

CRYSTALLIZATION KINETICS OF POLYAMIDE 6 CONTAINING PIGMENTS

*M. Eder and A. Włochowicz**

TEXTILE INSTITUTE, TECHNICAL UNIVERSITY OF ŁÓDŹ,
FINDERA 32, POLAND

(Received February 21, 1988)

In terms of the Avrami equation, the effects of selected organic pigments on the kinetic parameters of the isothermal crystallization of coloured polyamide 6 were examined in the temperature range 468–478 K. It was found that B Blue and BB Red are active nucleating agents, which is ascribed to their crystalline structure. G Orange slightly accelerates the crystallization of PA 6 at lower temperatures and concentrations, whereas in other conditions its effect is the opposite.

The isothermal data were confirmed by the results of non-isothermal crystallization. The degree of supercooling corresponding to the peak of the DSC curve was the measured feature in this case.

It was found that B Blue and BB Red reduce the free energy of formation of critical-size nuclei by 20 and 12%, respectively, which is reflected in the rates of crystallization.

Studies of the crystallization kinetics of pure polyamide 6 and of forms containing different additives has already been the subject of many papers [1–8]. In the early investigations of the effects of solid additives on the crystallization behaviour of polymer melts [9, 10], interfacial interactions were assumed to be responsible for the observed changes and were thought to cause no structural changes in the polymer matrix. Depending on their size, shape and concentration, the surface energy of the particles and their distribution within the bulk of the crystallizing polymer, added foreign substances affect the supermolecular structure of the polymer. At low concentrations, the additives exert an influence on the kinetics and thermodynamics of crystallization, changing the rate of growth and decreasing the sizes of spherulites [11, 12]. In turn, the mechanical properties of the polyamide are governed by the morphology of the supermolecular formations [13].

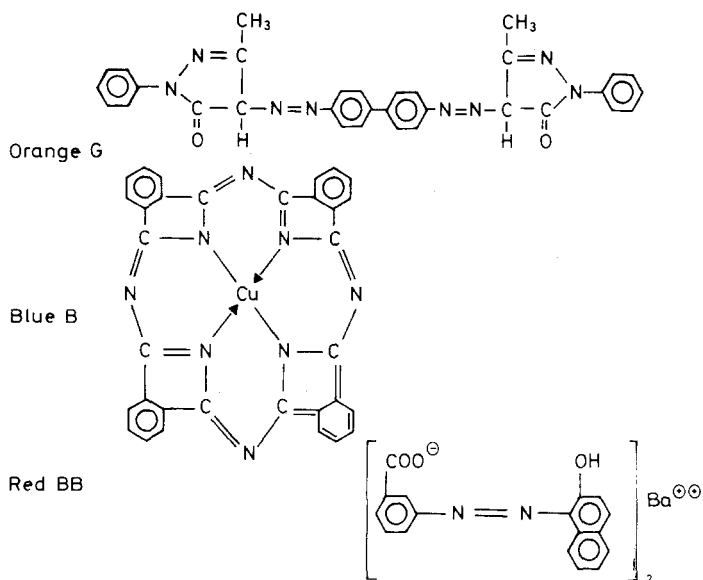
The purpose of this paper is to determine the effects of some selected organic pigments on the rate of crystallization of polyamide 6 by the use of differential

* Correspondence author.

scanning calorimetry (DSC). Since isothermal crystallization conditions are seldom employed, it was desirable to examine how dyed samples of the polyamide crystallize in the course of their cooling from the melt at constant cooling rate. Data on the kinetics, mechanism and energetic parameters of the crystallization describe the effects of the used pigments on the properties of polyamide 6.

Experimental

The following pigments were chosen as nucleating agents for polyamide 6:



These pigments are produced by Wolskie Zakłady Przemysłu Barwników in Poland. The homogeneous blending of the additives into the base polymer was attained by melt mixing in the Brabender laboratory extruder.

