



Transient nucleation in isothermal crystallization of poly(3-hydroxybutyrate)

Paweł Sajkiewicz,^{1*} Maria Laura Di Lorenzo,² Arkadiusz Gradys¹

^{1*}Institute of Fundamental Technological Research, Polish Academy of Sciences, Swietokrzyska 21, 00-049 Warsaw, Poland; fax: +48-22-8269815; e-mail: Pawel.Sajkiewicz@ippt.gov.pl

²Institute of Chemistry and Technology of Polymers (CNR) – c/o Compresorio Olivetti, Via Campi Flegrei, 34-80078 Pozzuoli (NA), Italy; fax: +39-081-8675059; e-mail: marialaura.dilorenzo@ictp.cnr.it

(Received: 05 November, 2008; published: 05 July, 2009)

Abstract: The time dependence of nucleation rate in isothermal crystallization of poly(3-hydroxybutyrate) was experimentally shown, both in heterogeneous and homogeneous nucleation. The time dependence of nucleation rate is one of the important limitations for the applicability of the simplified form of Kolmogoroff-Avrami-Evans model with time independent kinetic characteristics. The presented results are interpreted in terms of non-steady-state cluster size distribution underlying transient nature of nucleation. The relaxation time needed for reaching a steady-state cluster size distribution and thus steady-state nucleation rate is relatively long, exceeding the time of exhaustion of heterogeneities. The relaxation time estimated from homogeneous process was tens of seconds in the temperature range between 83 and 120 °C. Application of Arrhenius law allows estimation of relaxation time in broader temperature range, showing an increase of relaxation time with decreasing temperature.

Introduction

The most general model for the analysis of crystallization kinetics was formulated originally by Kolmogoroff [1], Avrami [2], Johnson and Mehl [3] and Evans [4] (KAE model). The degree of transformation, $x(t)$ is determined by the volume of phantom crystals, nucleated and grown during the period $(0, t)$

$$x(t) = 1 - \exp[-E(t)] \quad (1)$$

If the growth is isotropic and proceeds independently in m dimensions:

$$E(t) = \text{const.} N_0 \left[\int_0^t \dot{R}(z) dz \right]^m + \text{const.} \int_0^t \dot{N}(s) \left[\int_s^t \dot{R}(z) dz \right]^m ds \quad (2)$$

where N_0 is number of predetermined nuclei present in unit volume at the instant $t = 0$, while $\dot{N}$, and $\dot{R}$ are thermal nucleation and linear growth rate, respectively. Assumption that the nucleation and growth rates are controlled by temperature only and are independent of time, results in reduction of eq. (2) to:

$$E(t) = \text{const.} (\dot{R})^m \left[N_0 t^m + \dot{N} t^{m+1} / (m+1) \right] \quad (3)$$

that can be written in more general form:

$$E(t) = kt^n \quad (4)$$

$$1 - x(t) = \exp(-kt^n) \quad (5)$$

where k is the crystallization rate constant, containing both nucleation and growth rate, and n is a constant exponent, depending on the type of nucleation and growth.

Eq. (5) is sometimes written in a different form:

$$1 - x(t) = \exp[-(Kt)^n] \quad (6)$$

$$\text{where } K = k^{1/n} \quad (7)$$

where the dimensionality of crystallization rate constant, K , is $1/t$, being independent of the exponent n .

Eq. (5) or (6), commonly called Avrami equation, in contrast to general KAE model, is a relatively simple model being a convenient way for the analysis of the kinetics of isothermal crystallization. It is usually written in double logarithmic form:

$$\log[-\ln(1 - x(t))] = n \log t + \log k \quad (8)$$

The exponent n , that provides indications on the mechanism of nucleation and of geometry of crystal growth, is usually determined as the slope of the plot of $\log[-\ln(1-x)]$ vs. $\log(t)$, which is expected to be linear. The crystallization rate constant, k , is obtained from the abscissa of the double logarithmic plot, or from the characteristic time, $t_{1/2}$, at which $x = 1/2$. However there are a lot of published results indicating the difficulties in fitting experimental data of isothermal crystallization to the simplified form of KAE model with time independent kinetic characteristics. The careful analysis of the experimental $\log[-\ln(1-x)]$ vs. $\log(t)$ for various polymers shows more or less non-linear character [5-13]. Such non-linearity was also reported for isothermal crystallization of deformed copper [14]. The non-linearity of the plot of $\log[-\ln(1-x)]$ vs. $\log(t)$ at the late stage of crystallization is due to inapplicability of the KAE model to the process of secondary crystallization, which often occurs in polymers. The non-linearity of the plot of $\log[-\ln(1-x)]$ vs. $\log(t)$ observed in the range of primary crystallization is commonly ignored or interpreted by a change of nucleation mechanism (heterogeneous to homogeneous) or geometry of growth, resulting in a change of the exponent n during crystallization. It will be shown in this contribution that non-linearity of Avrami analysis is to be linked to the non-steady-state character of nucleation of polymeric crystals.

The nucleation process is the production of nuclei with critical size occurring from subcritical clusters and thus strongly related to distribution of cluster sizes. Practically all models applied for the analysis of crystallization kinetics assume that the cluster size distribution approaches steady-state for actual temperature instantaneously, resulting in a time-independent nucleation rate. In many cases, however, the change of external conditions during phase formation is so fast, that the steady-state density cannot be maintained, resulting in a time-dependent, or transient, nucleation rate. Transient nucleation rates have been reported so far for vapor condensation [15], crystallization of undercooled liquids [16], as well as in various glass forming systems, like metallic [17] and silicate glasses [18-22], or glass-ceramic materials [23]. In the case of polymers with large and less mobile crystallizing elements, it is expected that the chain rearrangements are so slow that even at relatively slow

changes of external conditions, cluster size distribution function approaches steady-state regime for apparent conditions not instantaneously but with some time lag, which can be relatively long. In such a case the rate of crystallization depends not only on the actual temperature but also on time. It has implications not only for non-isothermal processes but also in isothermal crystallization when the material is transferred relatively fast from amorphous state to constant temperature characterized by particular cluster size distribution function. An attempt to investigate a transient nature of nucleation of polymers was performed by Dobrev et al. for poly(ethylene terephthalate) [24].

According to Ziabicki [25-27] cluster size distribution, $\rho(v,t)$, in the crystallization conditions has a form with a simple material characteristic, relaxation time τ

$$\rho(v,t) = \rho_{st} + (\rho_0 - \rho_{st}) e^{-t/\tau} \quad (9)$$

where ρ_{st} is steady-state distribution at crystallization temperature and ρ_0 is initial distribution, transferred from previous conditions. Consequently, for isothermal conditions, time-dependent nucleation rate, $\dot{N}(t,T)$, and crystallization rate, $K(t,T)$, are written as:

$$\dot{N}(t,T) = \dot{N}_{st}(T) + \left(\dot{N}_0(t,T) - \dot{N}_{st}(T) \right) e^{-t/\tau} \quad (10)$$

$$K(t,T) = K_{st}(T) + \left(K_0(t,T) - K_{st}(T) \right) e^{-t/\tau} \quad (11)$$

where $\dot{N}_{st}(T)$ and $K_{st}(T)$ is the steady-state (saturation) nucleation and crystallization rate, respectively approached through a monotonical increase of the rate starting from $\dot{N}_0(t,T)$ and $K_0(t,T)$ values. Such relaxation assumption introduced by Ziabicki has been inspired by the theory of non-steady state nucleation rate formulated by Zeldovich [28, 29], Frenkel [30], Collins [31], and Kaschchiev [32], followed then by other treatments [33].

