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Non-isothermal crystallization kinetics of poly(phenylene sulfide)/Vectra-B blends

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The non-isothermal crystallization behaviour of blends of poly(phenylene sulfide) (PPS) with the thermotropic liquid-crystalline copoly(ester amide) Vectra-B950 (VB) was studied by means of differential scanning calorimetry. The PPS crystallization temperature and the crystallization rate coefficient were found to increase markedly upon addition of 2–50% VB. It was shown that the Ozawa equation is valid not only for neat PPS but also for the blends. The values of the Avrami exponents are in fair agreement with those found previously by isothermal analysis, and do not depend on the presence and the concentration of VB. It has been suggested that the slope of the plots of the cooling crystallization function *versus* T can be a criterion for the overall non-isothermal crystallization rate. It has been concluded that the non-isothermal crystallization of PPS is strongly accelerated by the presence of the VB phase, whereas the type of nucleation and the geometry of crystal growth do not change, and no reduction of the PPS degree of crystallinity could be noticed.

(Keywords: poly(phenylene sulfide); Vectra; crystallization kinetics)

INTRODUCTION

The study of non-isothermal crystallization of polymers is of great technological significance, since most practical processing techniques proceed under non-isothermal conditions. Moreover, from a scientific point of view, non-isothermal experiments may mean a great deal in view of the understanding of the crystallization behaviour of polymers, because the more used isothermal methods are often restricted to narrow temperature ranges.

In previous reports[1–3], the isothermal crystallization behaviour of blends of poly(phenylene sulfide) (PPS) with the thermotropic liquid-crystalline copoly(ester amide) Vectra-B950 (VB; Hoechst-Celanese) was described. The blends were shown to be biphasic, and the two components to be practically immiscible. The isothermal crystallization of PPS was found to be strongly accelerated by the presence of the VB phase, as a result of an increased nucleation density, whereas no reduction of the PPS degree of crystallinity could be noticed. Moreover, a scanning electron microscope investigation of these blends showed that there is a fairly good interphase adhesion between PPS and VB. Therefore, taking into account that the addition of a liquid-crystalline polymer (LCP) may appreciably reduce the melt viscosity of most thermoplastic materials, thus enhancing their processability[4], one might expect an improvement of PPS performance by blending it with VB.

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The crystallization behaviour of neat PPS[5], of PPS filled with solid fillers[6–8] and of PPS blended with thermoplastic polymers[9,10] has already been studied extensively, by isothermal methods. The only study of the non-isothermal crystallization kinetics of PPS described so far is that by Lopez and Wilkes[11], dealing with linear and branched PPS samples. These authors showed that the Avrami exponents, determined by the Ozawa equation[12] from non-isothermal measurements, are in good agreement with those achieved by isothermal methods.

We considered it of interest to study the non-isothermal crystallization behaviour of PPS in blends with an LCP, in order to compare the relevant results with those found by isothermal measurements[1–3], and to test the validity of the Ozawa equation for this system, too.

EXPERIMENTAL

Poly(phenylene sulfide) (PPS) was a pale amber, pelletized polymer, kindly supplied by Phillips Petroleum International SRL, Milano, and designated as Ryton GR02. The melt flow index (*MFI*) of this material was 97.8 g/10 min (ASTM 1238, 5 kg, 316°C).

Vectra-B950 (VB) was a wholly aromatic LC copoly(ester amide), produced by Hoechst-Celanese, containing 20% 4-aminophenol, 20% terephthalic acid and 60% 2-hydroxy-6-naphthoic acid units.

Both polymers were dried in a vacuum oven, at 120°C for 48 h, before use.

The PPS/VB blends, with a VB content in the range 2–50% w/w, were prepared in a 30 ml mixer attached to a Brabender Plasticorder, at 290°C and 100 rpm, for 3–4 min, under nitrogen. Blank samples of both PPS and VB were subjected to the same treatment.

Non-isothermal measurements were made using a Perkin–Elmer DSC-7 differential scanning calorimeter. The apparatus was calibrated with indium and tin standards, at different scanning rates. The lag between sample and pan holder temperatures was also taken into account, and computed through indium crystallization tests, as described by Eder and Wlochowicz[13].

