EFFICIENCY SCALE FOR POLYMER NUCLEATING AGENTS

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Abstract

Nucleation of crystallizable polymers is quantified through an efficiency scale obtained and calculated using differential scanning calorimetry (DSC). This scale, defined in self-nucleation experiments, is a simple, convenient and reliable calorimetric efficiency scale. Typical nucleating agents for isotactic polypropylene are evaluated; they rate at best at 60 to = 70% on this efficiency scale.

Keywords: DSC, nucleating agents, polymers

Introduction

Nucleating additives are widely used in industrial practice. They shorten the processing time in injection moulding; they reduce the average size of the spherulites, and hence, they improve the mechanical properties and reduce the haze [1]. The nucleating agents have various chemical structures [2, 3] (minerals (talcs...), organic salts (e.g. sodium benzoate), organics (e.g. DBS: dibenzylidene sorbitol)) and in the case of polyolefines they usually act via epitaxial interactions [4].

Generally, the efficiency of nucleating agents is characterized in two different ways: either in an anisothermal experiment by measuring the increase in crystallization temperature (the variables are the nuclei concentration N and the growth rate G) or in an isothermal experiment by evaluating the reduction of the crystallization half-time (the only variable is N since G is constant). In both cases, comparison is made with a 'reference' which is the 'virgin polymer', the polymer with no nucleating agents but submitted to the same processing conditions used to incorporate the nucleating agents (e.g. melt blending, etc...).

The above evaluations have however an intrinsic weakness as they use only a single reference, the virgin polymer, which happens to be the lower limit regarding the crystalline nucleus density. A more satisfactory evaluation would require to define an upper limit for the crystalline nuclei density.

In this paper, we first define the upper limit obtained with an 'ideally' nu-cleated polymer attainable via self nucleation [5]. Second, in an anisothermal crystallization carried out by DSC, an efficiency scale for nucleating additives is introduced. This scale is then used to evaluate the efficiency of several addi-tives known to promote the crystallization of isotactic iPP. Finally, in isothermal crystallization, we establish a correlation between both the observed crystal-lization temperature and spherulite size (or nuclei concentration), i.e. the effi-ciency coefficients are expressed by the physically more telling variables: spherulite size or nuclei concentration.

Experimental

Materials

All experiments are performed with the same polypropylene sample highly isotactic produced by SNEAP France, ref. 3030 BN1, with $Mw = 315.10^3$ and polydispersity 5.5.

The nucleating agents tested are mostly of commercial origin. Selection is based on several criteria: actual use in industry or reported efficiency in pub-lished literature.

Techniques

Experimental techniques are essentially DSC crystallization experiments performed under anisothermal and isothermal conditions. For anisothermal ex-periments, the heating and cooling rates are 10 deg·min^{-1}. Optical microscopy uses crossed polarizers. To determine small spherulite sizes, electron micros-copy has been used to observe shadowed replica of polymer film treated with permanganic etchant.

Results and discussion

Upper temperature limit of crystallization (self-nucleated polymer)

In polymer crystallization, the self-nucleation procedure is known to pro-duce numerous nuclei. Via this procedure, polymer crystal fragments which be-have as ideal nuclei in terms of both their interactions (chemical and crystallographic) and their state of dispersion can be obtained. This process takes place by partial melting of the original crystalline lamellae.

Four thermal steps are necessary to control the self nucleation procedure (Fig. 1).

1) Erasure of previous thermal history

The iPP sample is completely melted at 210°C (40°C above its melting temperature) for 10 min (Fig. 1 step A). This initial melting step eliminates all nuclei except for those which are temperature resistant (residues of catalysts, etc...).
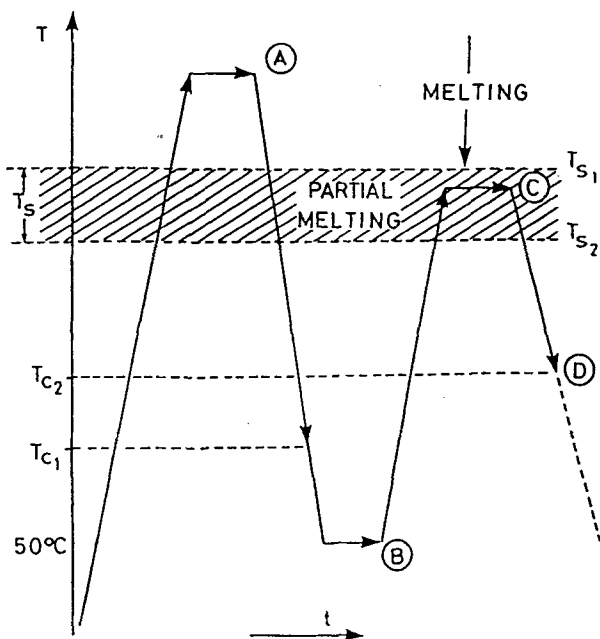

