

Effects of Predetermined Nuclei and Limited Transformation on Polymorphic Crystallization in a Model Polymer

Beata Misztal-Faraj, Andrzej Ziabicki

Institute of Fundamental Technological Research, Polish Academy of Sciences, Pawinskiego 5B, 02-106, Warsaw, Poland

Received 30 November 2011; accepted 30 November 2011

DOI 10.1002/app.36566

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Formation of different polymorphic structures plays important role in crystallization of some polymers, like polypropylene, polycapromamide, poly(vinylidene difluoride), and others. Physical properties of such materials depend on phase structure, that is, fractions of different polymorphs. Basing on the model of many-phase transitions (Ziabicki, *J Chem Phys* 2005, 123, 174103; Ziabicki and Misztal-Faraj, *J Mater Res*, 2011, 26, 1585) a model system consisting of an amorphous phase, stable solid phase, and metastable polymorphic phase was analyzed. Two effects in the kinetics of polymorphic crystalli-

zation have been analyzed: effect of the presence of universal and/or selective predetermined nuclei and limited crystallizability resulting from molecular constraints in high-molecular systems. Conditions in which different phase compositions (i.e., different proportions of individual phases) have been discussed. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: polymorphic phase transitions; phase composition; sporadic nucleation; predetermined nucleation; limited degree of transformation

INTRODUCTION

Many polymers, like isotactic polypropylene, poly(vinylidene difluoride), Nylon 6, and others exhibit polymorphism. Depending on crystallization conditions, different phases are created in different proportions. Physical properties of such polymers strongly depend on the phase composition. One of the polymorphic forms of PVDF is piezoelectric and its contents controls electric properties. Understanding the rules governing formation of various polymorphic structures makes possible adjusting crystallization conditions to obtain desired properties. Ziabicki^{1,2} developed a model of the kinetics of polymorphic phase transitions in many-phase systems. In this article, we will analyze development of phase composition in a three-phase monotropic system consisting of an amorphous (liquid) phase “0,” a metastable high-temperature solid “1,” and low-temperature stable solid “2.” Two effects in transformation kinetics will be discussed. First, effect of predetermined nuclei: fragments of unmelted crystals, foreign particles (pigments, catalysts, etc.) present in the polymer at the start of the process. Second, effect of molecular constraints in flexible-

chain polymer systems resulting in incomplete crystallization. Maximum degree of crystallinity, x_{\max} , dependent on molecular structure, will be incorporated in the crystallization model and its effect on the development of phase composition will be discussed.

THE MODEL

Figure 1 presents linearized isobaric phase diagram of the system. According to the classification by Mitscherlich³ the system is monotropic, that is, only two (out of three) phases are thermodynamically stable and appear in thermodynamic equilibrium. Below the temperature T_{02} stable phase is low-temperature solid “2,” above T_{02} : amorphous (liquid) phase “0.” The high-temperature phase “1” is metastable. There is no temperature in which phase “1” would exhibit minimum free energy.

Thermodynamically admissible transitions at any given temperature are defined as ones associated with reduction of the Gibbs' free energy:

$$\Delta G_{ij} = G_j - G_i < 0 \Leftrightarrow "i" \rightarrow "j" \quad (1)$$

It is evident in Figure 1 that in low temperatures, $T < T_{01}$ the admissible transitions include direct crystallization of the amorphous phase “0” and polymorphic transition between the two solids

Correspondence to: B. Misztal-Faraj (bfaraj@ippt.gov.pl).

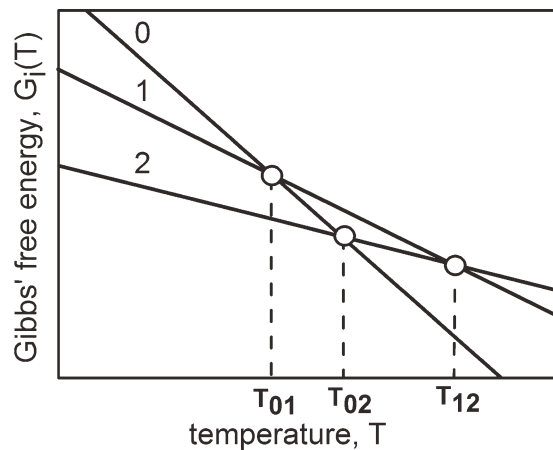


Figure 1 Isobaric Gibbs' free energy for a three-phase monotropic system. "0": liquid (amorphous) phase, "1": metastable, high-temperature solid, and "2": stable, low-temperature solid.

$$\begin{aligned}
 T < T_{01} : \\
 "0" &\rightarrow "1" \\
 "0" &\rightarrow "2" \\
 "1" &\rightarrow "2"
 \end{aligned}
 \quad (2)$$

Material characteristics used in the simulations, based on those for isotactic polypropylene⁴ are collected in Table I.

Characteristics identified as primary—heats of melting of phases "1" and "2," transition temperatures T_{01} , T_{02} , and average interface tension, σ_{20} —have been taken from the literature.⁴ Other characteristics, unavailable from direct experiments (in particular those concerned with polymorphic transition "1" \rightarrow "2"), were calculated from pri-

mary data using basic relations between thermodynamic functions

$$\begin{aligned}
 \Delta H_{ik} &= \Delta H_{ij} + \Delta H_{jk} \\
 \Delta S_{ik} &= \Delta S_{ij} + \Delta S_{jk} \\
 \Delta G_{ik} &= \Delta G_{ij} + \Delta G_{jk} \\
 T_{ik} &= \frac{\Delta H_{ik}}{\Delta S_{ik}} = \frac{(\Delta H_{ij} + \Delta H_{jk}) T_{ij} T_{jk}}{\Delta H_{ij} T_{jk} + \Delta H_{jk} T_{ij}}
 \end{aligned}
 \quad (3)$$

and correlation between interface tensions and transition enthalpies

$$\frac{\sigma_{ij}}{\sigma_{jk}} = \left| \frac{\Delta h_{ij}}{\Delta h_{jk}} \right|
 \quad (4)$$

