigma_{sf} - (\sigma^* + E_d) \quad (4)$$

In the above equations,  $\sigma_{sf}$  and  $\sigma^*$  are the surface energies at the substrate/melt and substrate/overgrowing crystal interfaces, respectively, and  $E_d$  is the total energy of misfit dislocations. According to van der Merve,<sup>6</sup>  $E_d$  is determined by the natural misfit  $f = (b_s - b_c)/b_s$  existing between the lattice parameters of the substrate and the overgrowing crystal;  $b_s$  and  $b_c$  are the lattice cell parameters of the substrate and the polymer crystal, respectively.

By applying van Laar’s formula connecting the adhesion energy at the crystal/substrate phase boundary and the cohesion forces in the substrate and the overgrowing crystal and the Born–Lande formula relating  $E_d$  with the cohesive forces, Dobrev and Gutzow<sup>4</sup> derived a simple expression which describes the dependence of the activity,  $\Phi$ , on the melting temperature of the substrate,  $T_{ms}$ :

$$\Phi = a_0 - a_1 \left( \frac{T_{ms}}{T_m} \right)^{1/2} + a_2 \left( \frac{T_{ms}}{T_m} \right) \quad (5)$$

Here, parameter  $a_2$  accounts for the influence of misfit effects while parameter  $a_1$  reflects the interaction energy across the substrate/overgrowing crystal-phase boundary. The constant  $a_0$  depends both on the cohesive forces as well as on the natural misfit. Equation (5) allows one to assess the

**Table I Melting Temperatures and Crystallographic Data for the Nucleating Agents Employed**

Substrate	$T_{ms}$ (K)	Crystal Structure	Lattice Parameters (Å)
AgBr	703	Cubic	5.776
AgI	830	Hexagonal	4.580
PbF <sub>2</sub>	1097	Cubic	5.942
Ag <sub>2</sub> S	1115	Cubic	4.900
LiF	1121	Cubic	4.028
CaF <sub>2</sub>	1691	Cubic	5.402

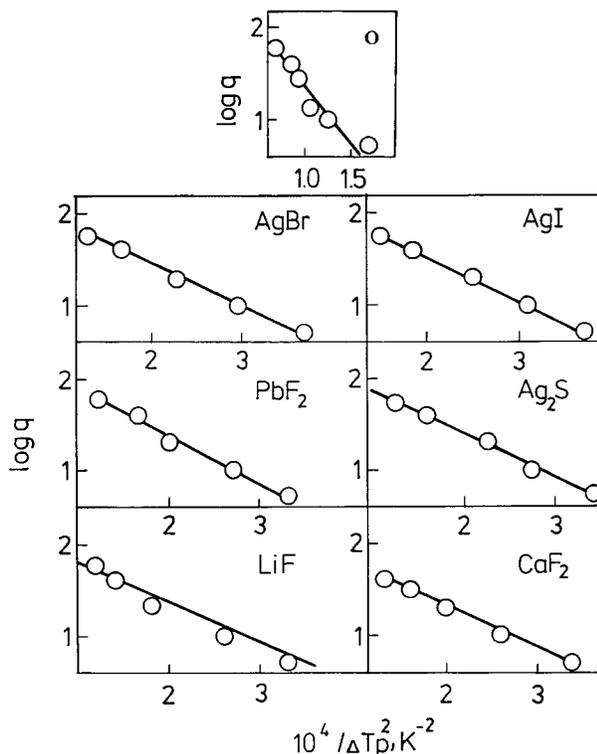
relative significance of the structural mismatch to the bonding energy.

## EXPERIMENTAL

PET was synthesized especially for the purpose of the present study without any fillers with an average viscosity molecular weight of 18,400. The melting temperature of the sample was determined in heating DSC runs as the temperature at which the last crystals melted. Thus, the measured value of  $T_m$  was found to be 548 K. PET has a triclinic crystal structure and  $a = 4.56$  Å,  $b = 5.94$  Å, and  $c = 10.74$  Å.