Fig. 1 Self-nucleation procedure as applied in DSC runs. Four steps (A), (B), (C), (D) are involved; heating and cooling rates are 10 deg·min^{-1}

2) Creation of the standard state (T_{c_i})

In anisothermal DSC procedure, this standard state is obtained by cooling the 'erased melt' at a determined cooling rate (10 deg·min^{-1}) down to some temperature T_1 ($T_1 = 50$°C here) (Fig. 1 step B). The crystallization takes place at the lower limit of the crystallization range (T_{c_i}). T_{c_i} depends on the molecular characteristics of the polymer and the concentration of temperature resistant nuclei.

3) Partial melting self-nucleation

The essential step of self-nucleation is carried out by heating the polymer to selected temperatures T_s (Fig. 1 step C). When T_s is located in the melting range (hatched zone), the formation of stabilized polymer crystal fragments re-

sults. The concentration of remaining crystal fragments varies dramatically, increasing as T_s decreases and reaching saturation for $T_s = T_{s_2}$.

4) Final crystallization (T_{c_2})

This second crystallization (Fig. 1, step D) is achieved by subsequent cooling of the sample and the crystallization peak is located at a temperature T_{c_2} ($T_{c_2} \geq T_{c_1}$). This increase in T_c indicates an increase in the concentration of nucleation sites induced by the self nucleation process.

In summary, the virgin sample (not self nucleated) crystallizes at the lowest temperature T_{c_1} whereas the best self nucleated sample crystallizes at the highest temperature $T_{c_{2max}}$.
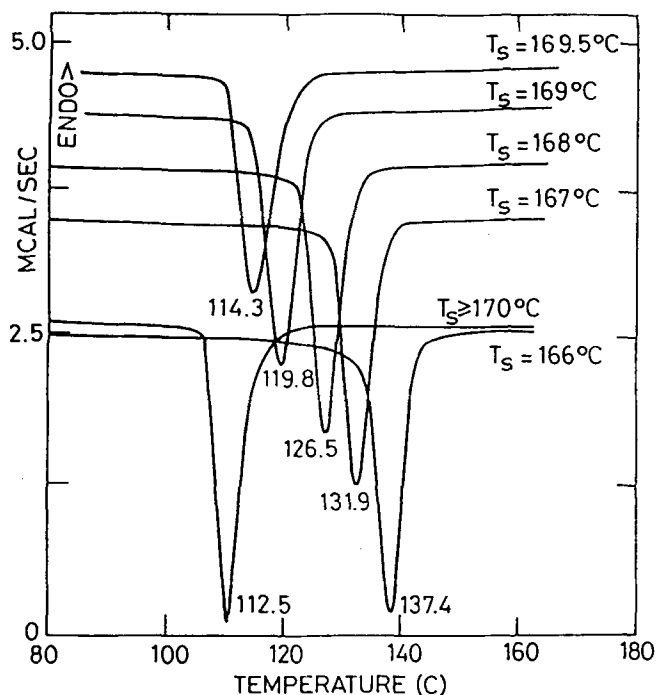

Fig. 2 Crystallization exotherms of iPP after melting at various T_s as indicated on the corresponding curves

Figure 2 illustrates the evolution of crystallization temperatures for iPP after self-nucleating experiments carried out at different temperatures and a fixed cooling rate (10 deg·min^{-1}) in a DSC run. The high temperature $T_{c_{2max}}$ is 137.4°C whereas the low temperature T_{c_1} is 112.5°C; a difference of 24.9°C. Corresponding concentration of nuclei varies between 10^6 cm^{-3} (spherulites diameter

≈ 100 µm) and 10^{12} cm^{-3} (spherulites diameter ≈ 1 µm); this size range is quite similar to that determined for other polymers in self-nucleation experiments [6].