The crystallization experiments were performed in an argon atmosphere, on blend samples previously held for 10 min at 330°C, in order to achieve the complete destruction of the crystalline nuclei[1]. The weight of the samples was held approximately constant (ca. 12 mg) throughout the study. The constant cooling rates used were 5, 10, 15, 20, 25 and 30°C min^{-1}.

RESULTS AND DISCUSSION

In *Figure 1* the d.s.c. traces obtained at a cooling rate of 20°C min^{-1} for neat PPS and its blends with a VB

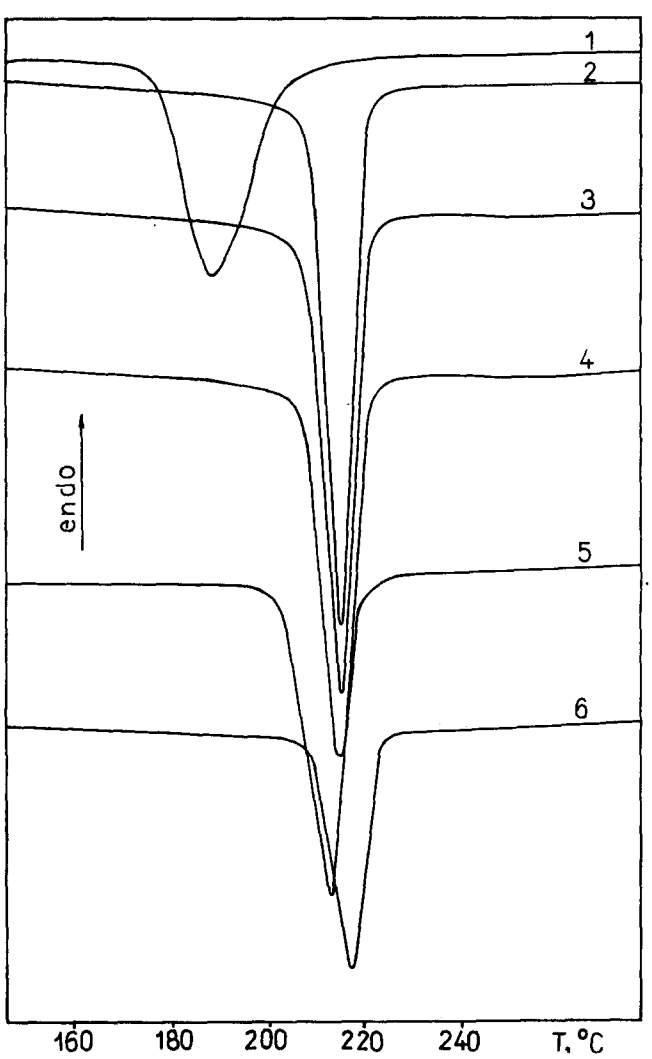

Figure 1 D.s.c. cooling traces of PPS/VB blends, recorded at 20°C min^{-1}: (1) 100/0; (2) 98/2; (3) 95/5; (4) 90/10; (5) 80/20; (6) 50/50

Table 1 Dependence of the crystallization temperature (T_{cr}), the degree of crystallinity (α), the half-width of the peak (ΔT_1), the crystallization rate coefficient (CRC) and the Avrami exponent (n) on the presence and the concentration of Vectra-B950 in the blends with PPS

No.	Blend PPS/VB	5°C min^{-1}			10°C min^{-1}			15°C min^{-1}			20°C min^{-1}			25°C min^{-1}			30°C min^{-1}			CRC (h^{-1})	n
		T_{cr} (°C)	α	ΔT_1 (°C)	T_{cr} (°C)	α	ΔT_1 (°C)	T_{cr} (°C)	α	ΔT_1 (°C)	T_{cr} (°C)	α	ΔT_1 (°C)	T_{cr} (°C)	α	ΔT_1 (°C)	T_{cr} (°C)	α	ΔT_1 (°C)		
1	100/0	213.1	0.28	10	208.0	0.29	13.2	200.6	0.27	14.3	193.8	0.25	14.3	189.8	0.26	15.7	185.8	0.26	17.1	52	3.1
2	98/2	228.3	0.30	4	223.8	0.30	5.0	221.8	0.30	5.0	219.7	0.30	5.0	218.9	0.30	5.7	217.8	0.32	5.7	150	2.9
3	95/5	229.6	0.30	4	224.9	0.29	5.7	222.5	0.31	5.7	220.7	0.30	6.4	218.9	0.29	7.8	217.4	0.29	7.8	150	2.8
4	90/10	229.5	0.29	4	225.4	0.29	5.7	223.7	0.30	5.7	220.7	0.29	7.1	219.8	0.30	7.8	217.8	0.29	8.6	150	2.9
5	80/20	225.5	0.29	6	222.8	0.28	7.1	220.9	0.29	6.4	217.9	0.29	7.8	217.8	0.29	10.0	214.9	0.29	10.0	150	2.9
6	50/50	231.9	0.29	5	227.4	0.30	6.0	223.1	0.31	6.4	223.3	0.31	7.1	222.3	0.31	7.1	219.4	0.29	7.1	150	3.1