According to the classical theory of phase transitions⁵⁻⁸ two basic classes of kinetic processes can be distinguished: m -dimensional growth (with a linear rate $\dot{R}_{ij} = dR_{ij}/dt$) of a constant number, N_0^{ij} , of pre-determined nuclei and sporadic nucleation (with a rate $\dot{N}_{ij} = dN_{ij}/dt$) followed by growth. The characteristic describing progress of the transition "i" \rightarrow "j" in time t is given by $E_{ij}^{\text{pre}}(t; T)$ in the case of pre-determined nucleation, and $E_{ij}^{\text{SPC}}(t; T)$ for sporadic nucleation

$$\begin{aligned}
 E_{ij}^{\text{pre}}(t; T) &= N_0^{ij} \left[\int_0^t \dot{R}_{ij}(s) ds \right]^m \\
 E_{ij}^{\text{SPC}}(t; T) &= \int_0^t \dot{N}_{ij}(s) \left[\int_s^t \dot{R}_{ij}(z) dz \right]^m ds
 \end{aligned}
 \quad (5)$$

TABLE I
Material Characteristics for the Model System⁴

Parameter	Characteristic	Value	Source
T_{01} (K)	Melting temperature of phase "1"	465.2	Primary
T_{02} (K)	Melting temperature of phase "2"	485.2	Primary
T_{12} (K)	Transition temperature "1" \rightarrow "2"	1221.6	Calculated [eq. (3)]
Δh_{10} (J/g)	Heat of melting phase "1"	194.9	Primary
Δh_{20} (J/g)	Heat of melting phase "2"	208.8	Primary
Δh_{21} (J/g)	Heat of the transition "2" \rightarrow "1"	13.9	Calculated [eq. (3)]
$E_D^{01} = E_D^{02}$ (kJ/mol)	Activation energy in the melt "0"	70	Assumed
$E_D^{12} = E_D^{10}$ (kJ/mol)	Activation energy in the solid phase "1"	110	Assumed
σ_{02} (J/cm ²)	Interface tension "2" vs. "0"	2.527×10^{-6}	Primary
σ_{01} (J/cm ²)	Interface tension "1" vs. "0"	2.3588×10^{-6}	Calculated [eq. (4)]
σ_{12} (J/cm ²)	Interface tension "1" vs. "2"	0.1682×10^{-6}	Calculated [eq. (4)]
v_0 (cm ³)	Volume of a single kinetic element	1.968×10^{-22}	Assumed
γ_0 (g/cm ³)	Density of the amorphous phase "0"	0.854	Primary
γ_1 (g/cm ³)	Density of solid phase "1"	0.939	Primary
γ_2 (g/cm ³)	Density of solid phase "2"	0.949	Primary

In steady-state isothermal conditions eq. (5) reduce to the Avrami equations

$$E_{ij}^{\text{pre}}(t; T) \xrightarrow{\text{isothermal}} N_0^{ij} \dot{R}_{ij}^m(T) t^m \quad (6)$$

$$E_{ij}^{\text{spc}}(t; T) \xrightarrow{\text{isothermal}} \frac{1}{m+1} \dot{N}_{ij}(T) \dot{R}_{ij}^m(T) t^{m+1}$$

where steady-state nucleation rate, \dot{N}_{ij}^{st} , of cubic clusters reads²

$$\dot{N}_{ij}^{\text{st}} = \frac{12\sigma_{ij}^{1/2}}{\sqrt{6\pi kT} v_0^{2/3}} \frac{kT}{h} e^{-\frac{E_D^{ij}}{kT}} \exp\left[\frac{-32 \sigma_{ij}^3}{kT \Delta g_{ij}^2}\right] \quad (7)$$

Similarly, linear growth rate, \dot{R}_{ij} , controlled by secondary nucleation on crystal surface is obtained in the form²

$$\dot{R}_{ij} = 2 v_0^{5/6} \left(\frac{|\Delta g_{ij}|}{\pi kT}\right)^{1/2} \frac{kT}{h} e^{-\frac{E_D^{ij}}{kT}} \exp\left[\frac{-4\sigma_{ij}^2 v_0^{1/3}}{kT |\Delta g_{ij}|}\right] \quad (8)$$

where $\Delta g_{ij} = \Delta h_{ij} \gamma_j (T_{ij} - T)/T_{ij}$ is free energy density providing driving force for the transition “i” → “j”.

KINETICS OF PHASE TRANSITIONS IN AN UNDERCOOLED SYSTEM

Consider behavior of a system undercooled to the temperature $T < T_{01}$ and containing at the start ($t = 0$) fractions x_0^0, x_1^0, x_2^0 of the individual phases. It has been demonstrated in our earlier articles² that the resulting phase composition at the instant t , reads

$$\begin{pmatrix} x_0^0 \\ x_1^0 \\ x_2^0 \end{pmatrix} \rightarrow \begin{pmatrix} x_0(t) \\ x_1(t) \\ x_2(t) \end{pmatrix} = \begin{pmatrix} x_0^0 e^{-E_{01}-E_{02}} \\ e^{-E_{12}(t)} \left[x_1^0 + \int_0^t e^{E_{12}(t')} x_0(t') \dot{E}_{01}(t') dt' \right] \\ x_2^0 + \int_0^t x_1(t') \dot{E}_{12}(t') dt' + \int_0^t x_0(t') \dot{E}_{02}(t') dt' \end{pmatrix} \quad (9)$$

In steady-state isothermal conditions and in the absence of predetermined nuclei, eq. (9) can be integrated to yield

$$\begin{pmatrix} x_0^0 \\ x_1^0 \\ x_2^0 \end{pmatrix} \rightarrow \begin{pmatrix} x_0(t) \\ x_1(t) \\ x_2(t) \end{pmatrix} = \begin{pmatrix} x_0^0 e^{-E_{01}-E_{02}} \\ x_1^0 e^{-E_{12}} + \frac{x_0^0 E_{01}}{E_{12}-E_{01}-E_{02}} (e^{-E_{01}-E_{02}} - e^{-E_{12}}) \\ x_2^0 + \frac{x_0^0 (E_{12}-E_{02})}{E_{12}-E_{01}-E_{02}} (1 - e^{-E_{01}-E_{02}}) + \left[x_1^0 - \frac{x_0^0 E_{01}}{E_{12}-E_{01}-E_{02}} \right] (1 - e^{-E_{12}}) \end{pmatrix} \quad (10)$$