The aim of the present work is to investigate quantitatively the transient nature of nucleation in isothermal crystallization of poly(3-hydroxybutyrate) (PHB) from the melt. This led to estimation of steady-state nucleation rate and relaxation time for PHB.

Results and discussion

The analysis by optical microscopy clearly shows that crystallization of PHB starts from a few nuclei appearing very early with a subsequent shorter or longer time gap preceding further nucleation. Fig. 1 presents a typical plot of the number of spherulites as a function of time during crystallization at 92 °C, while Fig. 2 the corresponding morphology at various times of crystallization.

It is seen that the first spherulites nucleate even before approaching of constant temperature (time < 0). The most probable explanation is that the early spherulites nucleate heterogeneously, even during cooling to T_c , while the spherulites appearing after the time gap are formed homogeneously. Thus, PHB provides excellent situation where heterogeneous nucleation is limited and well separated from the homogeneous process, which allows quantitative analysis of both processes.

The measurements of the radius of all registered spherulites on the sequences of micrographs show that the growth rate of each spherulite is constant until impingement occurs. Fig. 3 illustrates typical time dependencies of the radius of spherulites during crystallization at 84 °C.

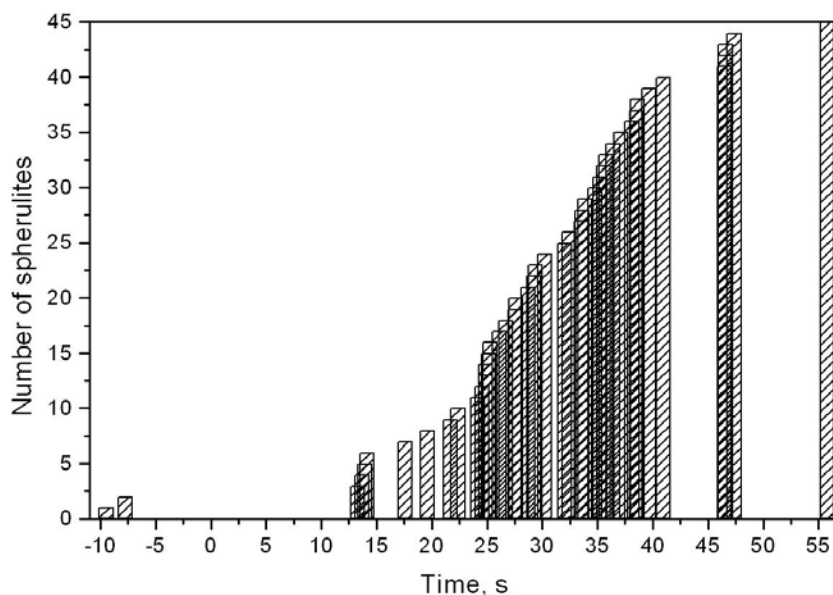


Fig. 1. Number of shperulites vs. time during crystallization at 92 °C.

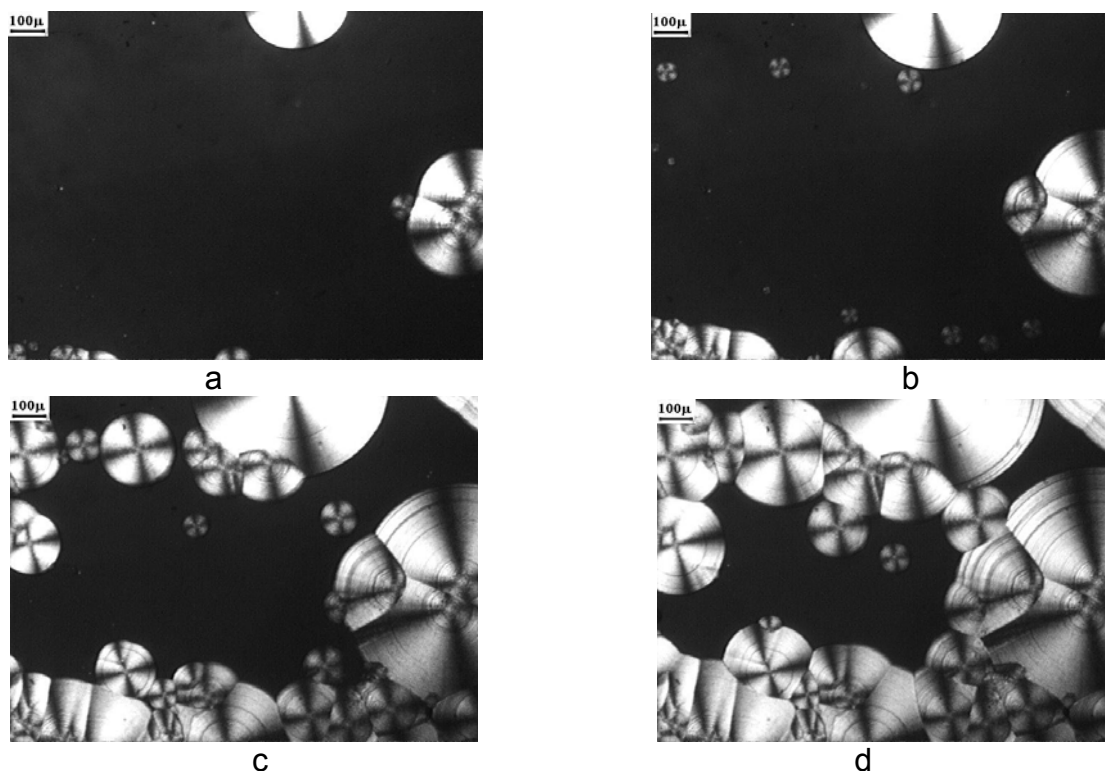


Fig. 2. Optical micrograph (crossed polars) registered after 20 (a), 30 (b), 40 (c), and 50 (d) seconds of crystallization at 92 °C.

The moment of nucleation of each spherulite was determined from linear extrapolation of the dependence of the radius vs. time to the zero radius. Fig. 4 presents a typical plot of the number of spherulitic nuclei appearing in the field of observation vs. time of crystallization, while Fig. 5 shows the corresponding nucleation density obtained by division of the number of spherulites by the actual volume of amorphous phase.