content of up to 50% are shown. The exothermic crystallization peaks are monomodal, and their shape shows that, as already found by Lopez and Wilkes[5] for PPS, secondary crystallization does not play an important role for these blends. It can be observed that the blend exotherms are much sharper than that of pure PPS, and are located at a higher temperature with respect to this latter.

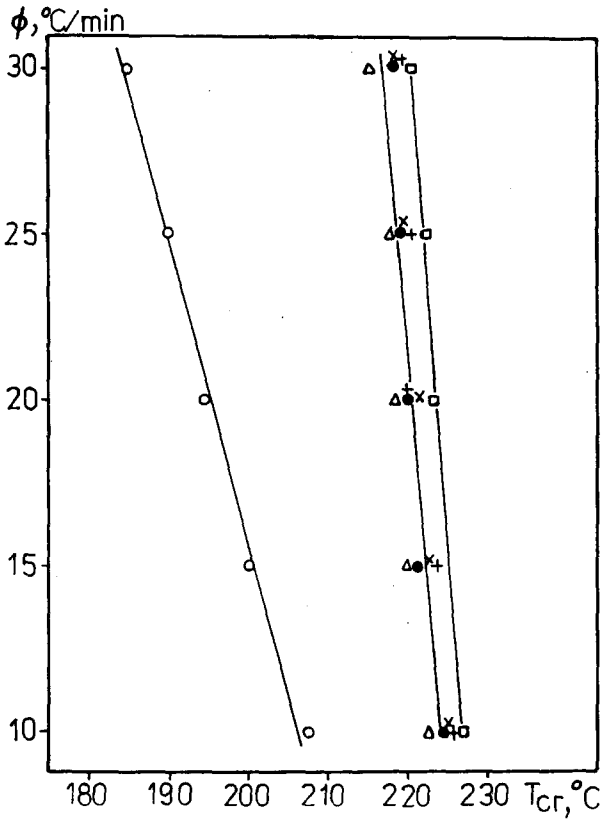

Figure 2 Cooling rate ϕ vs. crystallization temperature T_{cr} for PPS/VB blends: (○) 100/0; (●) 98/2; (×) 95/5; (+) 90/10; (△) 80/20; (□) 50/50

The crystallization temperatures T_{cr}, the half-widths of the crystallization peaks ΔT_1 and the degrees of crystallinity α of the PPS phase obtained at different cooling rates for the blends with a VB content in the range 2–50% are collected in *Table 1*. Here, the crystallization temperatures T_{cr} are those corresponding to the exothermic peak maxima, corrected as described by Eder and Wlochowicz[13]. The degree of crystallinity α has been calculated from the enthalpy of crystallization, normalized to the PPS content, assuming that the contribution of the LCP phase is negligible[3], and using the value of 146.2 J g^{-1} estimated by Maemura *et al.*[14] for the enthalpy of fusion of 100% crystalline PPS. It may be noticed that α remains approximately constant, or increases slightly, as a result of the addition of the LCP to PPS.

From the T_{cr} and ΔT_1 data, the following conclusions can be drawn: (i) T_{cr} increases strongly upon addition of VB to PPS; (ii) T_{cr} decreases on increasing the cooling rate, as could be expected for polymer crystallization controlled by nucleation[11]; this dependence of T_{cr} on cooling rate is much stronger for neat PPS than for the blends; (iii) the sharpness of the crystallization peaks, as measured by ΔT_1, is considerably higher for the blends than for pure PPS. These conclusions suggest that the rate of non-isothermal crystallization of PPS increases appreciably in the presence of VB.