To compare various effects in crystallization kinetics we will introduce two time-independent characteristics describing transition rates. The frequency of a process controlled by predetermined nucleation

$$v_{ij}^{\text{pre}} = \left(E_{ij}^{\text{pre}}/t^3\right)^{1/3} = 2 v_0^{5/6} N_0^{1/3} \left(\frac{|\Delta g_{ij}|}{\pi kT}\right)^{1/2} \frac{kT}{h} e^{-\frac{E_D^{ij}}{kT}} \exp\left[\frac{-4 \sigma_{ij}^2 v_0^{1/3}}{kT |\Delta g_{ij}|}\right] \quad (11)$$

Similarly, for sporadic nucleation

$$v_{ij}^{\text{spc}} = (E_{ij}^{\text{spc}}/t^4)^{1/4} = 96^{1/8} \frac{\sigma_{ij}^{1/8} |\Delta g_{ij}|^{3/8} v_0^{11/24} kT}{(\pi kT)^{1/2}} \frac{kT}{h} e^{-\frac{E_D^{ij}}{kT}} \exp\left[\frac{-8 \sigma_{ij}^3}{kT \Delta g_{ij}^2}\right] \exp\left[\frac{-3 \sigma_{ij}^2 v_0^{1/3}}{kT |\Delta g_{ij}|}\right] \quad (12)$$

SPORADIC NUCLEATION VERSUS PREDETERMINED NUCLEATION

An important role in the kinetics of phase transitions is played by predetermined nuclei. The number of such nuclei effective in the transition “i” → “j,” depends on the target phase, “j,” that is,

$$N_0^{ij} = N_0^j \quad (13)$$

Predetermined nuclei can consist of incompletely melted crystals, structural defects, or various foreign particles, like pigments, catalysts, dyestuffs, etc. Some (universal) additives are effective in formation of various phases; others behave in a selective way, stimulating formation of a specific polymorphic phase.⁹ The presence of predetermined nuclei converts isothermal transition rate into a sum of predetermined and sporadic mechanisms. Assuming three-dimensional growth, $m = 3$, we obtain

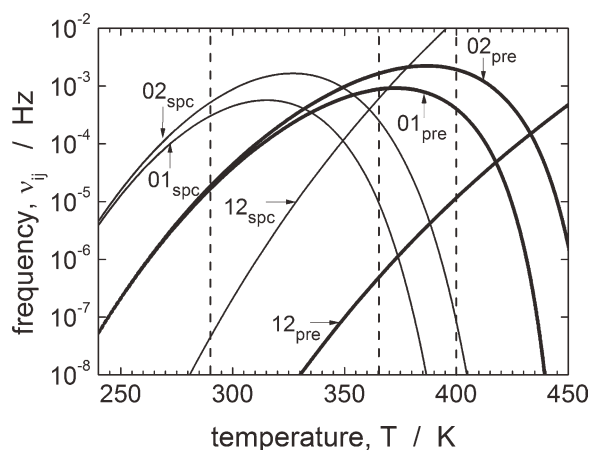


Figure 2 Frequencies of individual transitions, v_{ij} , for predetermined (pre) and sporadic nucleation (spc). Concentrations of predetermined nuclei: $N_0^{01} = N_0^{02} = N_0^{12} = 10^{12} \text{ cm}^{-3}$. Dashed lines indicate temperatures for which phase development was calculated.

$$E_{ij}^{\text{total}}(t, T) = E_{ij}^{\text{pre}}(t; T) + E_{ij}^{\text{spc}}(t; T) \quad (14)$$

$$E_{ij}^{\text{total}}(t, T) \xrightarrow{\text{isothermal}} \left[N_0^j + \frac{1}{4} \dot{N}_{ij} \cdot t \right] \dot{R}_{ij}^3(T) t^3$$

Concentration of predetermined nuclei, N_0^{ij} , can vary in a wide range dependently on the nature of additives, thermal history of the system, etc. Experiments based on the size of spherulites or single crystals [one spherulite (crystal)–one nucleus] yield values of the order of 10^7 cm^{-3} up to 10^{14} cm^{-3} .^{10,11} Realizing that in addition to starting a spherulite, predetermined nuclei may be effective in creating smaller crystal units, the above figures can be higher.

For the sake of simplicity an ideal system is assumed ($x_{\text{max}} = 1$). We will start our analysis with comparing sporadic and predetermined frequencies

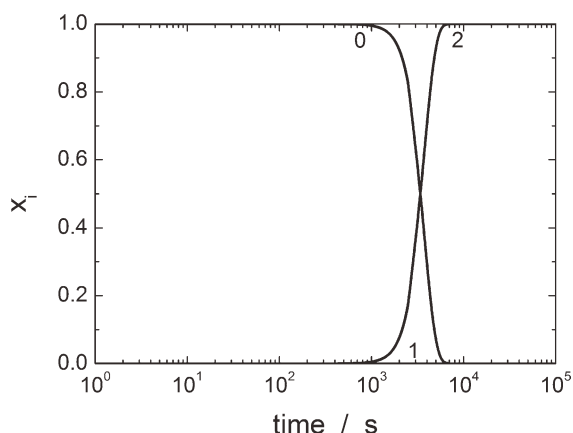


Figure 3 Development of phase composition at $T = 365 \text{ K}$ based on purely sporadic nucleation $N_0^{01} = N_0^{02} = N_0^{12} = 0$.