The kinetics of crystallization of PA 6 samples containing various amounts of organic pigments was investigated in a standard DSC cell of the DuPont 990 thermal analyzer. The measurements were carried out in a protective nitrogen atmosphere in order to reduce the thermal degradation of PA 6. Samples of 5 mg were heated at a rate of 10 deg/min from ambient temperature up to 530 K, and kept at this temperature for 5 minutes. The polymer melt was then cooled to the desired crystallization temperature with the aid of a Quick device. The time base and the amplification of the DSC record were adapted to the rate of crystallization and the intensity of crystallization heat release. The rate of isothermal crystalliza-

tion was determined in the temperature range 468–478 K. From the DSC curves of isothermally crystallized samples, melting points were determined. The parameters of the non-isothermal crystallization of PA 6 containing the organic pigments were determined by cooling molten samples at a constant rate. The cooling rates used were 1, 2, 5 and 10 deg/min. All calculations were performed with the aid of a minicomputer.

Results and discussion

Isothermal crystallization

In Fig. 1, some typical exotherms of crystallization at a temperature of 471 K for pure polyamide 6 and polyamide 6 coloured with organic pigments are presented.

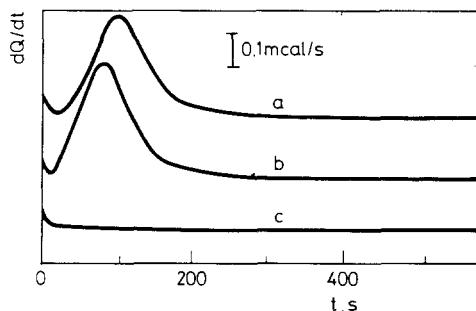


Fig. 1 Exotherms of isothermal crystallization at 471 K: a) polyamide 6, b) polyamide 6 containing 1% of BB Red, c) experimental baseline

Similar curves were obtained for all samples. Experimental data were analyzed in terms of the Avrami equation [14]:

$$\ln(1 - x_t/x_\infty) = -Kt^n \quad (1)$$

where x_t is the degree of crystallinity after time t , x_∞ is the equilibrium degree of crystallinity, K is the crystallization rate constant dependent on temperature, and n is a dimensionless exponent depending on the type of nucleation and on the geometry of crystallite growth. The relative degrees of crystallinity $\frac{x_t}{x_\infty}$ referred to the state of equilibrium were calculated from the ratio $\frac{A_t}{A_\infty}$, whereas A_t is the area under the crystallization exotherm up to time t , whereas A_∞ is the total area under the crystallization curve. In view of the extreme sensitivity of the measured

parameters K and n to the numerical values of A_t , especially at low degrees of transformation, the method of plotting the baseline is of great importance. In the present study, the DSC trace of the molten sample recorded at 510 K was accepted as baseline. At this temperature, the polymer did not crystallize. This procedure ensured the good reproducibility of the results. The standard plots of $\log [-\ln(1-x/x_\infty)]$ vs. $\log t$ for polyamide 6 containing 0.5% of BB Red at several temperatures of crystallization are presented in Fig. 2, whereas in Fig. 3 data are shown concerning the crystallization at 471 K of pure polymer, as well as polymer containing 2% of G Orange, 1% of B Blue and 1% of BB Red. The kinetic parameters of the crystallization are listed in Table 1. As can be seen from the data obtained, the isothermal crystallization of coloured polyamide can be described by Eq. (1) only in the initial stages of development of crystallinity. Above a degree of conversion of 0.5, a certain slowdown and departure from the values predicted by the Avrami equation were found. This additional process is normally referred to as secondary crystallization, which is considered to involve either further growth, or improvement of the degree of crystallinity, or filling-up of the holes remaining after primary crystallization.

The initial portions of the crystallization isotherms of pure polyamide 6 can be fitted to the Avrami function with exponents ranging from 3.4 to 3.8 which formally corresponds to three-dimensional growth of the crystalline structures on thermal and athermal nuclei. The same results were obtained by Gurato [3] and Ishibashi

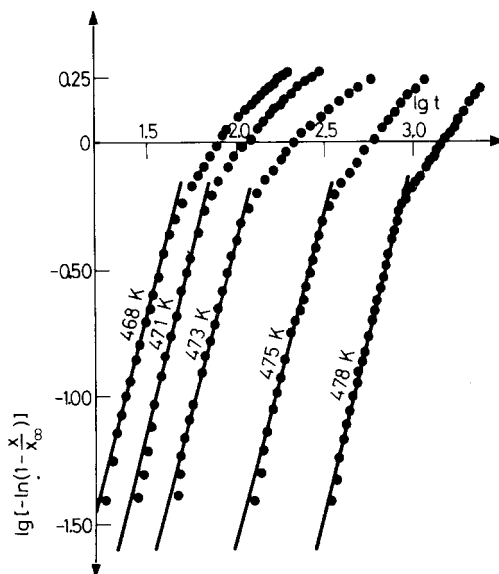


Fig. 2 Crystallization isotherms in Avrami co-ordinates of PA 6 coloured with 0.5% of BB Red