Efficiency scale for nucleating agents in anisothermal experiments

As mentioned above, the range of experimentally attainable nuclei concentrations in iPP can be characterized by the variation of T_{c_2} i.e. $\Delta T = T_{c_{2max}} - T_{c_1}$. The virgin sample and the best self nucleated sample, crystallized respectively at T_{c_1} and $T_{c_{2max}}$, provide the two extreme limit needed to define an efficiency scale for a given polymer.

Table 1 Crystallization temperatures T_c of the polymer and nucleation efficiency *NE* for some nucleating agents *NA* at various concentrations *C* in isotactic polypropylene

Nucleating agents and concentration	T_ciPP/°C	Nucleation efficiency *NE*/%
4-biphenyl carboxylic acid, 2%	128.8	66
2-naphtoic acid, 1%	127.8	62
Nicotinic acid, 1%	125.7	52
Thymin, 1%	125.3	50
DBS (dibenzylidene sorbitol), 0.4%	123.2	41
9-anthracene carboxylic acid, 1%	122.7	38
Talc, 1%	121.4	32
Sodium benzoate, 1%	121.2	31
9-fluorene carboxylic acid, 1%	118.4	18
2-hydroxy 3-naphtoic acid, 1%	116.0	7
2,4-(bis butylamine)6-hydroxy, 1,3,5 triazine, 1%	115.5	5

Similarly, the nucleated polymer crystallizes at a temperature T_c higher than T_{c_1} if the nucleating agent has any efficiency at all. The improvement introduced by the nucleating agent may be quantified by:

$$NE = 100 \frac{T_c - T_{c_1}}{T_{c_{2max}} - T_{c_1}} = 100 \frac{\Delta T_{NA}}{\Delta T}$$

The nucleating efficiency (*NE*) is thus equal to 0 for no nucleating action and 100 for optimum efficiency. In order to evaluate *NE* for known nucleating agents of isotactic polypropylene [2, 3], several known agents are studied (talc, sodium benzoate, dibenzylidene sorbitol (DBS),...). Typical values of *NE* range from 5 to 70% (Table 1). For example, a well known nucleating agent like DBS has a moderate efficiency (i.e. *NE* = 41%). The best nucleating agents com-

monly used in industrial practice are only rated at 40 to 60% on the present scale.

Compared to earlier methods of evaluation, based on the determination of T_c and the temperature difference ΔT_{NA} [7], the most significant improvement of the present scale rests in the introduction of an upper limit, expressed by $T_{c_{2max}}$. Further, this new method based on anisothermal experiments is more versatile and closer to industrial processing conditions.

Evaluation of nuclei concentration in isothermal experiments

In the present section, a similar approach to that mentioned above is proposed to evaluate nucleating agents. This is a comparison of number nuclei and/or size of nuclei for different samples (virgin polymer, nucleated or self-nucleated polymer).
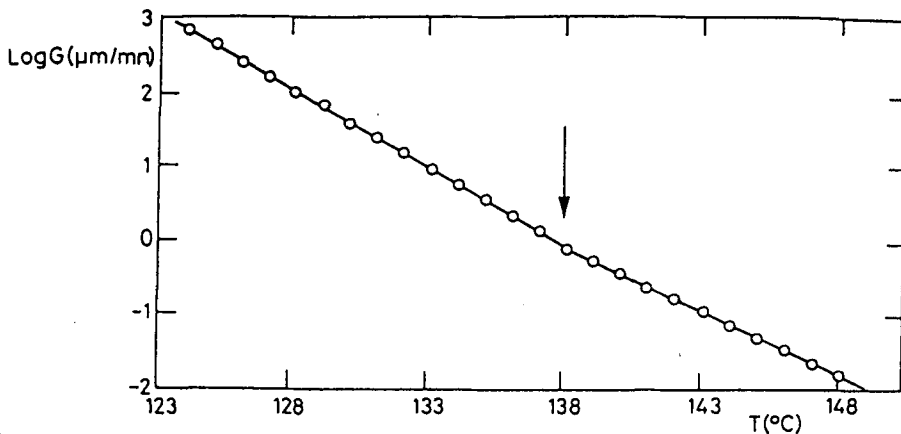

Fig. 3 Variation of growth rate (G) with temperature as determined in isothermal experiments (arrowed break, see text)

In fact, spherulite sizes measured by optical microscopy can be used to determine nuclei concentrations up to $= 10^8/cm^3$. For spherulite sizes smaller than a few µm, analysis of crystallization kinetics with the Avrami equation is necessary.