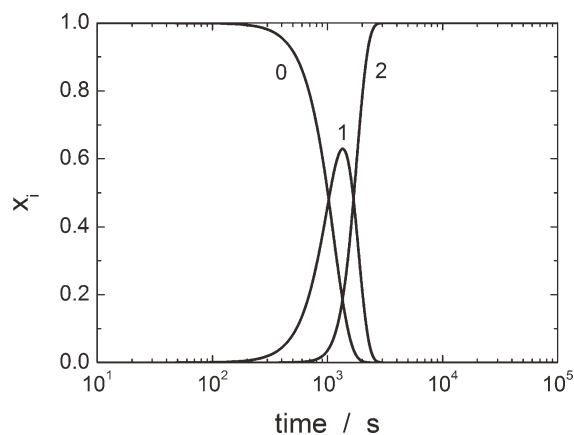


Figure 4 Development of phase composition at $T = 365 \text{ K}$ based on sporadic and predetermined nucleation. Predetermined nuclei, selective to phase “1.” $N_0^{01} = 10^{12} \text{ cm}^{-3}$. $N_0^{02} = N_0^{12} = 0$.

of the three transitions thermodynamically admissible at $T < T_{01}$.

Figure 2 presents sporadic and predetermined frequencies of individual transitions in the temperature range $280 < T < 410 \text{ K}$. In the region of low temperatures (below 330 K) frequencies of the direct transitions “0” → “1” and “0” → “2” based on sporadic nucleation are higher than those for predetermined nuclei. Consequently, effect of predetermined nuclei can be expected to be small. Above 355 K frequency of predetermined nucleation is higher than that for sporadic mechanism and in the vicinity of melting temperature ($T_{01} = 465.2 \text{ K}$) kinetics of crystallization are controlled solely by predetermined nucleation. Frequency of predetermined polymorphic transition “1” → “2” is much higher than that for sporadically nucleated process, in the entire range of temperatures.

Figure 3 presents development of phase composition at 365 K , in the absence of predetermined nuclei (purely sporadic mechanism). Crystallization starts at about 10^3 s and ends at about $6 \times 10^3 \text{ s}$. The amorphous phase “0” is converted into thermodynamically stable phase “2” and there is no evidence of the metastable phase “1.” It is consistent with Figure 2, which shows frequency of the sporadic “0” → “1” transition, about 36 times smaller than that of the sporadic “0” → “2” transition. Phase “1” created in small amounts from the amorphous phase is immediately converted into phase “2” due to high rate of the polymorphic transition “1” → “2.” In the temperature range investigated, formation of phase “1” can be stimulated by adding predetermined nuclei N_0^{01} selective to phase “1.”

Figure 4 shows development of phases “1” and “2” in a mixed process including sporadic nucleation and $N_0^{01} = 10^{12} \text{ cm}^{-3}$ predetermined nuclei selective to phase “1.” Conversion of the amorphous phase

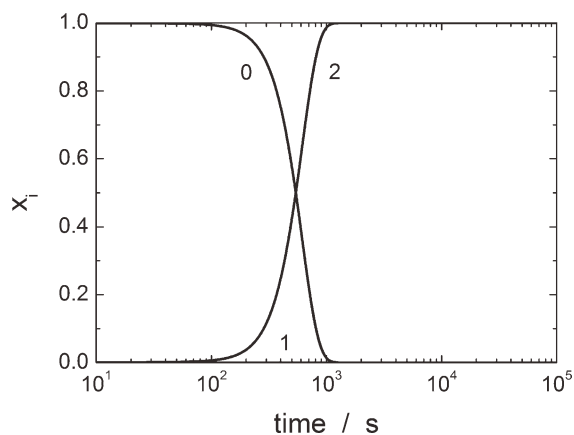


Figure 5 Development of phase composition at $T = 365$ K based on sporadic and predetermined nucleation. Predetermined nuclei selective for phase "2." $N_0^{02} = N_0^{12} = 10^{12} \text{ cm}^{-3}$; $N_0^{01} = 0$.

into phase "1" starts at about $2 \cdot 10^2$ s and phase "2" appears earlier than in a purely sporadic process (Fig. 3) because of rapid polymorphic transition "1" \rightarrow "2." The fraction of phase "1" reaches maximum at 1355 s and then falls down to zero, converted into the stable solid via polymorphic transition "1" \rightarrow "2." The level of the amorphous phase reaches zero around 2500 s. From this time on, phase "2" is created only in the polymorphic transition, and around 3070 s full crystallinity is reached ($x_2 = 1$).

Now, effect of nuclei selective for phase "2" will be discussed (Fig. 5). The transition "0" \rightarrow "2" starts below 100 s and lasts about one decade of time. The high-temperature solid "1" does not appear. In the absence of predetermined nuclei selective to phase "1," the only way of creating phase "1" is direct crystallization from the amorphous state based on sporadic nucleation. However, the frequency v_{01}^{spc} is small compared to v_{02}^{spc} and the kinetics are dominated by the "0" \rightarrow "2" transition, based on combined, sporadic and predetermined nucleation.

Nuclei specific for phase "2," $N_0^{02} = N_0^{12}$, do not contribute to creation of phase "1." However, the combined rate of polymorphic transition, v_{12} , increased by the presence of predetermined nuclei N_0^{12} , speeds-up conversion of phase "1," however small amount of it was created. In Figure 5 phase "1" does not appear.

Last, not least, we will consider effect of universal nuclei, equally effective in all transitions. Figure 6 presents development of phase composition at $T = 396$ K. It can be seen that conversion of the amorphous phase into phase "2" starts at the time of 100 s, comparable with the behavior shown in Figure 5. At the same time, universal predetermined nuclei speed up the transition "0" \rightarrow "1" as well as "0" \rightarrow "2." When the amorphous phase is exhausted ($x_0 = 0$), creation of phase "2" results from polymorphic

transition "1" \rightarrow "2." The latter is controlled by sporadic nucleation, whose frequency v_{12}^{spc} is nearly four orders of magnitude higher than v_{12}^{pre} .