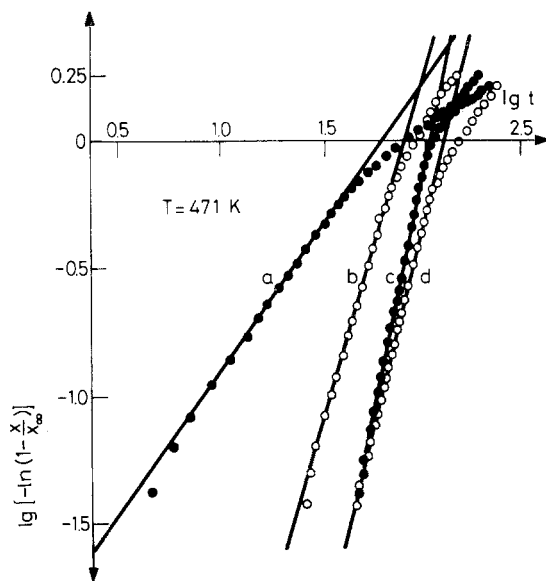


Fig. 3 Crystallization isotherms at 471 K: a) PA 6 with 1% of B Blue, b) PA 6 with 1% of BB Red, c) colourless PA 6, d) PA 6 with 2% of G Orange

[15]. In some papers [1, 2, 16], values of n up to 10 have been reported for the initial stages of transformation. However, those results can be described with the Avrami equation with $n = 4$ from the start of crystallization if the initial point is taken as the onset of crystal nucleation, i.e. if the time scale is corrected for the induction period.

The presence of pigments lowers the value of the Avrami exponent, since the content of heterogeneous nuclei is increased, and the crystallization gradually turns into a process controlled by diffusion. Moreover, the pattern of n evolution with time is found to be dependent on the amount of pigment. In the case of pure polyamide 6, the linear portions of the isotherms usually persisted to above the half-time of crystallization; for the coloured polyamides, this stage gradually became shorter with increasing content of pigment and the secondary crystallization started earlier (Figs 2 and 3).

The temperature-dependence of the overall isothermal crystallization was considered as the sum of the temperature coefficients of nucleation and growth of spherulites. According to the theory of nucleation [5], the rate of growth of the crystalline phase fits the equation:

$$G = G_0 \exp(-\Delta E/kT) \exp(-\Delta G^*/kT) \quad (2)$$

where ΔE is the activation energy for transport across the liquid-crystal interface, ΔG^* is the free energy of formation of a critical-size crystallization nucleus, k is the Boltzmann constant, and G_0 is a constant.

Table 1 Kinetic parameters of isothermal crystallization of PA 6 as functions of crystallization temperature and organic pigment content

Sample	468 K			471 K			473 K			475 K			478 K		
	log K	n	t, 1/2	log K	n	t, 1/2	log K	n	t, 1/2	log K	n	t, 1/2	log K	n	t, 1/2
Colourless PA 6	-6.35	3.4	66.3	-7.56	3.7	100.3	-8.62	3.8	168.9	-10.20	3.8	446	-11.82	3.7	1421
G Orange 0.5%	-4.55	2.6	48.3	-5.08	2.5	93.7	-6.28	2.6	228.0	-7.42	2.7	490	-8.81	2.7	1609
G Orange 1%	-4.88	2.7	56.1	-5.72	2.7	115.2	-7.15	2.8	316.2	-7.85	2.7	708	-9.12	2.8	1630
G Orange 2%	-5.47	3.0	59.3	-6.32	3.0	118.5	-8.16	3.2	324.1	-9.14	3.1	792	-9.83	3.0	1673
B Blue 0.5%	-1.66	1.0	31.8	-1.91	1.0	56.3	-2.55	1.2	99.1	-2.93	1.1	335	-3.79	1.2	1060
B Blue 1%	-1.76	1.1	28.5	-2.01	1.1	48.8	-2.72	1.3	92.4	-3.36	1.3	296	-4.05	1.3	983
B Blue 2%	-1.69	1.1	25.9	-1.82	1.2	44.9	-2.48	1.2	89.0	-3.09	1.2	288	-3.70	1.2	901
BB Red 0.5%	-4.28	2.4	58.2	-5.10	2.5	94.8	-5.52	2.5	140.4	-6.91	2.6	395	-7.75	2.5	1097
BB Red 1%	-4.60	2.6	51.4	-5.18	2.7	71.3	-5.59	2.6	123.3	-6.57	2.5	370	-8.21	2.7	965