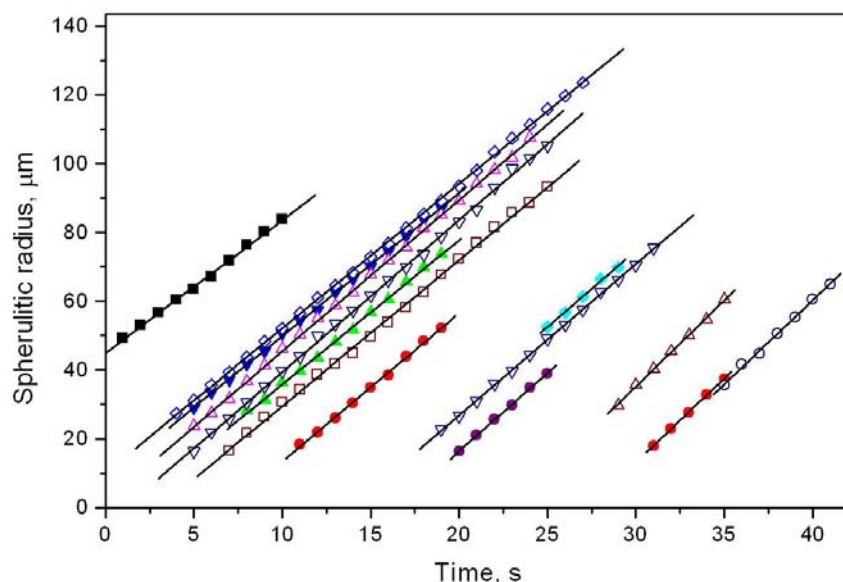


Fig. 3. Radius of PHB spherulites vs. time upon isothermal crystallization at 84 °C.

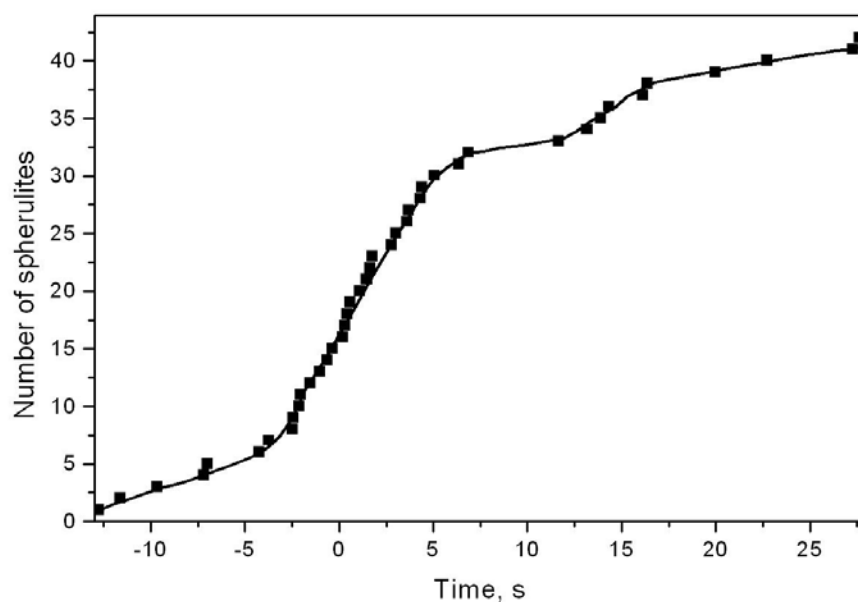


Fig. 4. Number of all spherulitic nucleus appearing in the field of observation vs. time of crystallization at 84 °C.

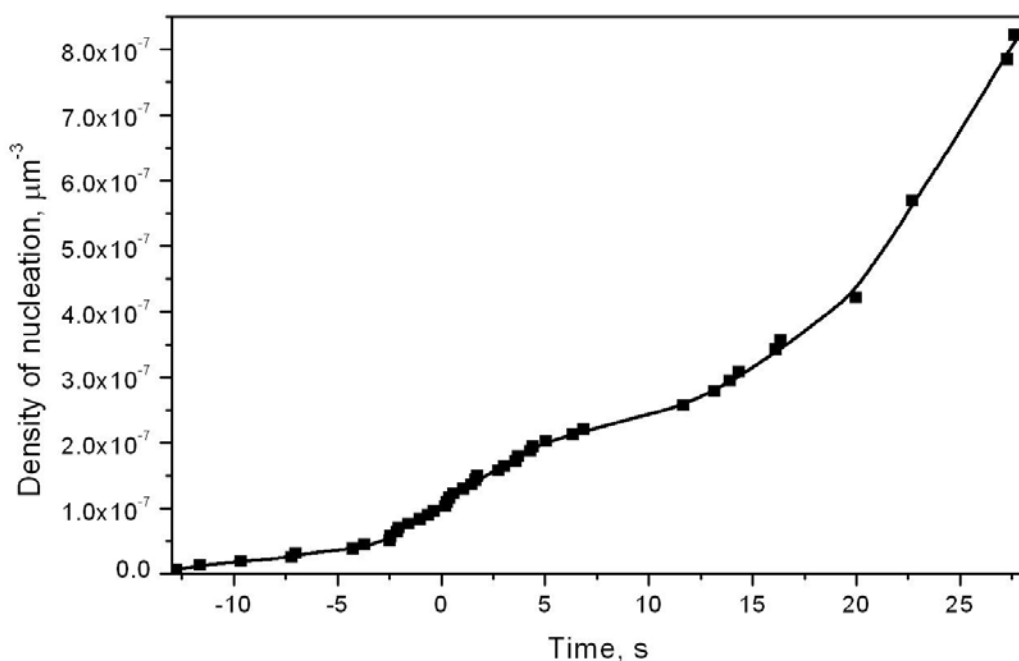


Fig. 5. Density of nucleation during crystallization at 84 °C.

The dependence of nucleation density on time presented in Fig. 5 is typical for all investigated temperatures, with early appearing heterogeneous nuclei (even before approaching of constant temperature, that is seen as time below 0), followed by a sizeable increase of the number of growing crystallites with time, due to the onset of homogeneous nucleation. Time differentiation of the plot of nucleation density leads to determination of the nucleation rate per unit volume of material. Fig. 6 shows the plots of nucleation rate vs. time of isothermal crystallization for a few selected temperatures.

It is evident from Fig. 6 that nucleation rate is not constant but depends strongly on time. There is sigmoidal increase of homogeneous nucleation rate to more or less constant value (line A in Fig. 6 for crystallization at 84 °C), with an additional maximum at low crystallization time related to heterogeneous nucleation (line B in Fig. 6). The end value of homogeneous nucleation rate is the steady-state nucleation rate, corresponding to the steady-state cluster size distribution. It may be argued that the levelling off homogeneous nucleation rate may be caused by termination of the phase transition, but in such a case one would expect a sudden decrease of the rate of appearing of new nuclei, rather than the attainment of a constant value. The increase of nucleation rate to the plateau value at the end of crystallization is caused by a delay in approaching of steady-state cluster size distribution at each temperature. This delay is linked to the low mobility of polymer molecules: after reaching the isothermal step, polymer chains still remember previous cluster distributions, inherited from higher temperatures, i.e. from the side of lower driving free energy. Cluster size distributions inherited from higher temperatures contain much smaller clusters compared to the steady-state cluster size distribution at the temperature of crystallization. This situation leads to transient nucleation rates that are lower than the steady-state rate. The increase of nucleation rate is faster for

heterogeneous nucleation (line B in Fig. 6), because of the smaller energy barrier than in homogeneous process. Contrary to the common assumption, our results demonstrate that heterogeneous nucleation is not an instant process, just because of transient process of approaching of steady-state distribution of clusters. As it is seen from line A in Fig. 6, the steady-state cluster size distribution is approached at the end of isothermal crystallization, and the steady-state nucleation rate for heterogeneous process is not reached because of the exhaustion of heterogeneities. The exhaustion of heterogeneities is manifested by approaching of the local maximum (line B in Fig. 6), followed by a decrease of the nucleation rate to the level characteristic for homogeneous nucleation.