LIMITED DEGREE OF TRANSFORMATION

The kinetic model described above concerned an ideal monotropic system in which thermodynamically admissible transitions resulted in complete transformation of the source phase into the thermodynamically stable target phase. Some systems, in particular organic polymers composed of long chain molecules, are unable to crystallize completely because of molecular constraints. It is well known that maximum achievable degree of crystallinity, x_{max} , in polyethylene, polypropylene, poly(ethylene terephthalate) and many other polymers is smaller than unity. Several attempts have been published¹²⁻¹⁴ to calculate theoretically the "equilibrium" (= maximum) degree of crystallinity from the statistics of chain conformation. Maximum degree of crystallinity depends on molecular weight of the polymer^{12,13} degree of branching¹⁵⁻¹⁸ and other characteristics of chain structure.

To account for the effect of limited crystallizability in crystallization kinetics we introduce the concept of two amorphous phases. One, unconstrained phase, x_{un} , can be crystallized, the other, constrained one, x_{con} , cannot be converted into any other phase.

$$x_0 = x_{\text{un}} + x_{\text{con}} \quad (15)$$

Consider crystallization of an undercooled amorphous system in a temperature $T < T_{01}$. The admissible transitions involve direct formation of solid phases "1" and "2" from the amorphous phase "0" and polymorphic transition of the high-temperature solid "1" into the low-temperature solid "2" (cf. Fig. 1).

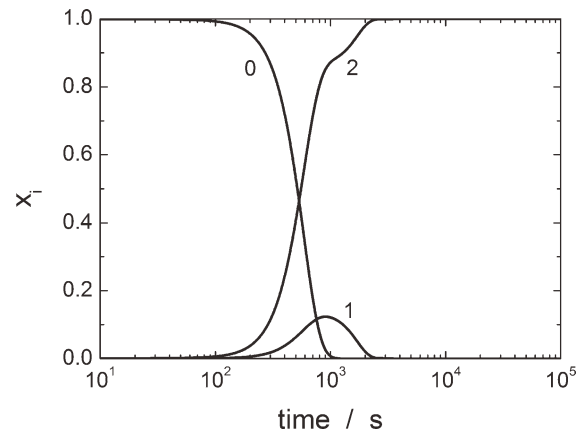
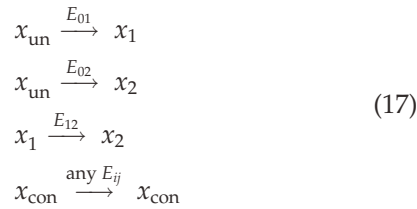


Figure 6 Development of phase composition at $T = 365$ K based on sporadic and predetermined nucleation. Universal predetermined nuclei effective in all transitions, $N_0^{01} = N_0^{02} = N_0^{12} = 10^{12} \times \text{cm}^{-3}$.

$$\begin{array}{l}
 x_0 \rightarrow x_1 \\
 x_0 \rightarrow x_2 \\
 x_1 \rightarrow x_2
 \end{array} \quad (16) \quad \begin{pmatrix} x_0 = x_{\text{un}} + x_{\text{con}} \\ x_1 \\ x_2 \end{pmatrix} \rightarrow \begin{pmatrix} x_{\text{un}} \\ x_1 \\ x_2 \\ x_{\text{con}} \end{pmatrix} \quad (18)$$

Realizing existence of two amorphous “phases,” different behavior of x_{un} and x_{con} should be considered. The admissible transitions read



The unconstrained amorphous phase can be converted into any of the solid phases. The constrained fraction is inert and does not participate in any transformations. The initial three-phase system should be analyzed as a pseudo-four-phase system.

The initial composition of the undercooled system depends on thermal history. For the sake of simplicity, we will assume that after cooling we are dealing with at a pure amorphous phase, $x_0^0 = 1$. Proportions of constrained and unconstrained fractions in the undercooled system are characterized by the material constant x_{max} .

$$\begin{pmatrix} x_{\text{un}}^0 = x_{\text{max}} \\ x_1^0 = 0 \\ x_2^0 = 0 \\ x_{\text{con}}^0 = 1 - x_{\text{max}} \end{pmatrix} \quad (19)$$

Applying eq. (10) to the first three components of the vector (19) one obtains

$$\begin{pmatrix} x_{\text{max}} \\ 0 \\ 0 \\ 1 - x_{\text{max}} \end{pmatrix} \xrightarrow{E_{01}, E_{02}, E_{12}} \begin{pmatrix} x_{\text{max}} e^{-E_{01}-E_{02}} \\ \frac{x_{\text{max}} E_{01}}{E_{12}-E_{01}-E_{02}} (e^{-E_{01}-E_{02}} - e^{-E_{12}}) \\ \frac{x_{\text{max}} (E_{12}-E_{02})}{E_{12}-E_{01}-E_{02}} (1 - e^{-E_{01}-E_{02}}) - \frac{x_{\text{max}} E_{01}}{E_{12}-E_{01}-E_{02}} (1 - e^{-E_{12}}) \\ 1 - x_{\text{max}} \end{pmatrix} \quad (20)$$

The fourth component, constrained amorphous phase, x_{con} , remains unchanged. The four-component vector of phase composition can be reduced to

three components by summation of the two virtual amorphous phases into one amorphous phase “0.”

$$\begin{pmatrix} x_0(t) \\ x_1(t) \\ x_2(t) \end{pmatrix} = \begin{pmatrix} 1 - x_{\text{max}} (1 - e^{-E_{01}-E_{02}}) \\ \frac{x_{\text{max}} E_{01}}{E_{12}-E_{01}-E_{02}} (e^{-E_{01}-E_{02}} - e^{-E_{12}}) \\ \frac{x_{\text{max}} (E_{12}-E_{02})}{E_{12}-E_{01}-E_{02}} (1 - e^{-E_{01}-E_{02}}) - \left[\frac{x_{\text{max}} E_{01}}{E_{12}-E_{01}-E_{02}} \right] (1 - e^{-E_{12}}) \end{pmatrix} \quad (21)$$

It is evident in eq. (21) that fractions of solid phases “1” and “2” are proportional to the material characteristic x_{max} . Fraction of the amorphous phase “0” does not disappear but asymptotically approaches fraction of the constrained part, $1 - x_{\text{max}}$.