On the assumption that the crystallization occurs only on heterogeneous crystal nuclei and is controlled by secondary sufficial nucleation, the surface free energy of fold-containing surfaces σ_e and the energy of the lateral surface σ were calculated:

$$\sigma_e = 6.24 \cdot 10^{-2} \text{ J/m}^2 \quad \text{and} \quad \sigma = 9.86 \cdot 10^{-3} \text{ J/m}^2$$

This result is in very good agreement with the value $\sigma_e = 6 \cdot 10^{-2}$ obtained by Magill [19] from spherulitic growth rates. The values used in calculations here were as follows: the effective thickness of the monolayer $b_0 = 4.25 \cdot 10^{-10}$ m [20], and the heat of fusion per unit volume $\Delta h_m = 2.32 \cdot 10^8$ J/m³ [5]. The equilibrium melting point T_m^0 was determined from the relationship between the melting point and the temperature of isothermal crystallization. The extrapolated experimental line $T_m = f(T_c)$ intersects the line $T = T_m$ at the point $T_m^0 = 512$ K (Fig. 4).

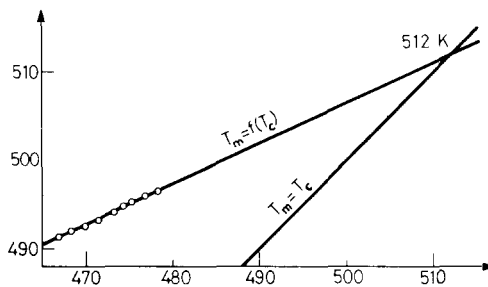


Fig. 4 Dependence of melting temperature on isothermal crystallization temperature for polyamide 6

The presence of organic pigments did not affect the equilibrium melting temperature of the glass transition temperature. Our results reveal different effects of the selected pigments on the crystallization rate, since their structures are dissimilar. Binsbergen [18] found that the active nucleating agents are insoluble in the polymer melt, and their physical state is a fine dispersion of small crystals or a thin crystalline layer adsorbed on dispersed particles of another substance. As regards their chemical nature, the agents consist of both hydrocarbon groups and either polar groups or a condensed aromatic structure. The hydrocarbon parts of the molecules do not carry polar substituents other than the acid groups. If one or more hydrogens are replaced by polar groups, such as $-\text{NH}_2$, $-\text{OH}$, $-\text{NO}_2$ or $-\text{OCH}_3$, the substance loses its nucleation ability. The crystals of active nucleating agents consist either of parallel layers or of parallel rows of molecules. As a result, such an arrangement of molecules enables the polymer molecules to assume a stretched confirmation over some distance, making crystallization much easier.

Among the selected pigments, B Blue pigment is the most active agent accelerating the crystallization of polyamid 6. In the case of polyamide 6 coloured

with this pigment, the half-times of crystallization are twice as short. Moreover, this agent causes changes in the mechanism of crystallization. The lower of the Avrami exponent (about 1) seems to depend on the high nucleating effect of this pigment. This would imply a morphology of the materials different from the spherulitic one. The presence of B Blue seems to induce only the development of fibrils, which subsequently do not organize into spherulites.

The activity of B Blue pigment [17] is probably connected with its structure, i.e. a regular packing of parallel stacks of flat ring systems, which corresponds to the model of Binsbergen [18]. BB Red can also be numbered among nucleating agents in the Binsbergen classification. However, in this case the presence of the polar —OH group in the hydrocarbon part of the molecule exerts an influence on the nucleation ability (Table 1). The Avrami exponent is in the range between 2.4 and 2.7. The different value obtained for this case is connected with a change in the crystallization mechanism. It probably corresponds to a disc-like growth from instantaneous nuclei or a rod-like growth from sporadic nuclei.