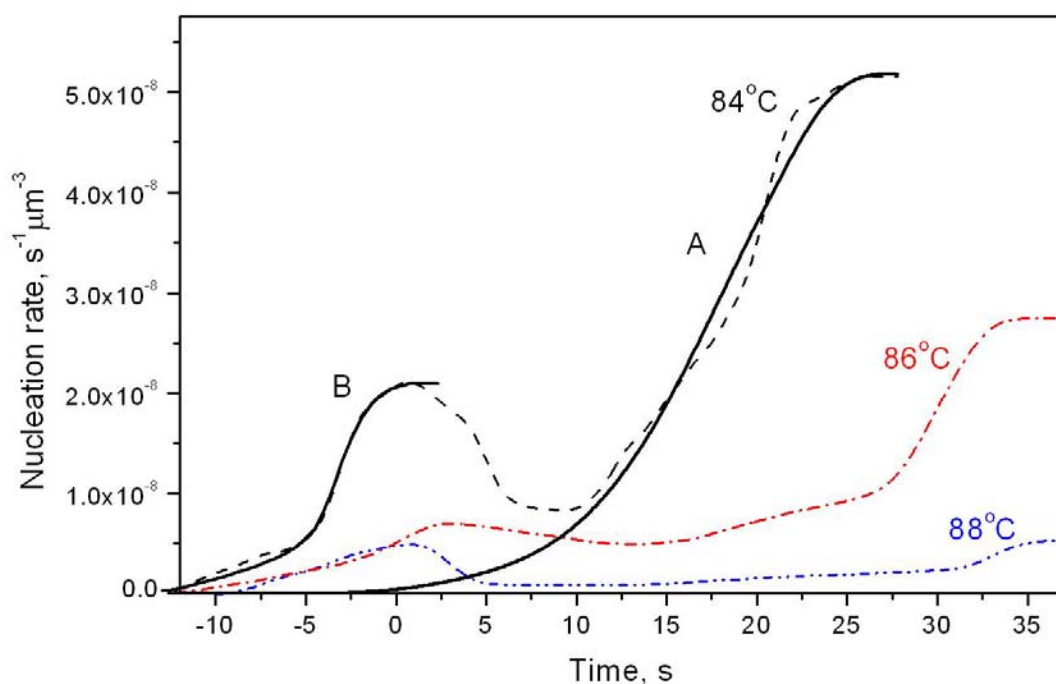


Fig. 6. Nucleation rate during crystallization at few temperatures (indicated). The dotted, dashed and dash-dotted lines represent the experimental data, and the solid lines are the estimated trends of homogeneous (line A) and heterogeneous (line B) nucleation rates for crystallization at 84 °C.

The parameters of transient nucleation in isothermal regime were estimated according to the procedure proposed by Ziabicki et al [26-27]. He proposed some experimental procedures for quantitative determination of time-dependent effects both from isothermal and non-isothermal experiments.

Summarizing, two main parameters that describe the transient character of nucleation are the steady-state rate reached at relatively long time and the relaxation time that is related to the delay in approaching the steady-state value. The steady-state cluster size distribution and the related nucleation rate were not reached in the heterogeneous process because of earlier exhaustion of nuclei, due to the high purity of PHB, therefore we have limited our estimation to homogeneous nucleation. The steady-state rate was estimated as a saturation value at the end of crystallization,

while the relaxation time was obtained from the inflexion point, t_{infl} , $\tau = 1.107336 t_{infl}$, as it was derived in Ref. [27], and results are illustrated in Figures 7 and 8.

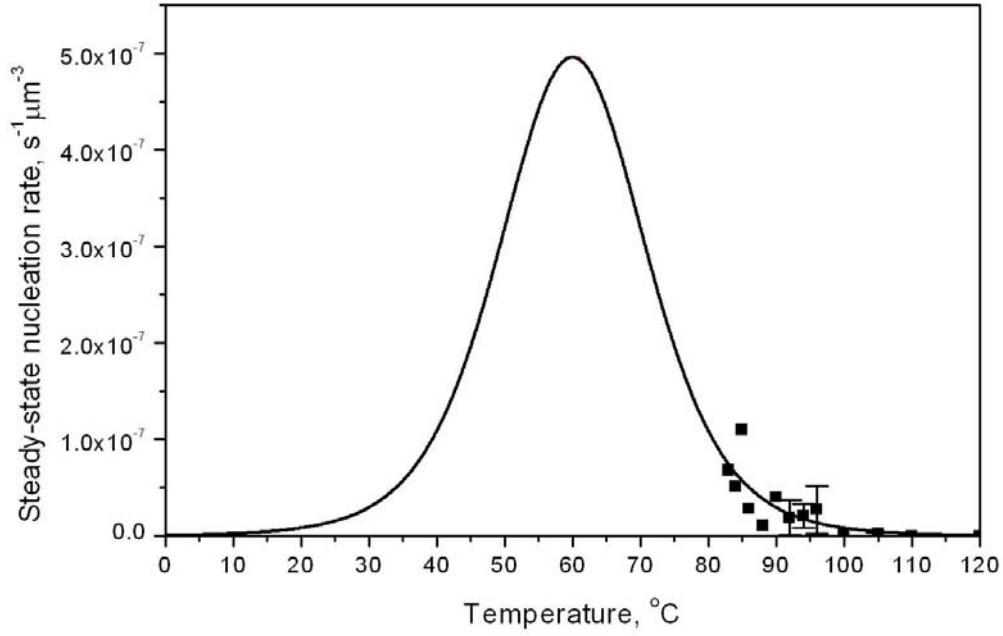


Fig. 7. Steady-state nucleation rate vs. temperature of isothermal crystallization.