The crystallization rate coefficient (*CRC*) suggested by Khanna[15] may be measured as the slope of the plot of the cooling rate ϕ (°C min^{-1}) vs. T_{cr}. These plots are shown in *Figure 2* for PPS and its blends, and the relevant *CRC* values are reported in *Table 1*. It may be seen that the blends have *CRC* values three times greater than that

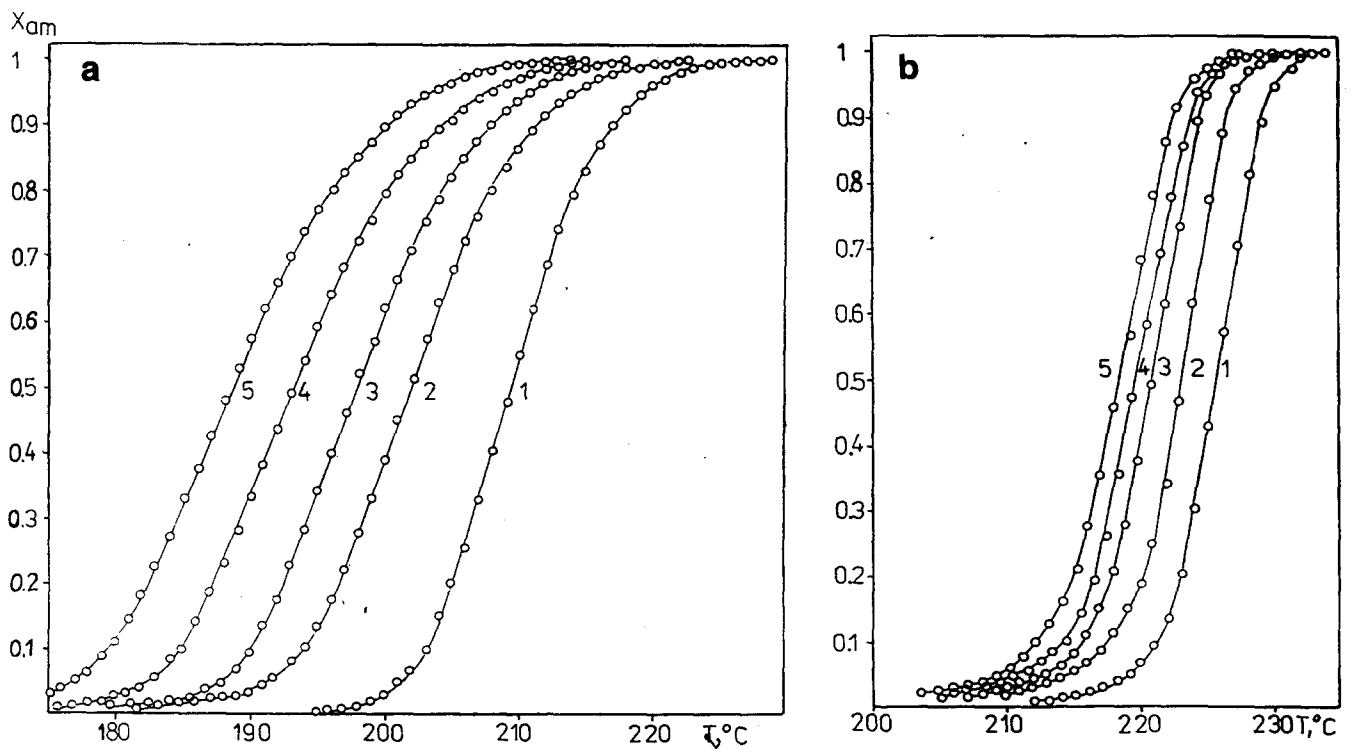

Figure 3 Amorphous fraction vs. temperature for (a) PPS and (b) 90/10 PPS/VB at different cooling rates: (1) 10°C min^{-1}; (2) 15°C min^{-1}; (3) 20°C min^{-1}; (4) 25°C min^{-1}; (5) 30°C min^{-1}