In other words, the observed effect can be due to a change in the growth process or to a change in the nucleation mechanism. Since nucleation on pre-existing nucleation sites appears to be a fairly general feature of polymer crystallization from the melt [5], a change in the growth process seems to be the case. G Orange does not form crystals with parallel layers or parallel rows of molecules and is not a nucleating agent. Only at low crystallization temperatures and at low concentrations does G Orange slightly accelerate crystallization; at higher temperatures it reduces the crystallization rate.

The particles of the tested nucleating pigments operate simultaneously at the onset of crystallization (athermal nucleation), since the exponent n is lower in the case of coloured polyamide than for pure polyamide 6. The presence of pigments causes an increase in nucleation density; they sometimes become active below a certain degree of supercooling.

Non-isothermal crystallization

Some typical DSC traces obtained for PA 6 at several constant cooling rates are shown in Fig. 5. In this case, the continuation of the straight portions of the DSC curve before and after crystallization was taken as baseline. The results of non-isothermal crystallization are in good agreement with the isothermal crystallization data.

For samples coloured with organic pigments, the temperatures of the maximum crystallization rates are shifted towards higher values, which testifies to smaller undercooling (faster crystallization). The temperatures of the DSC peaks listed in Table 2 as functions of sample composition and cooling rate reflect the nucleation

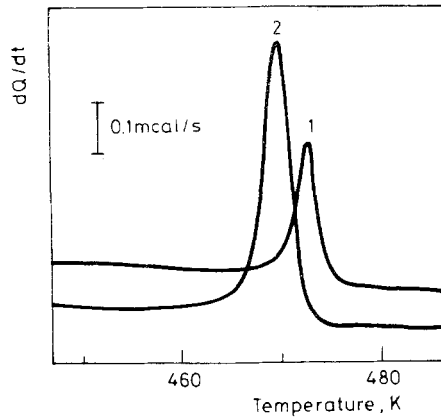


Fig. 5 DSC traces of non-isothermal crystallization of PA 6 at cooling rates of 1 K/min and 2 K/min

Table 2 Temperatures of DSC peaks of non-isothermal PA 6 crystallization as functions of cooling rate and pigment content

Cooling rate, deg/min	Colourless, PA 6	G Orange			B Blue			BB Red	
		0.5%	1%	2%	0.5%	1%	2%	0.5%	1%
1	472.7	472.5	472.7	472.2	476.2	476.5	476.5	473.9	474.6
2	470.0	469.6	470.2	469.5	473.8	473.9	473.9	471.7	471.6
5	464.6	464.7	464.6	464.6	469.7	470.2	470.2	466.8	466.7
10	461.8	460.6	460.9	460.2	466.6	466.9	467.7	463.7	461.8

abilities of B Blue and BB Red. B Blue is more active than BB Red. The effect of G Orange on PA 6 crystallization is complicated. At lower concentrations and cooling rates, it slightly accelerates crystallization, whereas at higher contents it causes a slowdown of PA 6 crystallization.

Ozawa [21] has extended the Avrami theory to the non-isothermal situation, assuming that the amorphous polymer is cooled at a constant rate. According to the Ozawa theory, the degree of conversion at temperature T is:

$$\ln(1 - x_T/x) = \varphi(T)/a^n \quad (3)$$

where x_T is the degree of crystallinity at temperature T , a is the cooling rate and $\varphi(T)$ is the cooling function.

Variation of the exponent n with the crystallization temperature (Table 1), the temperature-dependence of the fold length and the secondary crystallization are factors which would result in an inadequacy of the Ozawa formalism in this case. In Fig. 6, experimental data obtained for PA 6 coloured with B Blue are presented.