Isothermal development of phase composition based on sporadic nucleation and eq. (21) at different values of the parameter x_{max} , will be discussed. The value $x_{\text{max}} = 0$ (no unconstrained, crystallizable phase) leaves unchanged constrained amorphous phase in the system. Such a behavior can be observed in polymers with high degree of branching.^{15,18} However, $x_{\text{max}} = 1$ (no constrained phase) returns kinetics of an ideal system.

In high temperatures, frequency of direct crystallization of the unconstrained amorphous phase into

phase “1” is very low (see Fig. 2) and only phase “2” is created. At $T = 400$ K and $x_{\text{max}} = 0.25$ (Fig. 7) crystallization starts at about 4.4×10^6 s and levels off around 1.7×10^7 s reaching saturation level $x_2 = 0.25$.

Maximum degree of crystallinity does not significantly affect time scale of the transition at $T = 400$ K. Crystallization starts and is finished in the same range of times. What changes is saturation level corresponding to x_{max} . This is evident in Figures 7 (saturation at $x_2 = x_{\text{max}} = 0.25$), 8 (saturation at $x_2 = x_{\text{max}} = 0.5$), and 9 (saturation at $x_2 = x_{\text{max}} = 1$).

In the range of low temperatures, frequencies of direct formation of crystalline phases “1” and “2” are of the same order of magnitude, while that of polymorphic transition “1” \rightarrow “2” is much smaller

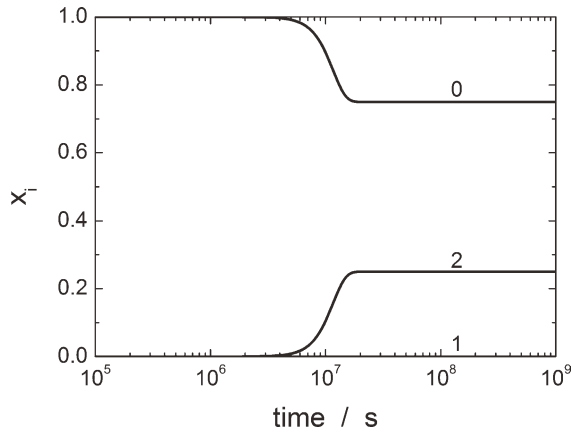


Figure 7 Development of phase composition at $T = 400$ K and maximum crystallinity, $x_{\max} = 0.25$.

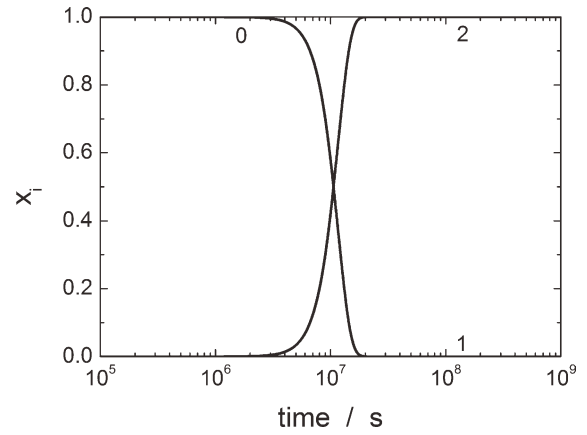


Figure 9 Development of phase composition at $T = 400$ K and maximum crystallinity, $x_{\max} = 1$.

(cf. Fig. 2). This makes the parameter x_{\max} affect kinetics in a more complicated way. We will consider development of phase composition at the temperature $T = 290$ K. Frequencies of transitions based on sporadic nucleation for an ideal system ($x_{\max} = 1$) are: $\nu_{01}^{\text{spc}} = 3.0 \times 10^{-4}$ Hz, $\nu_{02}^{\text{spc}} = 5.1 \times 10^{-4}$ Hz, and $\nu_{12}^{\text{spc}} = 4.2 \times 10^{-8}$ Hz. Figure 10 presents development of phase composition for maximum crystallinity $x_{\max} = 0.25$. Conversion of the unconstrained amorphous phase into phases “1” and “2” starts around 590 s. After 3.2×10^3 s all phases reach a plateau. Amorphous phase “0” levels off at $x_0 = 0.75$, phase “1” at $x_1 = 0.026$, and phase “2” at $x_1 = 0.224$. A period of “waiting” up to 10^7 s is followed by polymorphic transition “1” \rightarrow “2” and the final, (asymptotic) composition: $x_0 = 0.75$, $x_1 = 0$, and $x_2 = 0.25$ is reached around 3×10^7 s.

In the range of low temperatures, and short times (up to and during the “waiting period”) polymorphic transition can be neglected compared to direct transitions.

$$\begin{aligned} E_{01}^{\text{spc}} &\gg E_{12}^{\text{spc}} \\ E_{02}^{\text{spc}} &\gg E_{12}^{\text{spc}} \end{aligned} \quad (22)$$

The relation (22) is evident in Figure 2 presenting frequencies, $\nu_{ij} = (E_{ij}/t^m)^{1/m}$ of individual transitions [cf. eqs. (11) and (12)]. Neglecting effect of the slow polymorphic transition the ratio of solid phase fractions reduces to a constant, independent of time and of the parameter x_{\max} . Substituting $E_{12}^{\text{spc}} = 0$ into eq. (21) we obtain,

$$\begin{aligned} \begin{pmatrix} x_0(t) \\ x_1(t) \\ x_2(t) \end{pmatrix} \xrightarrow{E_{12} \rightarrow 0} &= \begin{pmatrix} 1 - x_{\max}(1 - e^{-E_{01} - E_{02}}) \\ \frac{x_{\max} E_{01}}{E_{01} + E_{02}} (1 - e^{-E_{01} - E_{02}}) \\ \frac{x_{\max} E_{02}}{E_{01} + E_{02}} (1 - e^{-E_{01} - E_{02}}) \end{pmatrix} \\ &\rightarrow \frac{x_1}{x_2} = \frac{E_{01}}{E_{02}} = \alpha(T) \end{aligned} \quad (23)$$

where α is a function of temperature. For $T = 290$ K, $\alpha = 0.12$.