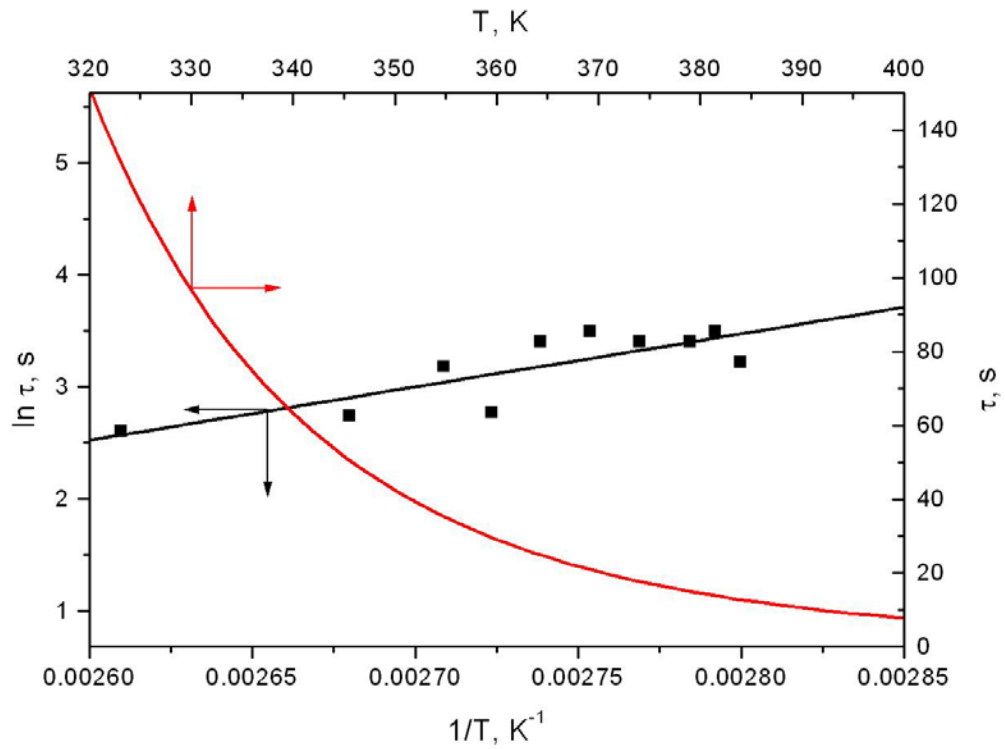


Fig. 8. Linear approximation of the plot of $\ln \tau$ vs. $1/T$ and extrapolated relaxation time, τ , vs. temperature in a wide range of temperatures.

The temperature dependence of the steady-state nucleation rate, presented in Figure 7, was fitted with a Gauss function, assuming the position of the peak at 60°C. This temperature was found previously as the temperature of maximum nucleation rate for PHB [34].

The important point for estimation of relaxation times is the choice of zero time. In the case of higher nucleation rates at lower temperatures, where heterogeneous and homogeneous nucleation can overlap, the starting point for homogeneous nucleation was determined using Boltzmann fitting applied for the range of nucleation after exhaustion of heterogeneous nuclei. In the case of lower nucleation rates at higher temperatures, the start of homogeneous nucleation is usually separated by long time gap from heterogeneous process. Although the scattering of relaxation times estimated from our experiments is relatively large, the plot of τ vs. T , illustrated in Figure 8, probes a tendency to increase of relaxation time with decreasing temperature of crystallization.

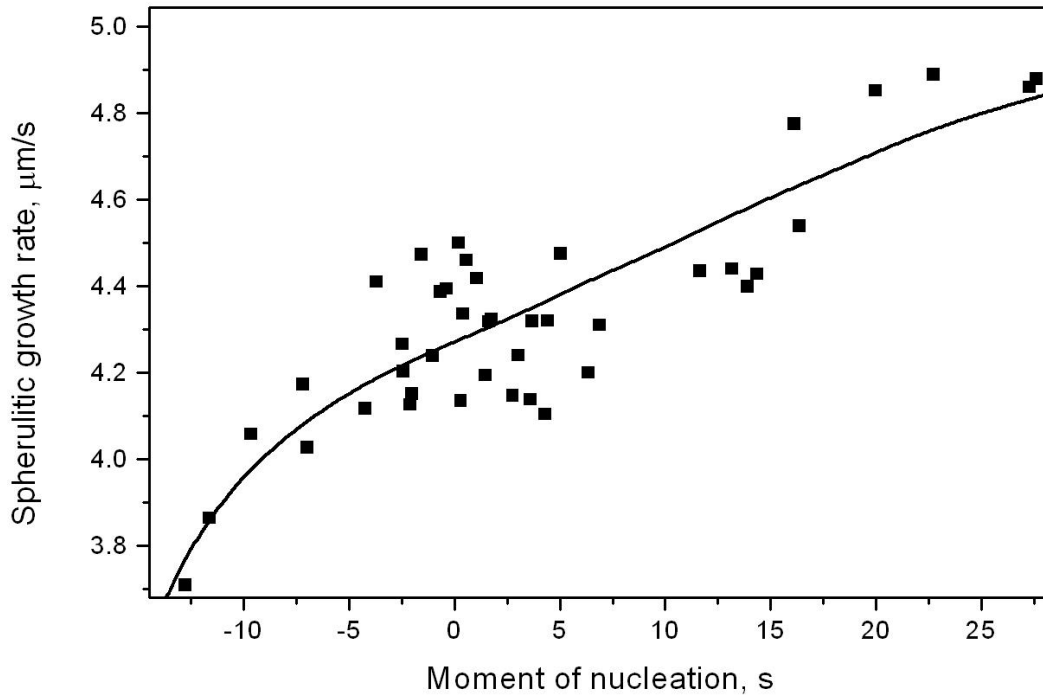


Fig. 9. Growth rate of spherulites as a function of the moment of nucleation for crystallization at 84 °C.

This trend is consistent with the theoretical predictions detailed in Ref. [27]. The temperature dependence of relaxation time is expected to be described by Arrhenius law:

$$\tau(T) = \tau_0 \exp[E_a / RT] \quad (12)$$

with the activation energy, E_a , and the pre-exponential factor, τ_0 . The activation energy estimated from the slope of the linear approximation of the experimental results of $\ln \tau$ vs. $1/T$ (Fig. 8) is 39 kJ/mole, which is the same order of magnitude as

activation energy for self-diffusion in polymers. For instance, the activation energy of the self-diffusion in polyethylene measured experimentally is 19.5 kJ/mole [35]. Linear approximation of the plot of $\ln(\tau)$ vs. $1/T$, allows estimation of relaxation times vs. temperature in a wide range of temperatures (Fig. 8).

Additional results, which can be also interpreted in terms of relaxation of cluster size distribution, were provided by the analysis of the growth rate of spherulites. As mentioned above, the growth rate of each particular spherulite is constant until impingement (see Fig. 3). On the other hand, we observed that the growth rate of each particular spherulite is the higher the later it was nucleated. This trend is exemplified in Figure 9 for crystallization at 84°C. Similar data were gained also at the other T_c s.