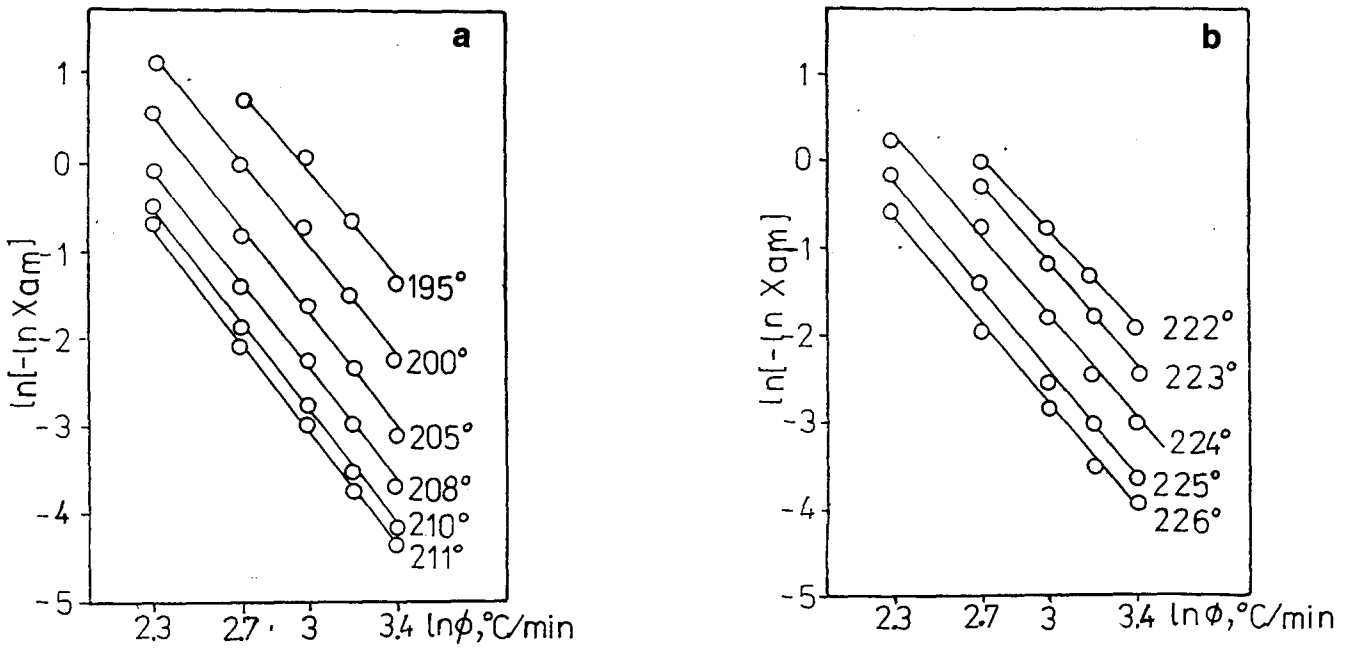

Figure 4 Double logarithm of the reciprocal amorphous fraction vs. logarithm of the cooling rate for (a) PPS and (b) 90/10 PPS/VB

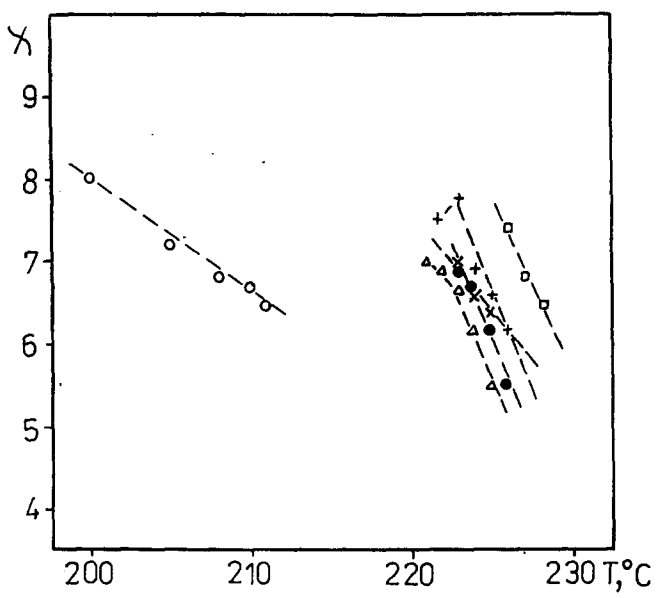

Figure 5 Cooling crystallization function vs. temperature for PPS/VB blends: (○) 100/0; (●) 98/2; (×) 95/5; (+) 90/10; (△) 80/20; (□) 50/50

of pure PPS. A comparison with the *CRC* figures given by Khanna[15] for various polymers shows that the *CRC* of PPS is approximately equal to that of nylon-6, whereas the PPS/VB blends have *CRC* values very close to that of polytetrafluoroethylene (PTFE), which is one of the fastest-crystallizing polymers.