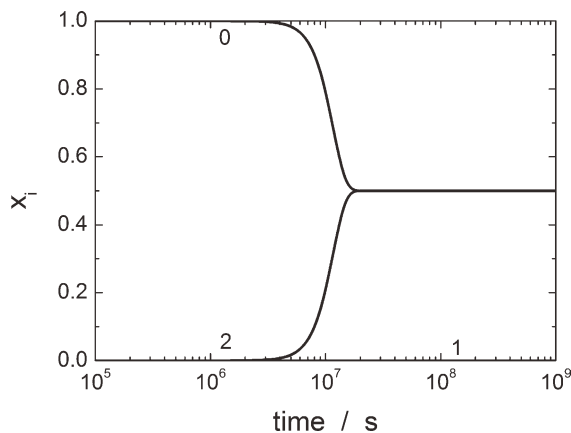


Figure 8 Development of phase composition at $T = 400$ K and maximum crystallinity, $x_{\max} = 0.5$.

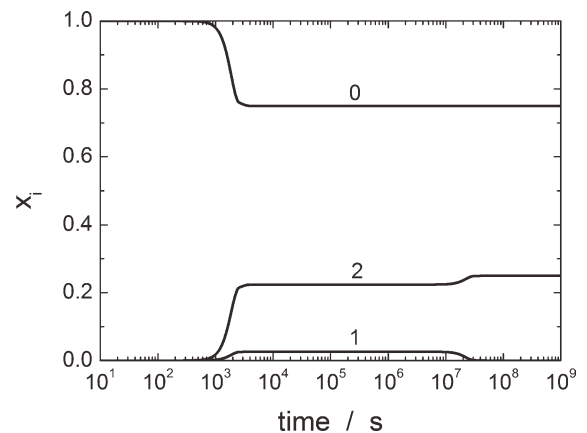


Figure 10 Development of phase composition at $T = 290$ K and maximum crystallinity, $x_{\max} = 0.25$.

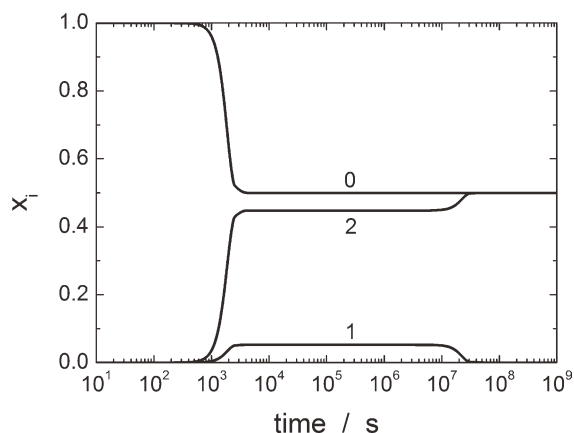


Figure 11 Development of phase composition at $T = 290$ K and maximum crystallinity, $x_{\max} = 0.5$.

The following relations between phase fractions up to, and during the “waiting period” are

$$\begin{aligned} x_0 &= 1 - x_{\max} \\ x_2 &= \frac{x_{\max}}{1 + \alpha} \\ x_1 &= \frac{\alpha \cdot x_{\max}}{1 + \alpha} \\ x_1/x_2 &= \alpha \end{aligned} \quad (24)$$

Asymptotic concentrations after the polymorphic transition is completed ($t \rightarrow \infty$)

$$\begin{aligned} x_0 &= 1 - x_{\max} \\ x_1 &= 0 \\ x_2 &= x_{\max} \end{aligned} \quad (25)$$

The above behavior is common for all values of x_{\max} (Figs. 10–12).

DISCUSSION

Simulations included in this article concern a typical three-phase model system composed of an amorphous phase “0,” a metastable, high-temperature solid “1” and stable, low-temperature solid “2” (Fig. 1). Thermodynamically admissible transitions in the temperature range $T < T_{01}$ include direct crystallization of the undercooled amorphous phase “0” into solid phases “1” and “2” as well as polymorphic transition of the metastable solid “1” into the stable polymorph “2.” The aim of the kinetic considerations is to define factors, which control phase composition and enable creation of the desired composition.

As evident in Figure 2 the rates (frequencies) of direct conversion of the undercooled amorphous phase, “0” \rightarrow “1” and “0” \rightarrow “2,” exhibit maxima vs. temperature. However, frequency of the polymor-

phic transition “1” \rightarrow “2” monotonically increases in the entire range of analyzed temperatures. Comparing direct transition frequencies based on sporadic nucleation with those characteristic for predetermined nucleation (Fig. 2) one can see that maximum frequencies based on predetermined nucleation are shifted to higher temperatures.

In the low temperature range, all transition frequencies, controlled by molecular mobility, are very low. For many materials, glass transition is observed. For the model discussed, all transition frequencies ν_{ij} are smaller than 10^{-5} Hz below $T = 245$ K, which would require conversion times longer than 27 h. Therefore, temperatures lower than 245 K will be excluded from our considerations. Existence of a low temperature limit of reasonably fast transitions applies to sporadically nucleated processes as well as ones based on predetermined nucleation. For the latter, the low temperature limit is shifted to higher temperatures, and the more so, the higher is concentration of sporadic nuclei, N_0^{ij} . In Figure 2, sporadically nucleated processes are compared those based on predetermined nuclei in the concentration $N_0^{ij} = 10^{12} \text{ cm}^{-3}$.

In the range of high temperatures, close to critical temperatures T_{01} and T_{02} (see Fig. 1) the respective transition rates “0” \rightarrow “1” and “0” \rightarrow “2,” are very small and tend to zero because of high thermodynamic barriers inversely proportional to the degree of undercooling. This applies to processes based on sporadic nucleation as well as those involving predetermined nuclei (Fig. 2). For our model we will assume the upper limit of direct transition rates at $T = 445$ K where the corresponding frequencies fall below 10^{-5} Hz. Unlike in low temperatures, frequencies of the polymorphic transition “1” \rightarrow “2” increase with temperature and reach relatively high values in a wide range of temperatures (Fig. 2).