AgBr, AgI, PbF<sub>2</sub>, Ag<sub>2</sub>S, LiF, and CaF<sub>2</sub> were used as nucleating agents. All of them were analytical grade, standard Merck samples. The nucleants were introduced in PET by an extrusion technique in the concentration of 0.3 wt %. The crystal structure, the lattice parameters, and the melting temperature of the substrates used are summarized in Table I.

DSC measurements were performed using a Mettler calorimeter Model TA 4000, DSC 30, controlled by a computer. Calibration of the instrument was done using standard procedures. The measurements were conducted with several constant cooling rates: 5, 10, 20, 30, 40, and 60 K/min. All runs were carried out in a stream of dried nitrogen. The dynamic temperature program was preceded by an isothermal period of 4 min approximately 20°C above the melting temperature for sporadic experiments and 4 min just at the melting temperature for athermal crystallization. These temperature regimes were chosen in accordance with our previous study<sup>5</sup> as well as with literature data,<sup>7</sup> where it was established that in the first type of experiments sporadic nucleation was, in fact, guaranteed while the second type



**Figure 1** Dependence of  $\log q$  on  $1/\Delta T_p^2$  for plain PET (○); PET + AgBr; PET + AgI; PET + PbF<sub>2</sub>; PET + Ag<sub>2</sub>S; PET + LiF; PET + CaF<sub>2</sub>.

of heat treatment led only to growth of existing athermal nuclei.

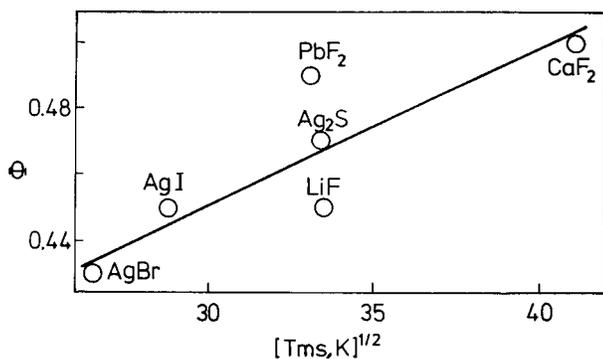
## RESULTS AND DISCUSSION

The results obtained for the rate dependence of the crystallization temperatures for plain and for nucleated PET are shown in Figure 1. The activity,  $\Phi$ , is calculated from the ratio of the slopes of the  $\log q - 1/\Delta T_p^2$  function for the homogeneous and the heterogeneous cases by virtue of eq. (2b). The values of the nucleating activity of the substrates used are listed in Table II.

It should be stated, however, that as far as there is some ambiguity in determining  $\Phi$  at large undercoolings, it is advisable to perform cooling

**Table II Nucleating Activity,  $\Phi$ , of Substrates in PET**

Substrate	AgBr	AgI	PbF <sub>2</sub>	Ag <sub>2</sub> S	LiF	CaF <sub>2</sub>
$\Phi$	0.43	0.45	0.49	0.47	0.45	0.5



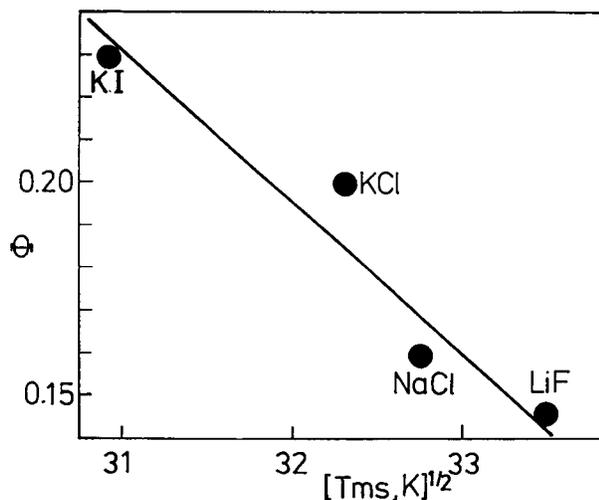
**Figure 2** Dependence of  $\Phi$  on  $T_{ms}^{1/2}$ .  $\Phi$  values are calculated from Figure 1. The line is drawn in a qualitative manner to show the tendency of decreasing activity.