This equation describes the overall progress of isothermal crystallization:

$$1 - \chi t = \exp(- Kt^n) \tag{1}$$

with: χt = crystalline fraction at time t, K = rate constant, n = Avrami exponent, which characterizes both the nucleation process and the geometry of the growth
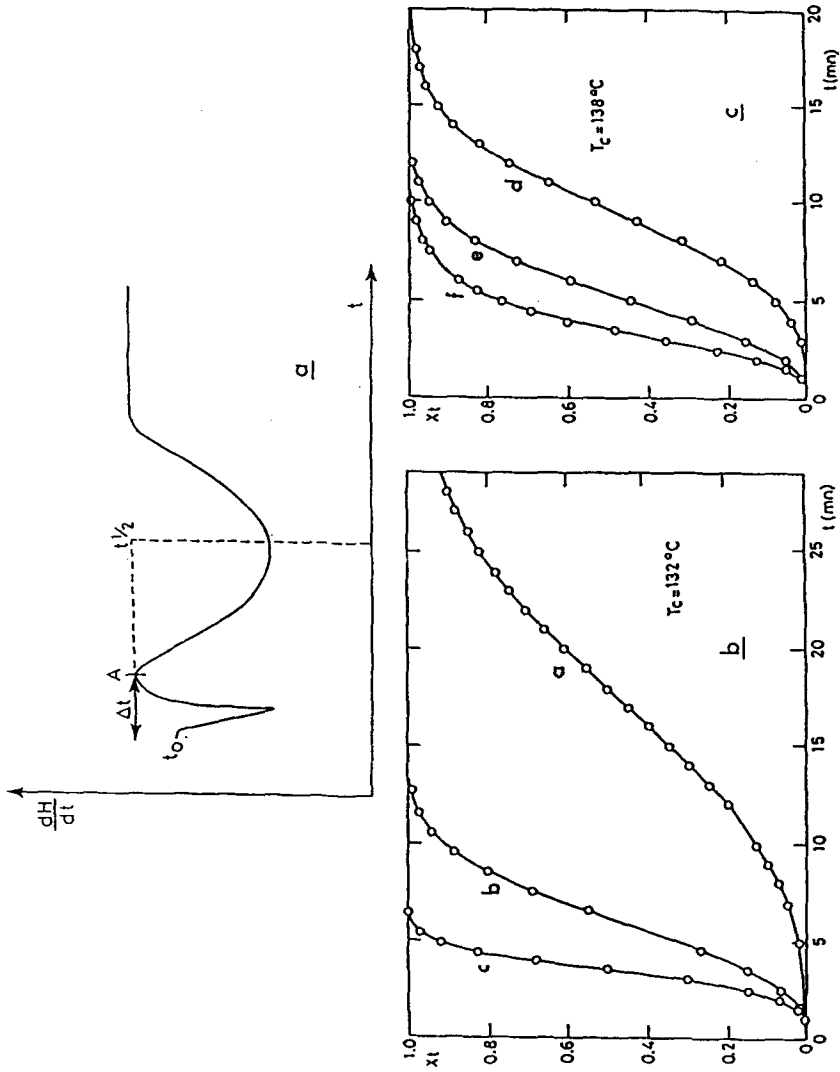
Fig. 4 a) Isothermal crystallization exotherm (schematic representation). Δt time needed to reach thermal equilibrium; $t_{1/2}$ half-time crystallization. b) and c) Isothermal crystallization kinetics curves respectively at 132 and 138°C (a to f curve subscripts see Table 2)

The rate constant K can be deduced from the crystallization half-time $(\chi t = 1/2)$:

$$K = \frac{\ln 2}{t_{1/2}^{n}} \tag{2}$$

Assuming three dimensional growth, K is proportional to the concentration of nuclei N:

$$K = \frac{4}{3} \pi N G^{3} \tag{3}$$

and

$$\frac{1}{N} = \frac{4\pi}{3} R^{3} \tag{4}$$

where G is the crystal linear growth rate measured by optical microscopy on virgin polymer at T_c and R the radius of spherulites. The measured growth rate for iPP is represented in Fig. 3, which features the characteristic change in slope at 138°C (arrowed), associated by several authors with a change in growth regime [8, 9].