The overall non-isothermal crystallization kinetics of PPS and its blends with VB was studied using the Ozawa formalism[12]. This is based on the equation:

$$\ln[-\ln(1-X)] = \chi - n\ln(\phi)$$

where X is the volume fraction of material crystallized at temperature T, ϕ is the constant cooling rate, n is the Avrami exponent and χ is the cooling crystallization function. This latter depends on the nucleation density and on the spherulitic radial growth rate, for both instantaneous and sporadic nucleation.

The amorphous fractions $1 - X(T)$ of the PPS phase of PPS/VB blends with VB content between 0 and 50% have been calculated from the d.s.c. traces, and plotted against T for different cooling rates. The plots drawn for pure PPS and for the 90/10 PPS/VB blend are shown in *Figure 3*. The double logarithm of the reciprocal amorphous fractions of the PPS phase can also be plotted against the cooling rate, for different temperatures, as shown in *Figure 4* for pure PPS and for the 90/10 blend. It may be seen that these plots as well as those (not shown) of all other blends studied represent straight lines, thus showing that the Ozawa equation describes satisfactorily the non-isothermal crystallization behaviour of the blends investigated.

The Avrami exponents n are ca. 3 for both PPS and the blends (*Table 1*). This value of n is in fair agreement with that found by Lopez and Wilkes for high-molecular-weight, unbranched PPS (ca. 2.8)[11], through non-isothermal measurements, and with those found previously by us[1] from isothermal experiments carried out on the same PPS/VB blends.

The finding that the Avrami exponents are insensitive to the presence and to the concentration of the VB phase blended with PPS demonstrates that the LCP does not influence the mechanism of crystallization of this latter polymer. This process seems to involve heterogeneous nucleation and three-dimensional crystal growth.

The cooling crystallization functions χ determined from the intercepts of the plots in *Figure 4* are presented in *Figure 5* as a function of temperature. The values of χ measured for PPS are in good agreement with those given by Lopez and Wilkes for high-molecular-weight, unbranched PPS[11]. In the temperature interval used by us, they decrease slowly on increasing the temperature, as found by Lopez *et al.* for PPS[11], by Ozawa for poly(ethylene terephthalate) (PET)[12] and by Eder *et al.*

for polypropylene[13]. The χ values measured for the blends are of the same order of magnitude as those obtained for pure PPS, but they appear on the plot in a higher temperature window, owing to the higher crystallization temperatures of the blends. It may be observed that the absolute value of the slope of the χ vs. T plots is much higher for the blends than for PPS. Lopez and Wilkes[11] suggested that the cooling crystallization function may be related to the overall rate of bulk crystallization, in the sense that it may give an indication of how fast the non-isothermal crystallization occurs. We believe that the slope of the χ vs. T plots is likely to be a more faithful indicator of the non-isothermal crystallization rate. In fact, this slope reflects both the retardation effect of the cooling rate on crystallization, and the temperature range at which crystallization occurs.

CONCLUSIONS

The study of the non-isothermal crystallization of PPS and of its blends with VB has shown that this LCP markedly accelerates PPS crystallization, not only under isothermal conditions as found earlier[1-3] but also under non-isothermal ones. The PPS crystallization rate coefficient CRC was found to increase three times upon addition of 2–50% VB. It was demonstrated that the Ozawa equation holds not only for neat PPS but for the blends as well. The values of the Avrami exponents n are close to 3, as found previously from isothermal analysis, and do not vary appreciably on addition of VB. This latter finding shows that the type of nucleation and the geometry of crystal growth do not change in the presence of VB. It has been suggested that the slope of the plots of the cooling crystallization function χ against T can be taken as an index of the overall rate of non-isothermal bulk crystallization.

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