crystallization runs near  $T_m$  as done in the present contribution. This temperature regime allows the direct calculation of the value of the nucleating activity of different substrates. Furthermore, in the considered temperature interval, the non-steady-state effects can be ignored.<sup>8</sup>

Figure 2 shows the dependence of  $\Phi$  on the melting temperature,  $T_{ms}$ , of the substrate. It is seen that the nucleating activity of substrates in PET decreases with increase of  $T_{ms}$ . According to eq. (5), such a dependence of  $\Phi$  on  $T_{ms}^{1/2}$  is an indication of considerable misfit values,  $f$ . On the contrary, for  $f \rightarrow 0$ , the reverse course of the  $\Phi - T_{ms}^{1/2}$  dependence is to be expected.

By using eqs. (1a) and (1c), the values of the lateral and the end surface energies were calculated. Thus,  $\sigma$  amounts to 6.5 erg/cm<sup>2</sup> and  $\sigma_e$  is 60 erg/cm<sup>2</sup>. In performing this calculation, the value  $\Delta S_m = 42.7 \text{ J K}^{-1} \text{ mol}^{-1}$  is used.<sup>9</sup> The lattice parameter  $b_c$  is calculated as a mean lattice parameter using the expression  $b_c = (V_m/N_a)^{1/3}$ ,  $N_a$  being Avogadro's number. Such an estimate when compared with existing data for lattice cell parameters (compiled by Wunderlich<sup>10</sup>) gives quite satisfactory results for polymer crystals if we calculate  $V_m$  as  $V_m = M_1/\rho$ , where  $M_1$  is the molecular weight per repeatable unit and  $\rho$  is the density of the crystalline material. It is calculated that  $V_m = 164.6 \text{ cm}^3/\text{mol}$  and  $b_c = 6.24 \times 10^{-8} \text{ cm}$ .

The value of  $n$  in eq. (2a) is taken from data



**Figure 3** Dependence of the activity  $\Phi$  on the melting temperature,  $T_{ms}^{1/2}$ , of substrates in the induced crystallization of PE nucleated with alkali halide crystals (according to data from ref. 11). The straight line is drawn by virtue of eq. (5).

from isothermal crystallization experiments. Dobrova et al.<sup>8</sup> obtained that at small undercoolings,  $n = 3$ . Keller et al.<sup>7</sup> also report that  $n = 3$  for PET crystallized in the temperature range under investigation.

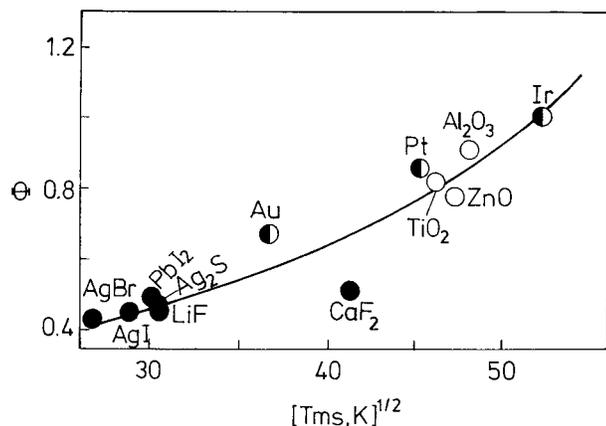
Thus, knowing the values of  $\sigma$  and  $\Phi$ , we can calculate the adhesion energy,  $\beta$  [cf. eq. (3)] and the energy difference  $\sigma_{sf} - (\sigma^* - E_d)$  [cf. eq. (4)]. The values of  $\beta$  and  $\sigma_{sf} - (\sigma^* - E_d)$  are given in Table III. It is seen from Table III that the values of  $\sigma_{sf} - (\sigma^* - E_d)$  are quite small. This finding implies that the total energy of misfit dislocations may have considerable values, so natural misfit may have a dominant influence on the nucleation capacity of the substrates in PET. The same conclusion has already been drawn on the basis of the analysis of the dependence of  $\Phi$  on  $T_{ms}^{1/2}$ .