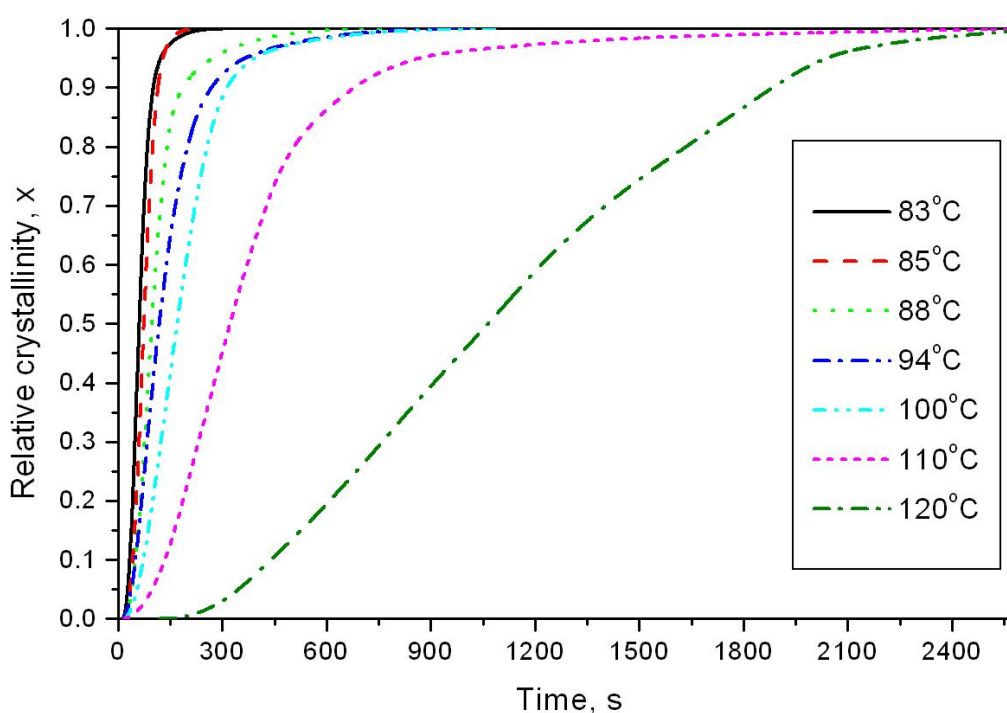


Fig. 10. Relative crystallinity, x , from DSC vs. time of isothermal crystallization.

We interpret this behavior as a change of cluster distribution with time toward steady-state value underlying in this case secondary nucleation. Approaching of steady-state nucleation rate occurs from cluster size distributions inherited from higher temperatures, containing thus relatively large number of small clusters. This situation leads to transient nucleation, also secondary one, with lower rate than the steady-state value approached at relatively long time. The observation that the growth rate of a particular spherulite remains constant can be explained by the fact that crystal growth occurs from the mother phase in the closest neighborhood around the spherulite, because of space limited molecular diffusion. It is expected that the local steady-state cluster size distribution in a nearest-neighbor shell is approached very fast because it is strongly affected by the growing spherulite. On the other hand, the next spherulite that nucleates later is sensitive to a global cluster size distribution,

tending to its steady-state. Such a new born spherulite meets another global apparent cluster size distribution, resulting in a different (higher) growth rate. Again, its growth rate is constant because of sensitivity to the local value of cluster size distribution.

Complementary results were obtained by DSC. Fig. 10 illustrates the changes of relative crystallinity vs. time for a few temperatures of crystallization.

Fig. 11 shows double logarithmic plots $\log[-\ln(1-x)]$ vs. $\log(t-t_i)$, where t_i is the induction time.

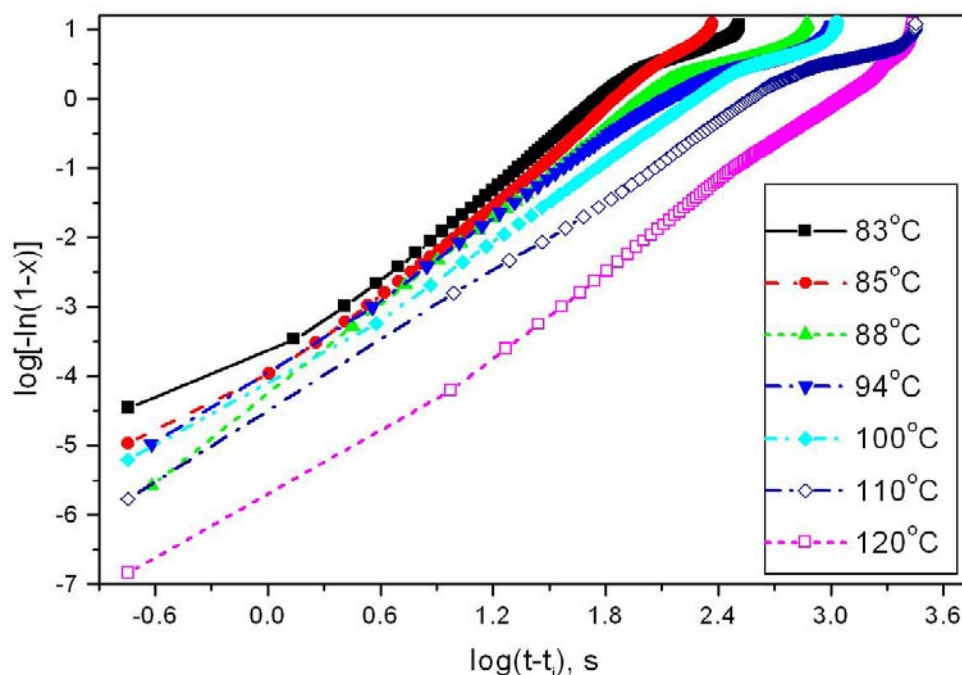


Fig. 11. Double logarithmic Avrami plot determined from DSC data for several temperatures of isothermal crystallization.

It is evident that the experimental double logarithmic Avrami plot is non-linear even when the induction time is subtracted, i.e. $\log(t-t_i)$ is used instead of time measured from the moment of approaching of isothermal step (Fig. 11). Strong non-linearity at the end of crystallization is caused by inapplicability of the KAE model to the secondary crystallization. The non-linearity of the double logarithmic plot occurs also in the range of primary crystallization. Non-linearity during primary crystallization is commonly ascribed to a change of the exponent n due to a variation in growth geometry, which was not observed by optical microscopy analysis during PHB crystallization. Both types of nucleation, heterogeneous and homogeneous, occur sporadically and the geometry of growth is the same irrespective of the type of nucleation. The non-linearity in the range of primary crystallization is, instead, related to the time dependence of nucleation rate. Considering this fact, crystallization rate, K , was determined using more general form of eq. (6), allowing time dependence of crystallization rate:

$$1 - x(t) = \exp \left[- \left(\int_0^t K(T, t') dt' \right)^n \right] \quad (13)$$

Rearrangement of eq. 13 allows determination of the actual value of crystallization rate, K , as a function of time:

$$K(t) = \frac{d \left\{ [-\ln(1-x(t))]^{1/n} \right\}}{dt} \quad (14)$$

This procedure has been applied previously int. al. in [26, 27]. It needs assumption of the exponent n . Although the plot of $\log[-\ln(1-x)]$ vs. $\log(t-t_i)$ is non-linear because it is loaded with the time dependence of crystallization rate as well as with secondary crystallization, it can be used for a rough estimation of the exponent n . The average value of the exponent n determined from the middle range of crystallization was equal to 2.

Fig. 12 shows the crystallization rate, K , vs time in the range of primary crystallization determined using eq. (14) with $n = 2$.