Although straight lines can be drawn through the experimental points in Ozawa co-ordinates, the slope is observed to change with decreasing temperature. For samples of PA 6 coloured with B Blue, n changes from 4 to 0.8, and in other cases from 6 to 1. These results reveal that the non-isothermal crystallization mechanism is modified during the process, and thus the data cannot be fitted by the Ozawa function. The high values of n obtained at high temperatures can be assigned to the sheaf-like

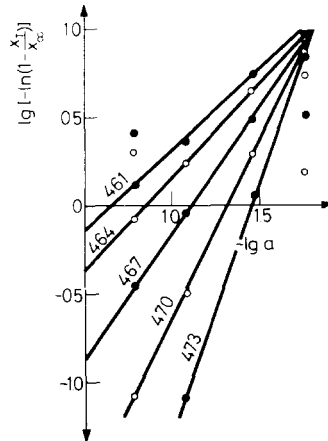


Fig. 6 Results of non-isothermal crystallization of PA 6 containing 1% of B Blue presented in Ozawa co-ordinates

crystallization of polyamide 6 in the γ -polymorphic modification, while lower n values are presumably a consequence of the simultaneous growth of α and γ -polymorphs [5]. The onset of crystallization, i.e. the crystallization of a small volume fraction of the melt, is given by [3]:

$$\frac{d\beta}{dt} = (1 - \beta) \exp\left(\frac{-\Delta E}{KT}\right) \exp\left(\frac{-\Delta G^*}{KT}\right) \quad (4)$$

If we assume that the ΔE term, connected with transport through the liquid-crystal interface, is independent of temperature in the vicinity of the melting point, i.e. at low undercoolings, the equation for cooling crystallization at constant rate can be given as

$$-\ln [a(2T_N - T_m^0)T_m^0/T_N^2(\Delta T)^2] = \frac{4b_0\sigma \cdot \sigma_e T_m^0}{K\Delta h_m T_N \Delta T} - \ln \frac{\text{const } K\Delta h_m}{4b_0\sigma \cdot \sigma_e} \quad (5)$$

where T_N is the temperature of deviation from the baseline on the curve, and ΔT is the degree of undercooling.

Tests of Eq. (5) are shown in Fig. 7 for pure PA 6 and for samples coloured with 1% of G Orange, B Blue and BB Red.

From the slope, the surface free energy of the fold surface σ_e was calculated for polyamide 6. The obtained value, $6.85 \cdot 10^{-2} \text{ J/m}^2$, is in satisfactory agreement with the isothermal result.

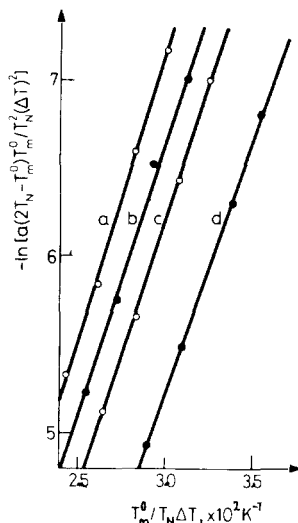


Fig. 7 Test of equation (5): for: a) PA 6 with 1% of G Orange, b) PA 6, c) PA 6, with 1% of BB Red, d) PA 6 with 1% of B Blue

It should be noted that the instrumental sensitivity is insufficient to detect the small amount of heat released as a result of the onset of nucleation. The temperature of nucleation should be higher by several degrees than the observed temperature T_N .

The basic assumption of most theories of heterogeneous nucleation is that the total interfacial free energy of the crystalline embryo is reduced by a foreign phase which provides part of the interface to be formed. This causes a reduction of the activation free energy and a decrease in the degree of supercooling required for nucleation. The extent of the reduction of the interfacial free energy is dependent on both the geometrical form of the foreign phase and its chemical nature.

The results of the non-isothermal crystallization of PA 6 coloured with pigments correspond to this idea, since the slopes of the straight lines in Fig. 6, connected with the free energy of formation of a critical-size crystallization nucleus, are different for PA 6 containing organic pigments. The apparent values of parameter σ_e calculated from Eq. (5): G Orange $7.36 \cdot 10^{-2}$, B Blue $5.41 \cdot 10^{-2}$, BB Red $6.02 \cdot 10^{-2} \text{ J/m}^2$. These are in good agreement with the observed rates of

crystallization. The surface free energy σ_e of polyamide 6 coloured with B Blue is reduced by 20%, which is reflected in a faster crystallization. The 7% increase in σ_e in the case of PA 6 coloured with G Orange causes the observed slowdown of the process. The nucleation abilities of the pigments can be arranged into the following series:

B Blue > BB Red > no pigment > G Orange

* * *

This work was supported by the Polish Academy of Science, goal 01.14.