The nuclei concentrations N are determined for the different nucleated samples by analysis of isothermal crystallization kinetics carried out by DSC. Figure 4a shows is schematic form the typical output of such isothermal crystallization runs. Integration of the curves yields the percentage of conversion χt vs. t. Six such curves are displayed in Figs 4b and 4c respectively.

The plot of log N vs. crystallization temperature (T) (Fig. 5) for each sample reveals the following features:

– for iPP without added nucleating agent (curves a, b, i), the range of N extends from = 10^{6} cm³ when pre-melting is above 170°C, i.e. for the virgin sample, to 10^{12} cm³ when optimal conditions for self-nucleation are attained,

– for nucleated samples, the range of N extends from 10^{7} cm³ for the less efficient nucleating agent to 10^{10} cm³ for the most efficient. On the graph, the most efficient nucleating agent are close to the upper right and least efficient ones to the lower left corner.

In Fig. 5 the dashed lines link experiments which give rise to equal crystallization half-times of iso $t_{1/2}$ = 4, 6 and 15 min. Since these 'iso $t_{1/2}$' lines cross all the curves, it is possible to define 'iso $t_{1/2}$' efficiency factors [NE_{an}] for all samples. For example, NE_{an} for iso $t_{1/2}$ = 4 min, is giving by 100 AB/AC. A, B, C being the intersection point of the 4 min dashed line with nuclei concentration curves respectively for the virgin polymer, the nucleated one and the op-

timally self-nucleated one. These efficiency coefficients are similar to those obtained from anisothermal experiments (Table 2 and section II).
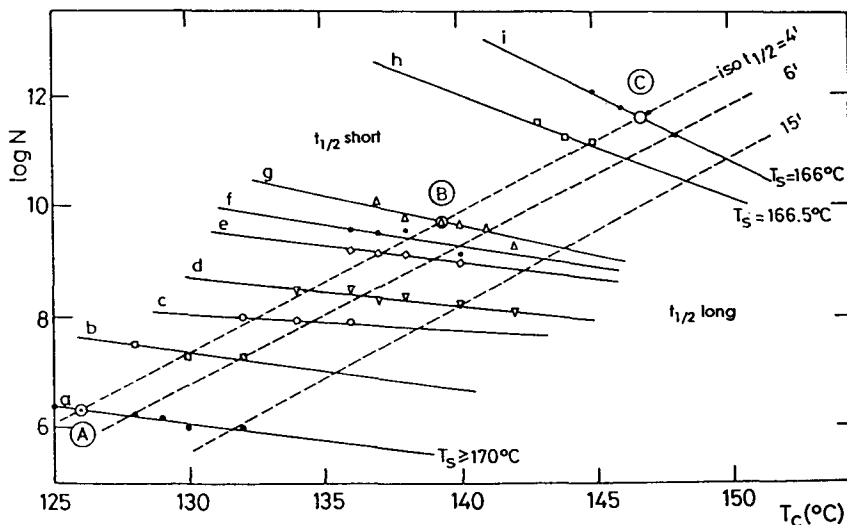

Fig. 5 Nuclei concentration N in cm^{-3} as a function of isothermal crystallization T_c (a to f subscripts, see Table 2). Dashed lines, half-time crystallization $t_{1/2}$ of 4, 6, 15 min as indicated on the curves

Table 2 Nucleation efficiency NE determined by anisothermal NE_{an} or isothermal NE_{iso} crystallization

Curve	Sample			$NE_{an}/$ %	$NE_{iso}/$ %
a	iPP 3030			0	0
b	iPP 3030	+	1% PTBBA	29	21
c	iPP 3030	+	0.4% DBS-AB	41	35
d	iPP 3030	+	0.5% PDG	41	43
e	iPP 3030	+	0.5% M888	48	56
f	iPP 3030	+	0.4% DBS + 0.5% PDG	63	62
g	iPP	+	2% ABPC	66	65
h	iPP		$T_s = 166.5°C$	90	91
i	iPP		$T_s = 166°C$	100	100