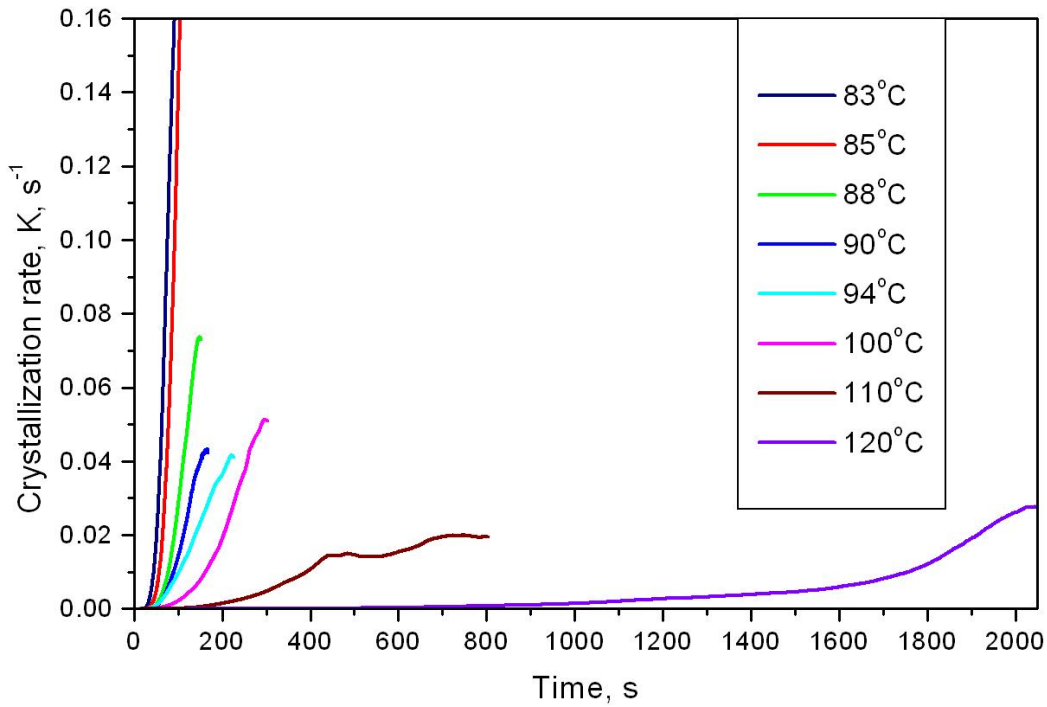


Fig. 12. Crystallization rate, K , vs. time at the indicated temperatures of isothermal crystallization.

It is evident that the crystallization rate K is indeed not constant but depends strongly on time. It increases with time of crystallization, following time dependence of nucleation rate.

Conclusions

Our experimental results obtained for poly(3-hydroxybutyrate) clearly show that the nucleation rate in isothermal crystallization of polymers is not constant, but depends on time. The time dependence of nucleation rate explains the problems with proper description of kinetic data using simplified form of Kolmogoroff-Avrami-Evans model with time independent kinetic characteristics that are often reported in literature. The treatment of nucleation as a steady-state process with a time-independent rate should be valid only for low molecular weight materials with small and mobile crystallizing elements (atoms), assuming additionally that the change of external conditions is relatively slow. The simplified form of Kolmogoroff-Avrami-Evans model with time independent kinetic characteristics can thus be used only as a very rough approximation of experimental data of polymer crystallization.

The interpretation of the time dependence of nucleation rate is based on the concept of transient time, which is needed for reaching the steady-state size distribution of clusters after changing of external conditions. In the case of isothermal crystallization, relatively fast cooling or heating usually precedes the constant temperature step. Time delay in approaching of steady-state cluster distribution implies significant time dependence for the rate of nucleation. Before reaching the steady-state value of nucleation rate, the apparent value of nucleation rate deviates from the steady-state rate. The presented data indicate that the relaxation time in approaching of steady-state cluster size distribution is relatively long, which results in delay in attainment of steady-state. In the case of heterogeneous nucleation, that is faster than homogeneous one because of the lower energy barrier for formation of critical nucleus, steady-state nucleation rate is not reached because of earlier exhaustion of heterogeneous centers for nucleation. In the case of homogeneous nucleation the end value is taken as the steady-state rate. The relaxation time estimated from homogeneous process using the procedure proposed in [27] is of the order of tens of seconds in the temperature range of investigated processes. Application of Arrhenius law allows estimation of relaxation time in broader temperature range, showing an increase of relaxation time with decreasing temperature.

Two other experimental facts observed in isothermal crystallization of poly(3-hydroxybutyrate), namely the sporadic nature of heterogeneous nucleation as well as the dependence of spherulitic growth rate on the moment of its nucleation, can also be interpreted by the non-steady-state cluster distribution during isothermal crystallization. The growth rate of each particular spherulite is constant until impingement, but it is determined by the moment of nucleation being higher leading to later nucleation. Also this time dependence is most probably due to a change of cluster distribution toward steady-state value. The constant value of the growth rate of each particular spherulite is due to its sensitivity to the very local value of cluster size distribution within nearest-neighbor shell.

Experimental part

Materials

Poly(3-hydroxybutyrate) (PHB) with molecular mass 435,000 Da was purchased from Aldrich Chemical Company, Inc. PHB, commercially produced by a batch fermentation process, is extremely pure material. High purity of PHB limits seriously heterogeneous nucleation providing excellent conditions for the analysis of homogeneous nucleation that is rather a rare case in polymers. It gives the possibility

to perform clear experiments allowing quantitative estimation of the time-dependent effects in polymer crystallization.

PHB foils were prepared by compression-molding with a Carver Laboratory Press at a temperature of 200 °C, first without any pressure for 2 minutes, to allow complete melting, then with a load of 0.5 ton for 2 min. Cooling to the room temperature was performed by means of cold water circulating in the plates of the press. Before pressing, PHB was dried under vacuum for 16 h.

Methods

Kinetics of crystallization of PHB was investigated in isothermal conditions. Two methods of investigations were applied – optical microscopy and differential scanning calorimetry, DSC, providing complementary information on the kinetics of transition. The use of optical microscope allows separate determination of nucleation and growth rate, while DSC provides information on the global kinetics of crystallization.

Optical investigations were performed with a Zeiss polarizing optical microscope equipped with a Linkam TMHS 600 hot stage and a Linkam CS 196 unit for fast cooling with liquid nitrogen. The sequences of photomicrographs were taken using a JVC TK-1085E Video Camera coupled with the software Image-Pro Plus 3.0. Samples were cooled from the melt state (193 °C, 3 min) to the constant temperature (T_c) in the range between 83 °C and 120 °C. Cooling rate to the isothermal step was 70 °C/min. A reliable determination of the moment of nucleation of each spherulite was performed by measurements of radius of particular spherulite on a sequence of micrographs and subsequent extrapolation to the zero radius. The nucleation rate was then determined in relation to the actual volume of amorphous phase outside the spherulites, an effective space for nucleation. The apparent volume of amorphous phase was estimated from the known thickness of a sample and the actual area of amorphous phase determined from registered micrographs.