References

- 1 F. Rybnikar, Collect. Czech. Commun., 27 (1962) 106.
- 2 E. Turska and S. Gogolewski, Polymer, 12 (1971) 616.
- 3 G. Gurato, D. Gaidano and R. Zannotti, Makromol. Chem., 179 (1978) 231.
- 4 F. De Candia, A. Tagliatalata and V. Vittoria, Kolloid-Z. u. Z. Polymere, 251 (1973) 61.
- 5 B. Wunderlich, Macromolecular Physics, Vol. II, Academic Press, New York 1976.
- 6 M. Inoue, J. Polymer Sci., A1 (1963) 2013.
- 7 A. Wlochowicz and M. Eder, Colloid and Polymer Sci., 261 (1983) 621.
- 8 W. Kozłowski, J. Polymer Sci., C38 (1972) 47.
- 9 F. P. Price, Nucleation, Ch. 8, p. 405, ed. by A. C. Zettlemoyer, Marcel Dekker Inc. New York 1969.
- 10 F. L. Binsbergen, J. Polym. Sci., Polym. Symp., 59 (1977) 11.
- 11 A. M. Chatterjee and F. P. Price, J. Polymer Sci., Polymer Phys. Ed., 13 (1975) 2369, 2385, 2391.
- 12 L. Mandelkern, Crystallization of Polymers, McGraw-Hill, New York 1964.
- 13 H. N. Beck and H. D. Ledbetter, J. Appl. Polymer Sci., 9 (1965) 2131.
- 14 M. J. Avrami, J. Chem. Phys., 7 (1939) 1103; 8 (1940) 212; 9 (1941) 177.
- 15 M. Ishibashi, Kobunshi Kagaku, 26 (1969) 199.
- 16 V. P. Privalko, T. Kawai and Y. S. Lipatov, Colloid and Polymer Sci., 257 (1979) 841.
- 17 B. Homigmann, H. U. Lenne and R. Schrödel, Z. Krist., 122 (1965) 185.
- 18 F. L. Binsbergen, Polymer, 11 (1970) 253.
- 19 J. H. Magill, Polymer, 6 (1965) 367.
- 20 V. P. Privalko, Macromolecules, 12 (1979) 122.
- 21 T. Ozawa, Polymer, 12 (1971) 150.

Zusammenfassung — Mit Hilfe der Avrami Gleichung wurde der Einfluß einiger ausgewählter organischer Pigmente auf die kinetischen Parameter der isothermen Kristallisation gefärbter Polyamide 6 im Temperaturbereich 468–478 K untersucht. B Blue und BB Red erwiesen sich als aktive Keimbilder, was mit Hilfe ihrer kristallinen Struktur erklärt werden kann. Bei niedrigeren Temperaturen und geringeren Konzentrationen wird die Kristallisation von PA 6 durch G Orange leicht beschleunigt, unter anderen Bedingungen kann das Gegenteil beobachtet werden. Die isothermen Daten wurden durch die Ergebnisse bei nichtisothermer Kristallisation bekräftigt. In diesem Falle wurde das dem DSC Peak entsprechende Maß an Unterkühlung untersucht. Es wurde gefunden, daß B Blue und BB Red die freie Energie zur Bildung von Keimen kritischer Größe um 20 bzw. 12% herabsetzen, was sich in den Kristallisationsgeschwindigkeiten widerspiegelt.

Резюме — Исходя из уравнения Аврами, исследовано влияние некоторых органических пигментов на кинетические параметры изотермической кристаллизации окрашенного полиамида-6 в интервале температур 468–478 К. Установлено, что голубой Б и красный ББ являются активными центрами кристаллизации, что обусловлено их собственной кристаллической структурой. Пигмент оранжевый Ж при более низких температурах и концентрациях в малой мере ускоряет кристаллизацию, тогда как в других условиях он вызывает противоположный эффект. Изотермические данные подтверждены данными неизотермической кристаллизации. Измерена степень переохлаждения соответствующего пика кривой ДСК. Найдено, что пигменты голубой Б и красный ББ понижают свободную энергию образования центров кристаллизации критической величины, соответственно, на 20 и 12%, что отражается на скоростях кристаллизации.