PTBBA = Para-tertiobutylbenzoic acid
DBS = Dibenzylidenesorbitol
AB = Benzoic acid
PDG = Diphenylglycine
M888 = a propriatory nucleating agent
ABPC = 4-Bephenylcaboxylic acid
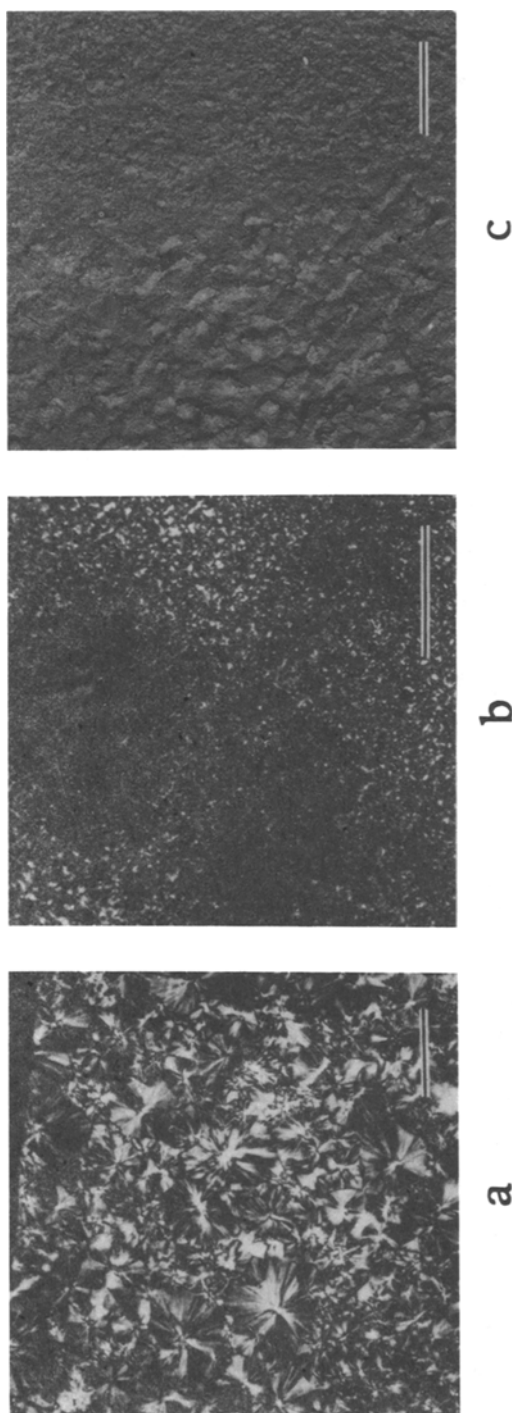
Fig. 6 Examples of spherulite morphology (section of thin films) for various nucleation states. a) Virgin polymer $2R \approx 100$ μm; b) iPP+0.4% DBS $2R \approx 20$ μm; c) Optimal self-nucleated iPP $2R \approx 1$ μm for the spherulites initially crystallized in the α-phase (left hand size), those initially crystallized in the β-phase are even smaller (right hand size). For detailed analysis of the β-phase self-nucleation see Ref. [10]. a) and b) Crossed polar optical micrographs, scale bars 100 μm. c) Electron microscopy micrograph of permanganic etched and Pt/C shadowed replica, scale bar 2.5 μm

Spherulite size for a given sample can either be calculated from values of N using expression [4] or measured directly by optical or electron microscopy (for the latter see Fig. 6). In fact, for both evaluation, the both evaluation, the spherulite size are roughly equivalent, varying from 1 μm (optimal self-nucleation) to 100 μm (virgin polymer).

Conclusion

To determine the efficiency of nucleating agent two limits are defined. The lower limit refers to the virgin polymer and the upper one to optimally nucleated polymer obtained via self-nucleation.

An efficiency coefficient (NE) expressed as a percentage of the above range has been defined in anisothermal DSC experiment and the effect of different NA on iPP have been gauged on this scale. The efficiency of nucleating agents for iPP varies greatly (5% for the worst and 66% for the best). Considerable improvements in the efficiency of such agents are therefore possible.

The proposed scale for nucleating additives is simple, fast, reliable. It has a physical meaning demonstrated through the equivalence of the results for isothermal and anisothermal experiments.

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Zusammenfassung — Anhand einer unter Einsatz von DSC erhaltenen und berechneten Effizienzskale wurde eine Quantifizierung der Keimbildung bei kristallisierbaren Polymeren vorgenommen. Diese in selbstkeimbildenden Experimenten definierte Skale ist eine einfache, praktische und sinnvolle kalorimetrische Effizienzskale. Für isotaktisches Polypropylen wurden typische Keimbildungsagenzien entwickelt, deren Bestgeschwindigkeit auf dieser Effizienzskale bei 60 bis 70% liegt.