In the case of DSC method, Perkin-Elmer Pyris 1 DSC equipped with Intracooler 2P was used. The instrument was calibrated in temperature with standard indium and zinc references, and in heat flow rate with indium. PHB film samples weighing c.a. 4 mg were melted at the same conditions as in the case of optical investigations, i.e. 193 °C for 3 min and then cooled at 70 °C/min to crystallization temperature, where the heat flow was registered as a function of time. The starting time at each T_c was determined from the temperature profile as an intercept of linear extrapolations of the cooling and the isothermal stages. Evaluation of the crystallization heat flow time-dependence was obtained with a fitting procedure using second order exponential decay function to simulate thermal equilibrating effect.

Taking into account high sensitivity of PHB to the thermal degradation, the important point of the experiments was to choose properly conditions of melting before crystallization. The results of additional experiments described elsewhere [36] show that melting at 193 °C for 3 minutes is sufficient to melt the polymer completely before crystallization from the one side and to minimize degradation of material from the other one. This temperature is close to the equilibrium melting temperature, T_m^0 , determined experimentally by Al-Salah (190 °C) [37], Avella et al. (194 °C) [38] and by Organ et al. [39], showing the molecular dependence of the equilibrium melting point, with $T_m^0=186$ °C for a PHB with molecular weight ca. 100,000 Da. Few authors have applied similar conditions of melting (190 °C for 5 minutes [40]), claiming that they are sufficient for destroying of previous thermal history. Our results showed that the

molecular weight, M_v , after compression-molding at 200 °C and then melting at 193 °C for 3 minutes was around 120,000 Da [36]. Molecular degradation in the range of crystallization temperatures (between 83 °C and 120 °C) can be neglected. According to Janigova et al. [41] only marginal degradation can occur below 170 °C.

Acknowledgements

Part of the investigations was performed at the Institute of Chemistry and Technology of Polymers (CNR) in Pozzuoli, Italy, in the frame of COST Action P12 "Structuring of Polymers" as the Short Term Scientific Mission COST-STSM-P12-02979. Early investigations were performed in the frame of Scientific and Technological Cooperation between the Italian Republic and the Republic of Poland for the years 2004 – 2006 as well as CNR Short Term Mobility Program.

References

- [1] Kolmogoroff, A.N. *Izvestija Akad. Nauk USSR, Ser. Math.* **1937**, *1*, 355 (in Russian).
- [2] Avrami, M. *J.Chem. Phys.* **1939**, *7*, 1103; *ibid*, **1940**, *8*, 212; *ibid*, **1941**, *9*, 177.
- [3] Johnson, W.A.; Mehl, R.F. *Trans. Am. Inst. Min. Met. Engs.* **1939**, *135*, 416.
- [4] Evans, U.R. *Trans. Faraday Soc.* **1945**, *41*, 365.
- [5] Gauthier, C.; Chailau, J.F.; Chauchard, J. *Polym.Polym.Compos.* **1993**, *1*, 309A.
- [6] Cebe, P.; Hong, S.D. *Polymer*, **1986**, *27*, 1183.
- [7] Tan, S.; Su, A.; Li, W.; Zhou, E. *J.Polym.Sci., Polym. Phys.* **2000**, *38*, 53.
- [8] Hong, S.M.; Kim, B.C.; Kim, K.U.; Chung, I.J. *Polymer J.* **1992**, *24*, 727.
- [9] Morita, K.; Masuko, T. *Sen-i Gakkaishi* **1993**, *49*, 609.
- [10] Mubarak, Y.; Harkin-Jones, E.M.A.; Martin, P.J.; Ahmad M. *Polymer* **2001**, *42*, 3171.
- [11] Mucha, M.; Marszałek, J.; Fidrych, A. *Polymer* **2000**, *41*, 4137.
- [12] Lu, X.F.; Hay, J.N. *Polymer* **2001**, *42*, 9423.
- [13] Li, Y.; Zhu, X.; Yan, D. *Polym.Eng.Sci.* **2000**, *40*, 1989.
- [14] Krüger, P. *J.Phys.Chem.Solids* **1993**, *54*, 1549.
- [15] Schelling, F.J.; Reiss, H.J. *J.Chem.Phys.* **1981**, *74*, 3527.
- [16] Gutzow, I. *Contemp. Phys.* **1980**, *21*, 243.
- [17] Buchwitz, M.; Adlwarth-Dieball, R.; Ryder, P.L. *Acta Metall. Mater.* **1983**, *41*, 1885.
- [18] Kelton, K.F. *Materials Sci. Eng.* **1997**, *A226-228*, 142.
- [19] Ray, C.S.; Day D.E.; Huang, W.; Narayan, K.L.; Cull, T.S.; Kelton, K.F. *J.Non-Crystal.Solids* **1996**, *204*, 1.
- [20] Fokin, V.M.; Kalinina, A.M.; Filipovich, V.N.; *J.Cryst.Growth*, **1981**, *52*, 115
- [21] Narayan, K.L.; Kelton, K.F. *Acta Materialia* **1998**, *46*, 3159.
- [22] James, P.F. *J. Non-Cryst. Solids* **1985**, *73*, 517.
- [23] Gutzow, I.; Zlateva, E.; Alyakov, S.; Kovatscheva, T. *J. Mater. Sci.* **1977**, *12*, 1190.
- [24] Dobрева, A.; Stoyanov, A.; Tzuparska, S.; Gutzow, I. *Thermochimica Acta* **1996**, *280/281*, 127.
- [25] Ziabicki, A.; Alfonso, G.C. *Colloid Polym. Sci.* **1994**, *272*, 1027.
- [26] Ziabicki, A. *Colloid Polym.Sci.* **1996**, *274*, 705.
- [27] Ziabicki, A.; Sajkiewicz, P. *Colloid & Polymer Sci.* **1998**, *276*, 680.
- [28] Zeldovich, B.J. *Zh. Eksp. Teor. Fiz.* (USSR) **1942**, *12*, 525 (in Russian).
- [29] Zeldovich, B.J. *Acta Physicochim. USSR* **1943**, *18*, 1.

- [30] Frenkel, J. *Kinetic Theory of Liquids*, Oxford University Press, Clarendon, Oxford **1946**.
- [31] Collins, F.C. Z. *Elektrochem.* **1955**, 59, 404.
- [32] Kashchiev, D.; *Surf. Sci.* **1969**, 1, 209.
- [33] Schneidman, V.A.; Weinberg, M.C. *J. Non-Cryst. Solids* **1996**, 194, 145.
- [34] Organ, S.J.; Barham, P.J. *J. Mater Sci* **1991**, 26, 1368.
- [35] Fleischer, G. *Polymer Bull.* **1984**, 11, 75.
- [36] Di Lorenzo, M.L; Sajkiewicz, P.; Gradys, A.; La Pietra P. *e-Polymers*, accepted **2009**.
- [37] Al-Salah, H. A. *Polymer Bulletin* **1998**, 41, 593.
- [38] Avella, M.; Martuscelli, E. *Polymer* **1989**, 29, 1731.
- [39] Organ. S.J.; Barham, P.J. *Polymer* **1993**, 34, 2169.
- [40] Gunaratne, L.M/W/K.; Shanks, R.A.; Amarasinghe, G. *Thermochimica Acta* **2004**, 423, 127.
- [41] Janigova, I.; Lacik, I.; Chodak, I. *Polym. Degrad. Stab.* **2002**, 77, 35.