To our knowledge, only Koutsky et al.<sup>11</sup> treated the nucleation ability of substrates in polymer melts in terms of adhesion energies. In ref. 11, heterogeneous nucleation of polyethylene (PE) catalyzed by LiF, NaCl, KCl, and KI was studied.

The dependence of the activity of nucleants in PE on the melting temperature, according to eq.

**Table III** Values of  $\beta$  and  $\sigma_{sf} - (\sigma^* - E_d)$  in PET

Substrate	AgBr	AgI	PbF <sub>2</sub>	Ag <sub>2</sub> S	LiF	CaF <sub>2</sub>
$\beta$ (erg/cm <sup>2</sup> )	7.40	7.15	6.63	6.89	7.15	6.50
$\sigma_{sf} - (\sigma^* - E_d)$ (erg/cm <sup>2</sup> )	0.90	0.65	0.13	0.39	0.65	0.00



**Figure 4**  $\Phi$  vs.  $T_{ms}^{1/2}$  for PET;  $\Phi$  data for  $TiO_2$ ,  $ZnO$ , and  $Al_2O_3$  are taken from ref. 3;  $\Phi$  data for  $Au$ ,  $Ir$ , and  $Pd$  were obtained by Gutzow et al.<sup>12</sup> The line is drawn in order to satisfy eq. (5).

(5), is shown on Figure 3. The values of  $\Phi$  are calculated from the values of  $\beta$ , reported by Koutsky et al.<sup>11</sup> by virtue of eq. (3). It is seen from Figure 3 that in this case the nucleant with the highest melting temperature ( $LiF$ ) is the most active. In terms of the formalism developed by Dobreva and Gutzow,<sup>4</sup> a decreasing  $\Phi - T_{ms}^{1/2}$  function corresponds to zero  $f$  values and to the absence of misfit effects. This experimental finding is confirmed also by the high values of the difference  $\sigma_{sf} - \sigma^*$  obtained by Koutsky et al.<sup>11</sup> In this case,  $E_d$  (i.e., misfit contribution) can be neglected.

Figure 4 summarizes all experimental data, known to us, for the activity of nucleants in PET. It includes  $\Phi$  data for  $Al_2O_3$ ,  $TiO_2$  (anatase), and  $ZnO$  in PET, obtained by Dobreva et al.<sup>3</sup> using the same nonisothermal method. The values of the activity of  $Ir$ ,  $Pt$ , and  $Au$  in PET were obtained by Gutzow et al.<sup>12</sup> by measuring the time necessary for the appearance of optical microscopically distinguishable crystallization at constant temperature. From Figure 4, it is seen that the nucleating activity of substrates in PET decreases with the increase of  $T_{ms}$ .

It is interesting to mention that Ibbotson and Sheldon<sup>13</sup> also found that the additive with the

highest melting temperature (boron nitride) from a series of nucleants is practically inactive with respect to the crystallization of PET melts.

## CONCLUSIONS

The present study shows that the nucleant with the lowest melting temperature ( $AgBr$ ) is the most active in catalyzing nucleation in PET melts. According to the theoretical concepts used, this is an indication that considerable misfit exists between the lattice parameters of the substrates and the PET crystals.

The authors are thankful to Prof. I. Gutzow for a number of helpful suggestions.

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