Excluding the low-temperature and high-temperature regions characterized by negligible transition

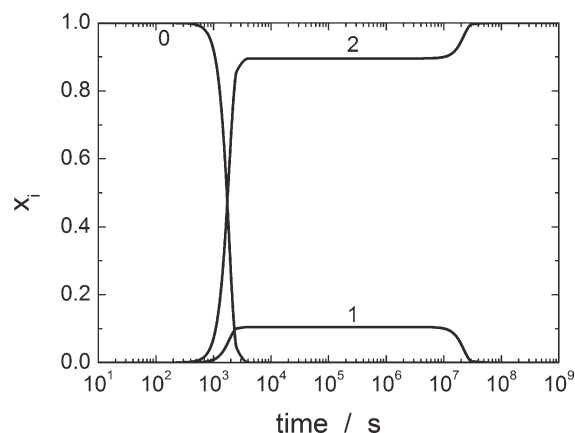


Figure 12 Development of phase composition at $T = 290$ K and maximum crystallinity, $x_{\max} = 1$.

rates, we will analyze the medium range of temperatures $245 < T < 445$ K where phase transitions proceed with reasonably high speeds. Two kinds of kinetic behavior can be distinguished.

Development of phase composition based on purely sporadic nucleation is illustrated by Figs. 3, 9, and 12. In low temperatures ($T = 290$ K; Fig. 12), phases "1" and "2" are created simultaneously from the amorphous phase and their fractions assume constant levels. After several decades of "waiting," slow polymorphic transition is switched on and phase "1" is converted into the target phase "2." With increasing temperature, the rates of direct crystallization pass maxima and fall down while the frequency v_{12}^{SPC} increases. A consequence of this is gradual contraction and disappearance of the "waiting period." In the middle ($T = 365$ K; Fig. 3) and high temperatures ($T = 400$ K; Fig. 9), phase "1" does not appear and crystallization is controlled by the direct process "0" \rightarrow "2." Slowly created small amounts of phase "1" are immediately converted into phase "2."

Effect of predetermined nuclei in the temperature $T = 365$ K will be considered. Addition of 10^{12} cm^{-3} predetermined selective nuclei effective for phase "2" speeds-up the "0" \rightarrow "2" transition by one order of magnitude (cf. Figs. 3 and 5). The same operation involving nuclei effective for phase "1" makes the latter to appear and stay for a period before it is converted by the polymorphic transition to phase "2" (cf. Figs. 3 and 4). When predetermined nuclei are universal (i.e., effective in creation phase "1" and "2") a mixture of both solid phases is obtained, fraction of phase "1" being reduced, compared to that created on the selective nuclei N_0^{01} .

Molecular constraints and limited crystallinity, x_{max} , do not affect transition frequencies, v_{ij} but reduce the resulting fractions of the solid phases "1" and "2" (Figs. 7–12).

CONCLUSIONS

Crystallization in a three-phase monotropic system consisting of an amorphous phase "0," high-temperature metastable solid phase "1" and stable polymorphic solid "2" strongly depends on temperature. In very low and very high temperatures, transition rates are negligibly small. In the middle temperature range, a mixture of solid phases is created followed

by polymorphic conversion of the metastable phase into the stable polymorph. In higher temperatures, there is no evidence of phase "1." Small amounts of the metastable phase are immediately converted into the stable phase "2."

- Addition of predetermined nuclei speeds-up individual transitions.
- Creation of the metastable solid can be stimulated by predetermined nuclei selective for this phase.
- There is no way, in which pure metastable phase "1" could be created in a monotropic system. Variable proportions between polymorphs "1" and "2" can be obtained temporarily by adjusting temperature and concentration of predetermined nuclei. The final phase composition consists of a pure solid "2" (for ideal systems, $x_{\text{max}} = 1$) and a mixture of the solid "2" and constrained, uncrystallizable amorphous phase (for $x_{\text{max}} < 1$).

References

1. Ziabicki, A. *J Chem Phys* 2005, 123, 174103.
2. Ziabicki, A.; Misztal-Faraj, B. *J Mater Res* 2011, 26, 1585.
3. Mitscherlich, E. *Ann Chim Phys* 1822, 19, 350.
4. Sajkiewicz, P.; Gradys, A.; Misztal-Faraj, B.; Ziabicki, A. *e-Polymers* 2010,124.
5. Kolmogoroff, A. N. *Izv Akad Nauk SSSR, Ser Math* 1937, 3, 353.
6. Johnson, W. A.; Mehl, R. F. *Trans AIME* 1939, 135, 416.
7. Avrami, M. *J Chem Phys* 1939, 7, 1103; *ibid.* 1940, 8, 212;1941, 9, 17.
8. Evans, U. R. *Trans Faraday Soc* 1945, 41, 365.
9. Varga, J.; Mudra, I.; Gottfried, W. E. *J Appl Polym Sci* 1999, 74, 2357.
10. Supaphol, P.; Spruiell, J. E. *J Appl Polym Sci* 2000, 75, 337.
11. Alfonso, G. C.; Valenti, B.; Pedemonte, E. *Makromol Chem* 1974, 175, 1917.
12. Roe, R. J.; Smith, K. J., Jr.; Krigbaum, W. R. *J Chem Phys* 1961, 35, 1306.
13. Des Cloizeaux, J. *J Polym Sci A2* 1970, 8, 1773.
14. Elyashevich, G. K.; Baranov, W. G.; Frenkel, S. Ya. *Fizika Tverdogo Tela* 1974, 16, 2075.
15. Cheng, S. Z. D. *Phase Transitions in Polymers*; Elsevier: Amsterdam, 2008; p 97.
16. Albrecht, T.; Strobl, G. R. *Macromolecules* 1995, 28, 5827.
17. Strobl, G. R.; Schneider, M. J.; Voigt-Martin, I. G. *J Polym Sci* 1980, 18, 1361.
18. Mai, Y.; Zhou, Y.; Yan, D.; Hou, J. *New J Phys* 2005, 7, 42.